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Novel Lanthanide Amides Incorporating Neutral Pyrrole Ligand in a Constrained Geometry Architecture: Synthesis, Characterization, Reaction, and Catalytic Activity

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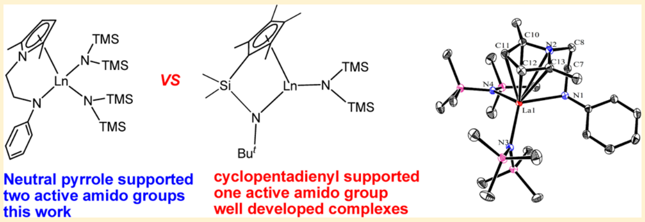
Supporting Information

ABSTRACT: The first series of lanthanide amido complexes incorporating a neutral pyrrole ligand in a constrained geometry architecture were synthesized, and their bonding, reactions, and catalytic activities were studied. Treatment of $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$ with 1 equiv of $(N\text{-}C_6H_5NHCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)$ (**1**) afforded the first example of bisamido lanthanide complexes having the neutral pyrrole η^5-bonded to the metal formulated as $[\eta^5{:}\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)]Ln[N(SiMe_3)_2]_2$ (Ln = La (**2**) and Nd (**3**)). Reaction of $[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ with 2 equiv of **1** produced the complex $[\eta^5{:}\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)][\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)]SmN(SiMe_3)_2$ (**4**). Treatment of **3** with 2 equiv of **1** gave the sandwich neodymium complex $[\eta^5{:}\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)]_2Nd[\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)]$ (**5**), in which two neutral pyrroles bonded with metal in an η^5 mode. Complex **5** could also be prepared by reaction of $[(Me_3Si)_2N]_3Nd(\mu\text{-Cl})Li(THF)_3$ with 3 equiv of **1**. Reactivities of the lanthanide bisamido complexes were further investigated. Reaction of complex **2** with pyrrolyl-functionalized imine $[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3N{=}CH)C_4H_3NH]$ afforded a mixed η^5-bonded neutral pyrrole and η^1-bonded anionic pyrrolyl lanthanum complex $[\eta^5{:}\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)]\{\eta^1\text{-}2\text{-}[(2,6\text{-}{}^iPr_2C_6H_3)NCH]C_4H_3N\}La[N(SiMe_3)_2]$ (**6**). Reactions of complexes **2** and **3** with pyrrolyl-functionalized secondary amine afforded the mixed η^5-bonded neutral pyrrole and the η^1-bonded anionic pyrrolyl lanthanide complexes $[\eta^5{:}\eta^1\text{-}(N\text{-}C_6H_5NCH_2CH_2)(2,5\text{-}Me_2C_4H_2N)][(\eta^1\text{-}2\text{-}{}^tBuNCH)\text{-}C_4H_3N]_2Ln$ (Ln = La (**7**), Nd (**8**)) with dehydrogenation of the secondary amine. Investigation of the catalytic properties of complexes **2**−**8** indicated that all complexes exhibited a high activity with a high chemo- and regioselectivity on the addition of dialkyl phosphite to α,β-unsaturated carbonyl derivatives. An interesting result was found that 1,2-hydrophosphonylation substrates could be catalytically converted to 1,4-hydrophosphinylation products when the substrates are the substituted benzylideneacetones by controlling the reaction conditions.



INTRODUCTION

The introduction of cyclopentadienyl ligand or its derivatives to rare-earth metals led to the development of a variety of homogeneous precatalysts[1] with findings of applications in different unsaturated molecules transformations such as polymerization of olefins,[2] hydroamination of alkenes and alkynes,[3] hydrosilylation of unsaturated compounds,[4,1b] hydrophosphinylation or hydrophosphonylation of unsaturated bonds,[5] hydroboration,[6] and the development of reagents for activation of small molecules such as N_2,[7] CO,[8] CO_2,[9] and so on. Among the cyclopentadienyl supported rare-earth metal complexes, the constrained geometry complexes (CGCs) have been found to exhibit a high activity for the polymerization of olefins (**A**, Chart 1).[10] The reactivity of anionic pyrrolyl supported complexes have been well developed, in which the anionic pyrrolyl (including poly pyrrolyl anions) ligands bonded with rare-earth metals in η^5 or η^1 or $\eta^5{:}\eta^1$ capability (**B**, Chart 1).[11] As the isolobal analogues to cyclopentadienyl anion,[12] the π-bonded neutral benzenes[13] or the π-bonded neutral pyrrole rare-earth metal complexes are known. Among the π-bonded neutral pyrrole rare-earth metal complexes, most of them are supported by multipyrrolyl moiety or appended with cyclopentadienyl anion.[14] To the best of our knowledge, lanthanide amides, alkyls, and hydrides containing a neutral pyrrole in the constrained geometry architecture similar to cyclopentadienyl and pyrrolyl anion supported analogues (**C**, Chart 1) have not been developed.

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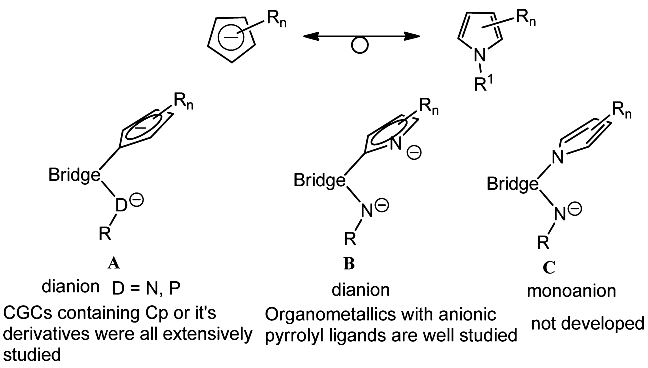
Chart 1

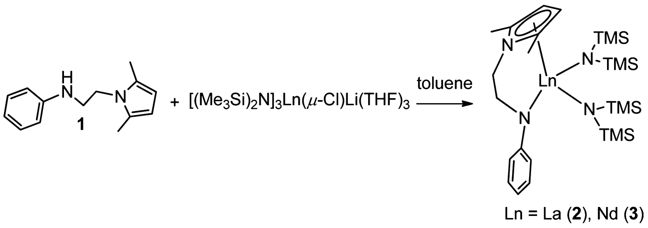


In this paper, we will for the first time report the synthesis of lanthanide amides incorporating the neutral pyrrole ligand in the constrained geometry architecture. Their bonding, reactions, and catalytic activities for the addition of diethyl phosphite to α,β-unsturated carbonyl compounds will also be reported.

RESULTS AND DISCUSSION

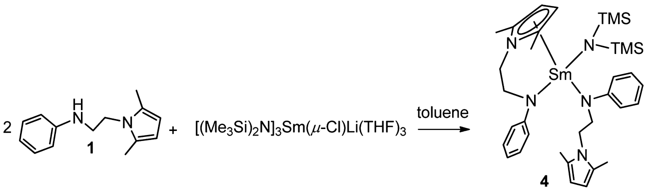
Synthesis, Characterization, and Reactivity of Constrained Geometry Lanthanide Amides Incorporating Neutral Pyrrole Ligand. Treatment of $[(\mathrm{Me_3Si})_2\mathrm{N}]_3\mathrm{Ln}(\mu\text{-}\mathrm{Cl})\mathrm{Li}(\mathrm{THF})_3$ (Ln = La, Nd) with 1 equiv of (N-$\mathrm{C_6H_5NHCH_2CH_2}$)(2,5-$\mathrm{Me_2C_4H_2N}$) (**1**) in toluene at 70−80 °C for 12 h, after workup, afforded the first example of neutral pyrrole incorporated constrained geometry lanthanide amides $[\eta^5{:}\eta^1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N})]\mathrm{Ln}[\mathrm{N}(\mathrm{SiMe_3})_2]_2$ (Ln = La (**2**), Nd (**3**)) (Scheme 1). Reaction of $[(\mathrm{Me_3Si})_2\mathrm{N}]_3\mathrm{Sm}(\mu\text{-}\mathrm{Cl})\mathrm{Li}(\mathrm{THF})_3$ with 2 equiv of **1** afforded the complex $[\eta^5{:}\eta^1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N})]\{\eta^1\text{-}[1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N}]\}\mathrm{SmN}(\mathrm{SiMe_3})_2$ (**4**) (Scheme 2). Several attempts for the syntheses of La and Nd complexes containing two neutral pyrrole ligands under the same conditions were tested but failed. Attempts with other ligands are still in progress.

Scheme 1. Synthesis of η^5 Bonded Neutral Pyrrole Lanthanide Amides

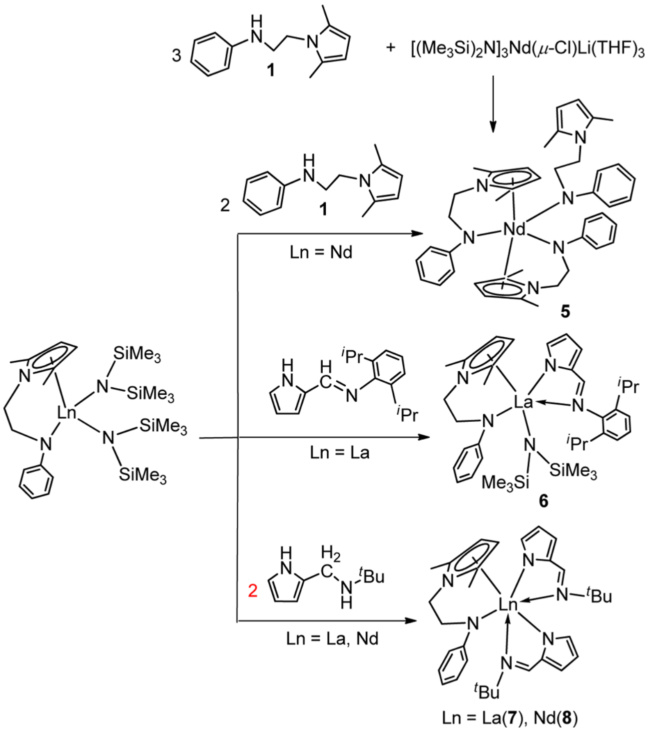


Reactivities of complexes **2** and **3** were then investigated. Treatment of **3** with 2 equiv of **1** produced the sandwich neodymium complex, $[\eta^5{:}\eta^1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N})]_2\mathrm{Nd}[\eta^1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N})]$ (**5**). This complex could also be prepared by treatment of $[(\mathrm{Me_3Si})_2\mathrm{N}]_3\mathrm{Nd}(\mu\text{-}\mathrm{Cl})\mathrm{Li}(\mathrm{THF})_3$ with 3 equiv of **1** (Scheme 3). Reaction of complex **2** with 1 equiv of imino-functionalized pyrrole $[2\text{-}(2,6\text{-}{}^i\mathrm{Pr_2C_6H_3N{=}CH})\mathrm{C_4H_3NH}]$ in toluene at 75 °C afforded the pyrrole deprotonated complex **6** in 80% yield. When the complexes **2** and **3** were respectively reacted with 2 equiv of amino-functionalized pyrrole $[2\text{-}({}^t\mathrm{BuNHCH_2})\text{-}\mathrm{C_4H_3NH}]$ in toluene at 90 °C for 24 h, the mixed η^5-bonded neutral pyrrole and η^1-bonded anionic pyrrolyl lanthanide complexes $[\eta^5{:}\eta^1\text{-}(N\text{-}\mathrm{C_6H_5NCH_2CH_2})(2,5\text{-}\mathrm{Me_2C_4H_2N})]\mathrm{Ln}\text{-}[(\eta^1\text{-}2\text{-}{}^t\mathrm{BuNCH})\mathrm{C_4H_3N}]_2$ (Ln = La (**7**), Nd (**8**)) were isolated (Scheme 3). In the reaction, the dehydrogenation of the pyrrolyl-functionalized secondary amines was found. The results of the dehydrogenation were supported by X-ray diffraction analyses and NMR spectral analyses. X-ray analyses revealed that the bond distance of N(4)−C(19) 1.286(8) Å and N(6)−C(28) 1.283(7) Å in **7**, C−N distances of 1.286(6) Å and 1.272(6) Å in **8** are in the range of normal C=N double bond, suggesting that the secondary amines were transformed to imines.[11n,p] ^{1}H NMR spectra of complexes **7** showed the clear resonances of the protons of the imine (N=CH) at about 8.10 and 8.01 ppm; the ^{13}C NMR spectra also displayed the resonances of the carbons of the imines (N=CH) at about 155 and 154 ppm (see Supporting Information).

Scheme 2. Synthesis of Samarium Complex 4

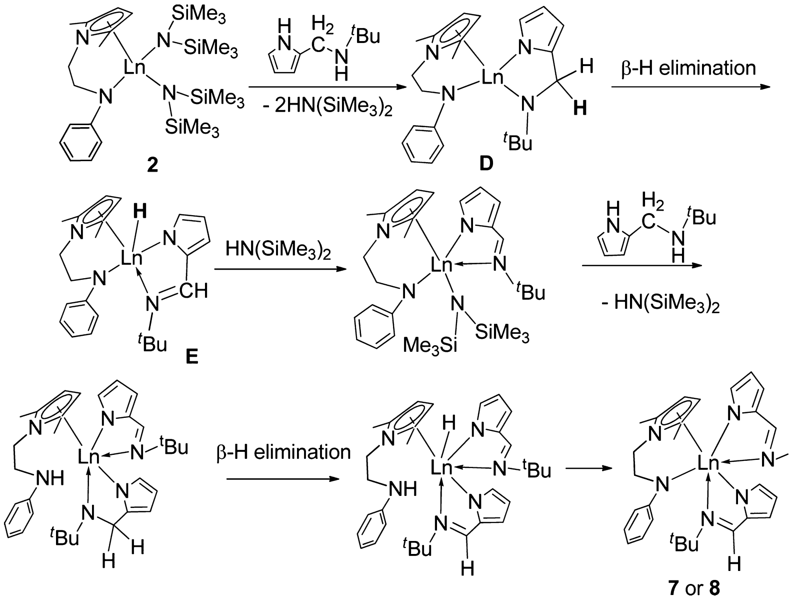


Scheme 3. Reactivities of the Neutral Pyrrole Incorporated Lanthanide Amides



We have demonstrated that the lithium amide $\mathrm{LiN(SiMe_3)_2}$ cannot promote the dehydrogenation of secondary amine to imine.[11n] The dehydrogenation pathway is proposed as follows (Scheme 4): Initial silylamine elimination of **2** gave the amido-appended pyrrolyl intermediate **D**, and the amido-appended intermediate underwent β-H elimination to give imine intermediate **E**. The intermediate **E** reacted with $\mathrm{HN(SiMe_3)_2}$

Scheme 4. Proposed Pathway for the Dehydrogenation Process



through a fast acid−base exchange process to produce the new amido intermediate, which then repeated the above processes of silylamine elimination and β-H elimination to afford the final products.

Structure and Bonding of the Complexes. The structures of all the above complexes were determined by single-crystal X-ray crystallographic analyses. X-ray analyses revealed that complexes **2** and **3** were isostructural constrained geometry organolanthanide bisamido complexes containing a neutral pyrrole ligand. A representative structure diagram is shown in Figure 1. In complexes **2** and **3**, the rare-earth metal adopts a distorted pseudotetrahedral geometry, and the neutral pyrrole appended amido ligand coordinated to rare-earth metal in η^5:η^1 modes, which is similar to the constrained geometry complexes having the cyclopentadienyl derivatives $[(\text{Bridge})(\text{DR})(\text{C}_5\text{Me}_4)]^{2-}$ (Bridge = Me_2Si, CH_2CH_2, etc; R = ^{t}Bu or Ar, D = N, P; as shown in Chart 1) bonded with metal in η^5:η^1 modes.[10] Different from the cyclopentadienyl supported CGCs having the cyclopentadienyl anion as a π supporting ligand, these series of complexes have the neutral pyrrole as the π supporting ligand. Complex **4** (Figure 2) contains one $\text{N(SiMe}_3)_2$, one neutral pyrrole appended amido ligand coordinated to rare-earth metal in η^5:η^1 modes, and another neutral pyrrole ligand serving as an amido ligand probably due to steric effects. Complex **5** (Figure 3) has two neutral pyrrole appended amido ligands bonded with metal in η^5:η^1 modes, and another neutral pyrrole appended amido ligand serves as amido ligand, thus forming a new kind of π-bonded neutral pyrrole sandwich amido complex. In complexes **6** (Figure 4), **7**, and **8** (complex **7** as a representative structure diagram in Figure 5), the anionic iminopyrrolyl ligands serve as donor ligands σ-bonded to the metal, suggesting the strong donating property of the anionic pyrrolyl ligand.

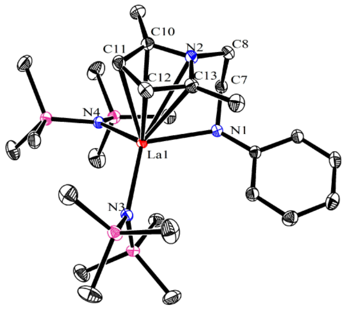


Figure 1. Representative molecular structure of complexes **2** and **3**. Hydrogen atoms were omitted for clarity.

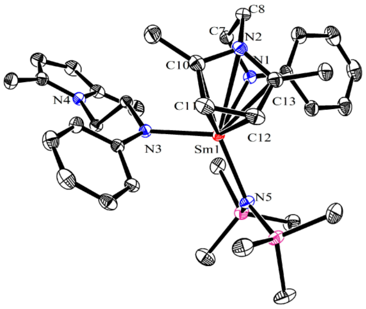


Figure 2. Molecular structure of complex **4**. Hydrogen atoms were omitted for clarity.

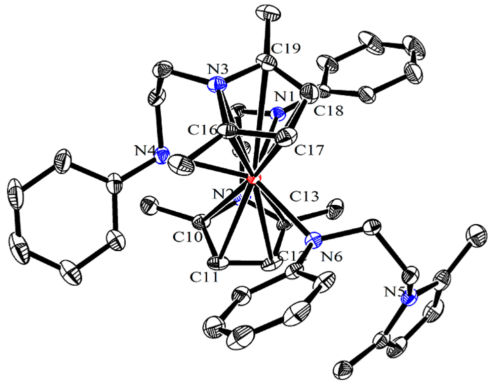


Figure 3. Molecular structure of complex **5**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): Nd−Pyr_{cent} (1), 2.845(6) Å, Nd−Pyr_{cent} (2), 3.012(7) Å. More bond distances and angles can be found in Supporting Information.

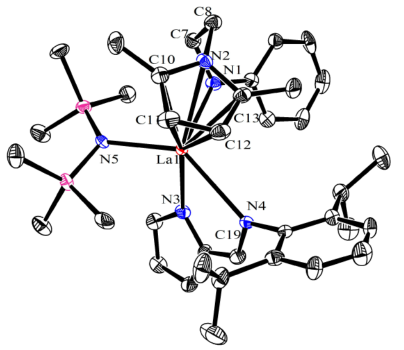


Figure 4. Molecular structure of complex **6**. Hydrogen atoms were omitted for clarity. C(19)−N(4), 1.33(2) Å.

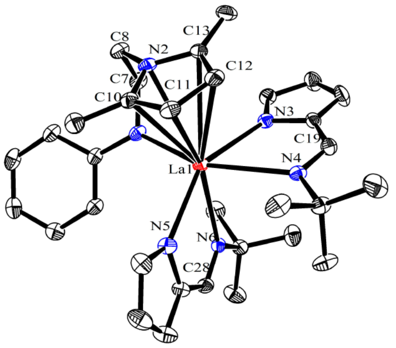


Figure 5. Molecular structure of complex **7**. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å): N(4)−C(19), 1.286(8) Å; N(6)−C(28), 1.283(7) Å; N(2)−C(8), 1.450(8) Å.

Complexes **2**, **3**, and **4** have the same coordination number, but complex **4** has different amido ligands. The Sm−Pyr$_{cent}$ distance of 2.704(3) Å in **4** is shorter than the Ln−Pyr$_{cent}$ distances of 2.847(5) Å in **2** and 2.793(3) Å in **3**, reflecting the lanthanide contraction sequence (ionic radii values for six-coordinate Ln^{3+}: La^{3+} 1.032 Å, Nd^{3+} 0.983 Å, Sm^{3+} 0.958 Å).[15] The Sm−Pyr$_{cent}$ distance in **4** is comparable with that found in *N,N′*-dimethyl substituted porphyrinogen samarium complex (2.69 Å),[14b] and is obviously longer than that found in the lower coordination number silyl-linked amido cyclopentadienyl complex [Me$_2$Si(C$_5$Me$_4$)(^{t}BuN)]SmN(SiMe$_3$)$_2$ (2.371 Å),[16] indicating the labile nature of the π-coordinated neutral pyrrole ring. The Pyr$_{cent}$−Sm−N(1) bond angle in **4** [84.62(8)°] is larger than the corresponding bond angle in **2** [79.97(6)°] and **3** [80.64(9)°].

The coordination geometry of complex **5** can be described as a distorted trigonal bipyramid, the three anion nitrogens are placed in the equatorial position, while centroids of two pyrrole rings are in axial positons. The bond distances of Nd−Pyr$_{cent}$(1) [2.845(6) Å] and Nd−Pyr$_{cent}$(2) [3.012(6) Å] (Table 1) with an average of 2.928(6) Å are comparable to one neutral pyrrole bonded with metal in η^5 modes of **2**, **3**, and **4** (taking account for iron radii of Nd^{3+} 0.983 Å for six coordinates, Nd^{3+} 1.163 Å for nine coordinates).[15]

In complexes **6**, **7**, and **8**, the neutral pyrrole appended amido ligand adopts η^5:η^1 bonding modes, and the anionic pyrrolyl ring bonded with metal in an η^1 fashion. The La−C$_{Pyr}$ distances in **6** fall in the same ranges of the η^6 La−C(arene) of [La(EtFormAlMe$_3$)(AlMe$_4$)$_2$] (Form = ArNCHNAr) (3.068(3)−3.144(4) Å).[13c] The distance of La−Pyr$_{cent}$ [2.850(2) Å] in **6** is longer than those found in **7** [2.794(6) Å] and **8** [Nd−Pyr$_{cent}$ 2.747(5) Å].

Catalytic Addition of Diethyl Phosphite to α,β-Unsaturated Carbonyl Derivatives. Various metal complexes have been demonstrated to be the effective catalysts for hydrophosphonylation of aldehydes, affording a direct and atomic efficient way for the synthesis of α-hydroxy phosphonates.[17] Recently, our group has reported hydrophosphonylation of both aromatic and aliphatic aldehydes, unactivated ketones, and substituted imines catalyzed by lanthanide amides with high catalytic activities.[5f,l,18] However, a few catalytic strategies for the catalytic addition of dialkyl phosphites to α,β-unsaturated carbonyl compounds have been developed, and the reported methods require high catalyst loadings (generally required 20 mol % catalyst loading) or stoichiometric amount in the case of CaO as catalyst,[19e] and the reported methods only focused on limited substrates (generally with one or two series of α,β-unsaturated carbonyl substrates).[19] So, highly efficient catalysts with high chemo- and regioselectivity suitable for catalytic addition of phosphites to all α,β-unsaturated carbonyl compounds are highly required. The addition reaction of diethyl phosphite to cinnamaldehyde was first investigated in the presence of neutral pyrrole supported lanthanide amido complexes, and the results are summarized in Table 2. Results showed that the addition of diethyl phosphite to cinnamaldehyde provided only 1,2-regioselective addition product **9c** in an excellent yield. Lowering or elevating reaction temperature did not affect the yield of product dramatically (compare the data in Table 2, entries 2, 7, and 8). Studies on the catalytic activities of the different lanthanide complexes revealed that complexes **2**−**8** exhibited high catalytic activities on the addition reaction, Complexes **2** and **3** displayed an excellent catalytic activity due to the leaving group of (Me$_3$Si)$_2$N. The differences in catalytic activities of these complexes are probably due to different amido groups, which displayed different reactivities in the catalytic transformation. It is worth noting that [(Me$_3$Si)$_2$N]$_3$Nd(μ-Cl)Li(THF)$_3$ as the catalyst displayed a slightly lower catalytic activity under the same conditions (Table 2, entry 15), suggesting the ligands' and coordination mode's effects on the catalytic activities.

Under the optimized reaction conditions, we next examined the substrate scope of the catalytic addition of diethyl phosphite to different α,β-unsaturated carbonyl derivatives in the presence of the neodymium amide **3** (Table 3). Results showed that only 1,2-addition products are isolated when the substrates are the α,β-unsaturated aldehydes, and 2-cyclohexen-1-one.

Interestingly, 1,2-regioselectivity products could be obtained when the benzylideneacetones were treated as substrates at temperature 0 °C. The 1,4-hydrophosphinylation products could be obtained when the catalytic reactions of benzylideneacetones with diethyl phosphite were carried out at a temperature of 40 °C in the presence of 5 mol % catalyst (Table 3, Scheme 5). It is also found that the 1,2-hydrophosphonylation products could be transformed to the 1,4-hydrophosphinylation products in the presence of 3 mol % catalyst at temperature of 40 °C.

It was documented that the α-hydroxy phosphonates readily underwent a retroreaction under basic conditions.[20] In order to understand the catalytic reaction, NMR technique was used to probe the process of the catalytic transformation of the 1,2-hydrophosphonylation product to the 1,4- hydrophosphinylation product. Upon addition of a catalytic amount of complex **2**

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg)

	2	3	4	5	6	7	8
Ln(1)−N(1)	2.384(18)	2.330(2)	2.295(2)	2.351(4)	2.371(15)	2.414(5)	2.367(4)
Ln(1)−N(2)	3.159(19)	3.064(4)	3.019(3)	3.143(4)	3.078(15)	3.025(4)	2.996(4)
Ln(1)−N(3)	2.396(18)	2.339(2)	2.293(18)	3.226(4)	2.508(15)	2.519(5)	2.459(4)
Ln(1)−N(4)	2.418(17)	2.363(2)		2.372(5)	2.800(15)	2.711(5)	2.675(4)
Ln(1)−N(5)			2.280(2)		2.401(15)	2.522(5)	2.675(4)
Ln(1)−N(6)				2.366(5)		2.656(4)	2.608(4)
C(10)−Ln(1), Ln−C(16)	3.079(2)	3.031(3)	2.998(3)	3.125(6), 3.183(5)	3.15(2)	2.972(5)	2.937(5)
C(11)−Ln(1), Ln−C(17)	2.995(2)	2.931(3)	2.899(3)	3.026(6), 3.202(7)	3.12(2)	2.876(6)	2.940(5)
C(12)−Ln(1), Ln−C(18)	3.026(2)	2.958(3)	2.872(3)	3.009(6), 3.250(7)	3.05(2)	3.074(6)	3.014(5)
C(13)−Ln(1), Ln−C(19)	3.141(2)	3.101(3)	2.962(3)	3.082(6), 3.291(6)	3.02(2)	3.100(5)	3.058(5)
C(19)−N(4), C(28)−N(6)					1.33(3)	1.288(8), 1.283(7)	1.272(6), 1.286(6)
Ln(1)−Pyr$_{\mathrm{av}}$(1), Ln(1)−Pyr$_{\mathrm{av}}$(2)	3.080(2)	3.050(3)	2.950(3)	3.230(4), 3.077(6)	3.083(2)	3.009(5)	2.989(5)
Ln(1)−Pyr$_{\mathrm{cent}}$(1), Ln(1)−Pyr$_{\mathrm{cent}}$(2)	2.847(5)	2.793(3)	2.704(3)	2.845(6), 3.012(6)	2.850(2)	2.794(6)	2.747(5)
Pyr$_{\mathrm{cent}}$−Ln(1)−N(1)	79.97(6)	80.64(9)	84.62(8)	80.82(18), 94.81(17)	83.95(6)	84.25(4)	85.35(14)
Pyr$_{\mathrm{cent}}$−Ln(1)−N(3)	118.84(6)	118.33(9)	109.31(8)			97.98(16)	98.61(13)
Pyr$_{\mathrm{cent}}$−Ln(1)−N(4)	112.38(6)	113.02(9)		98.36(15), 79.25(18)	95.47(5)	93.46(17)	93.84(13)
Pyr$_{\mathrm{cent}}$−Ln(1)−N(5)			128.21(8)		109.65(6)	105.41(17)	103.85(15)
Pyr$_{\mathrm{cent}}$−Ln(1)−N(6)				95.42(16), 89.67(17)		172.33(16)	172.32(14)
Pyr$_{\mathrm{cent}}$(1)−Ln(1)−Pyr$_{\mathrm{cent}}$(2)				174.63(6)			
N(1)−Ln(1)−N(3)	112.98(6)	112.90(9)	104.79(7)			91.14(17)	91.82(14)
N(1)−Ln(1)−N(4)	112.01(6)	111.47(9)			114.6(5)		
N(3)−Ln(1)−N(4)	115.54(6)	115.49(9)			65.0(5)	66.71(15)	67.98(12)
N(1)−Ln(1)−N(5)			114.55(8)		100.9(6)		
N(3)−Ln(1)−N(5)			110.77(7)		84.5(5)		
N(1)−Ln(1)−N(6)				125.74(16)			
N(4)−Ln(1)−N(6)				133.66 (13)			
N(5)−Ln(1)−N(6)						67.02(15)	68.56(13)
C(7)−N(1)−Ln(1)	107.68(14)	107.41(18)	106.68(15)	107.7(3)	111.5(13)	114.1(4)	112.5(3)

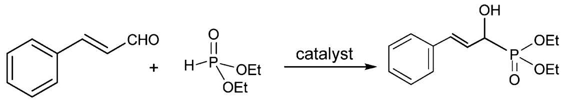
(for the paramagnetic property of complex **3**, so we used complex **2** instead of complex **3** in the probing experiments) to diethyl 2-hydroxy-4-phenylbut-3-en-2-ylphosphonate (**9e**) in C_6D_6, the mixture was heated to 40 °C. The disappearance of resonances of the protons on double bonds of **9e** at 6.62 and 7.36 ppm and methyl (CH_3CHOH−) at 2.0 ppm and appearance of the protons of the methyl (CH_3CO−) of diethyl 3-oxo-1-phenylbutylphosphonate (**10a**) at 1.60 ppm can be recorded in 5 min. The transformation of **9e** to **10a** can be finished in 2 h by comparison of the ^{1}H NMR spectra with the purified **10a**. At the same time, we tested the temperature or catalyst effects on this transformation. Compound **9e** was heated to 40 or 60 °C for 2 h, even 12 h, and no 1,4-hydrophosphinylation product was found upon analysis of the ^{1}H NMR spectra. However, **9e** can be almost completely transformed to **10a** in the presence of a catalytic amount of complex **2** at 10 °C, but it required 6 h (see Supporting Information), indicating that catalyst played a key role in the transformation of 1,2-addition products to 1,4-addition products. On the basis of experimental results, the catalytic transformation pathway of the 1,2-hydrophosphonylation products to the 1,4-hydrophosphinylation products is proposed involving acid−base interaction to give intermediate **F**, followed by intramolecular addition of phosphorus to the C═C to produce the intermediate **G** similar to the retroaddition.[20] This intermediate reacted with amine to produce the final product (Scheme 6).

It is found that the catalytic addition of diethyl phosphite to 2-cyclopenten-1-one, *α*,*β*-unsaturated chalcones, amides, and esters in the presence of 1.0 mol % of **3** produced only 1,4-regioselective addition products in good to high yields. However, the catalytic reaction generally required 120 min for the *α*,*β*-unsaturated chalcones and ester substrates to give satisfactory yields of the products, suggesting these substrates are relatively unactivated compared to other ones. It is found that the electronic nature and steric hindrance of substituents have an effect on the reactivity. For example, when electron-donating substituents such as Me and OMe were used, good yields of products **10k** and **10l** were isolated (entries 16 and 17), and the addition of diethyl phosphite to 4-nitrochalcone produced the product in 80% yield, while the addition of diethyl phosphite to 2-nitrochalcone gave the product in only 50% yield. For comparison, the catalytic activity of the cyclopentadienyl-free neodymium amide $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ was tested by running catalytic addition of diethyl phosphite to some relatively unreactive substrates such as *α*,*β*-unsaturated chalcones. Results (Table 3, entries 14, 16, 18, and 19) indicated the above neutral pyrrole incorporated constrained geometry lanthanide amido complexes generally exhibited a higher activity than the $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ did, indicating the advantage of the neutral pyrrole incorporated constrained geometry lanthanide amido complexes. High catalytic activity with a low catalyst loading (1 mol %) for the catalytic addition of phosphites to *α*,*β*-unsaturated carbonyl derivatives is for the first time reported in this field comparable to the literature's results.[19]

■ CONCLUSIONS

In summary, we have for the first time synthesized and characterized a series of rare-earth metal amides incorporating

Table 2. Optimization of the Conditions on the Reaction of Cinnamaldehyde with Diethyl Phosphite[a]



entry	cat. (mol %)	solvent	temp (°C)	time	yield (%)[b]
1	**3** (1 mol %)	*n*-hexane	rt	5 min	93
2	**3** (1 mol %)	toluene	rt	5 min	90
				20 min	97
3	**3** (1 mol %)	THF	rt	5 min	92
				20 min	95
4	**3** (1 mol %)	solvent free	rt	20 min	98
5	**3** (0.5 mol %)	toluene	rt	24 h	30
6	**3** (0.25 mol %)	toluene	rt	24 h	trace
7	**3** (1 mol %)	toluene	0	20 min	95
8	**3** (1 mol %)	toluene	40	20 min	97
10	**2** (1 mol %)	toluene	rt	20 min	95
11	**4** (1 mol %)	toluene	rt	20 min	85
				2 h	98
12	**5** (1 mol %)	toluene	rt	20 min	80
				4 h	95
13	**6** (1 mol %)	toluene	rt	20 min	88
14	**7** (1 mol %)	toluene	rt	20 min	92
16	**8** (1 mol %)	toluene	rt	20 min	93
15	Nd[N]$_3$[c] (1 mol %)	toluene	rt	20 min	88
				2 h	95

[a] Reaction conditions: cinnamaldehyde (2.0 mmol), diethyl phosphite (2.4 mmol), solvent (2 mL) or solvent free, room temperature. [b] Isolated yields. [c] Nd[N]$_3$: [(Me$_3$Si)$_2$N]$_3$Nd(μ-Cl)Li(THF)$_3$.

neutral pyrrole appended amido ligand in the constrained geometry architecture. X-ray diffraction analyses indicated the neutral pyrrole bonded with rare-earth metal ions in an η^5 mode. This work may open the chemistry of constrained geometry organolanthanide complexes with π-bonded neutral pyrrole ligands. Reactions of the neutral pyrrole supported lanthanide bisamido complexes with imino and secondary amine functionalized pyrroles were studied, and results indicated that the neutral pyrrole still bonded with the rare-earth metal ions in the η^5 mode, while the anionic pyrrolyl ligands bonded with the rare-earth metal ions as σ-donationg ligands. Additionally, reactions of the neutral pyrrole supported bisamido rare-earth complexes with secondary amine functionalized pyrrole led to the dehydrogenation of secondary amine to imine through the proposed β-H elimination process. The neutral pyrrole supported rare-earth complexes exhibited a high chemo- and regioselectivity in catalytic addition of diethyl phosphite to α,β-unsaturated carbonyl derivatives. The catalytic reactions provided only 1,4-regioselectivity addition for α,β-unsaturated esters, amide, chalcones, and 2-cyclopenten-1-one, and 1,2-addition for α,β-unsaturated aldehydes and 2-cyclohexen-1-one. It is interesting to find that the reaction conditions have a great effect on the regioselectivity for the catalytic addition of diethyl phosphite to substituted benzylideneacetones: the 1,2-regioselective addition products were obtained when the reactions were run at 0 °C, while 1,4-addition products could be separated when the reactions were carried out at or above 40 °C, and the 1,2-addition products could be transferred to the 1,4-addition products at or above 40 °C in the presence of the neutral pyrrole supported lanthanide amides as catalysts. Further works on neutral pyrrole or indole supported rare-earth metal complexes are in progress.

EXPERIMENTAL SECTION

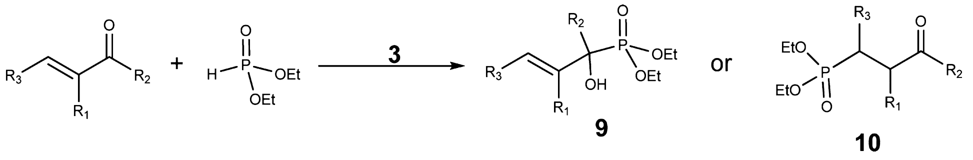
General Remarks. All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (Ln = Nd, Sm, La),[21] 2-[(2,6-^{i}Pr$_2$C$_6$H$_3$)NCH]C$_4$H$_3$NH, and 2-(^{t}BuNCH$_2$)C$_4$H$_3$NH were prepared according to literature methods.[11p] Acetonylacetone and *N*-phenylethylenediamine were purchased and used without purification. Solid α,β-unsaturated carbonyl derivatives were used directly, and liquid derivatives were distilled before use. Elemental analysis data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ^{1}H; 75.0 MHz for ^{13}C; 121 MHz for ^{31}P NMR) in C$_6$D$_6$ 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 FTIR-8400s spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT-MS spectrometer. Melting points were determined in capillaries and were uncorrected.

Preparation of *N*-Anilinoethyl-2,5-dimethylpyrrole (1). *N*-Phenylethylenediamine (7.6 g, 0.05 mol), acetonylacetone (2.7 g, 0.05 mol), and sufficient toluene were placed in a round-bottom flask with a water separator and heated at reflux overnight. The water produced during the reaction was removed as a toluene azeotrope. The toluene was removed in vacuo after the reaction was completed. Recrystallization of crude product from hexane and ethyl acetate (1:3) gave the product (**1**) (9.6 g, 90% yield). Mp: 74−76 °C. ^{1}H NMR (300 MHz, CDCl$_3$, ppm,): δ 7.19−7.10 (m, 2H, C$_6$H$_5$), 6.67−6.55 (m, 1H, C$_6$H$_5$), 6.53−6.52 (m, 2H, C$_6$H$_5$), 5.73 (s, 2H, pyr), 3.90 (t, *J* = 6.6 Hz, 2H, CH$_2$), 3.33 (t, *J* = 6.6 Hz, 2H, CH$_2$), 2.14 (s, 6H, CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ 147.5, 129.6, 127.9, 117.8, 112.7, 105.7, 44.0, 42.9, 12.8. IR (KBr pellets, cm^{-1}): ν 3435 (s), 3356 (s), 2974 (m), 2910 (w), 2580 (w), 1600 (s), 1508 (s), 1406 (s), 1325 (s), 1257 (w), 1114 (w), 881 (w), 752 (s), 690 (s). HRMS (ESI) calcd for C$_{14}$H$_{19}$N$_2$ (M + H$^+$): 215.1548. Found: 215.1548.

Preparation of [η^5:η^1-(*N*-C$_6$H$_5$NCH$_2$CH$_2$)(2,5-Me$_2$C$_4$H$_2$N)]La[N(SiMe$_3$)$_2$]$_2$ (2). To a toluene (20.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$La(μ-Cl)Li(THF)$_3$ (1.072 g, 1.2 mmol) was added a toluene (10.0 mL) solution of ligand **1** (0.257 g, 1.2 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 2 h, the mixture was stirred at 70 °C for 24 h. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (2 × 10.0 mL). The extracts were combined and concentrated to about 10.0 mL. Pale yellow crystals were obtained by recrystallization from the concentrated *n*-hexane solution at 0 °C (0.62 g, 77% yield). Mp: 178−180 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$, ppm): δ 7.37−7.31 (m, 2H, C$_6$H$_5$), 6.91−6.88 (m, 2H, C$_6$H$_5$), 6.75−6.70 (m, 1H, C$_6$H$_5$), 5.80 (s, 2H, pyr), 3.23 (t, *J* = 4.5 Hz, 2H, CH$_2$), 2.91 (t, *J* = 4.8 Hz, 2H, CH$_2$), 1.66 (s, 6H, CH$_3$), 0.37 (s, 36H, CH$_3$). ^{13}C NMR (75.0 MHz, C$_6$D$_6$, ppm): δ 153.3, 132.0, 128.8, 114.4, 112.9, 106.8, 46.6, 41.8, 11.3, 4.1. IR (KBr pellets, cm^{-1}): ν 2974 (w), 2910 (w), 1602 (s), 1498 (w), 1406 (w), 1327 (s), 1257 (m), 1178 (s), 1124 (s), 1001 (m), 937 (s), 831(m), 752 (s). Anal. Calcd for C$_{26}$H$_{53}$N$_4$LaSi$_4$ + (1/2)C$_6$H$_{14}$: C, 48.64; H, 8.45; N, 7.82. Found: C, 48.47; H, 8.58; N, 7.42.

Preparation of [η^5:η^1-(*N*-C$_6$H$_5$NCH$_2$CH$_2$)(2,5-Me$_2$C$_4$H$_2$N)]Nd[N(SiMe$_3$)$_2$]$_2$ (3). This compound was prepared as blue crystals in 85% (0.616 g) yield by treatment of HL (**1**) (0.23 g, 1.07 mmol) with [(Me$_3$Si)$_2$N]$_3$Nd^{III}(μ-Cl)Li(THF)$_3$ (0.945 g, 1.07 mmol) using procedures similar to those described above for preparation of **2**. Mp: 170−172 °C. IR (KBr pellet, cm^{-1}): ν 2941 (s), 2902 (s), 2850 (s), 1602 (m), 1510 (m), 1406 (m), 1327 (s), 1273 (m), 1178 (s), 1124 (s), 1018 (s), 935 (s), 842 (s), 775(s), 690 (m). Anal. Calcd for C$_{26}$H$_{53}$N$_4$NdSi$_4$: C, 46.04; H, 7.88; N, 8.26. Found: C, 45.84; H, 7.81; N, 8.32.

Table 3. Addition of Diethyl Phosphite to Various Unsaturated Carbonyl Compounds Catalyzed by Catalyst 3[a]



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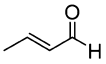
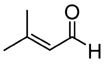
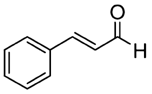
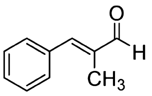
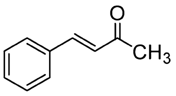
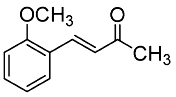
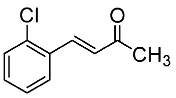
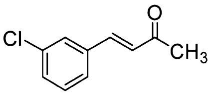
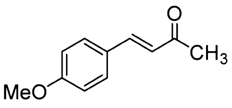
1		none	20	**9a**	95
2		none	20	**9b**	95
3		none	20	**9c**	98
4		none	20	**9d**	95
5		toluene	20	**9e**	97
			120	**10a**[c]	95
6		toluene	120	**10b**[c]	93
			20	**9f**	92
7		toluene	120	**10c**[c]	88
			20	**9g**	85
8		toluene	120	**10d**[c]	80
			20	**9h**	90
9		toluene	120	**10e**[c]	89
			20	**9i**	90

Table 3. continued

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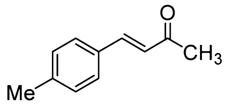
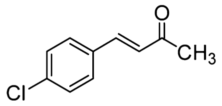
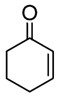
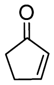
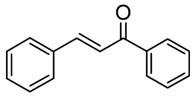
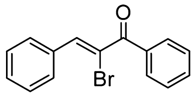
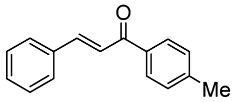
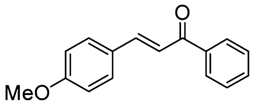
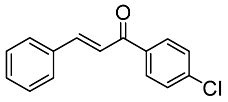
10		toluene	120	**10f**[c]	88
			20	**9j**	89
11		toluene	60	**10g**[c]	88
			20	**9k**	90
12		toluene	120	**9l**	86
13		toluene	120	**10h**	84
14		toluene	120	**10i**	95 (90)
15		toluene	120	**10j**	92
16		toluene	120	**10k**	92 (82)
17		toluene	120	**10l**	90
18		toluene	120	**10m**	90 (80)

Table 3. continued

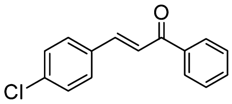
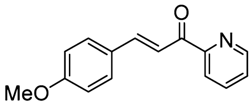
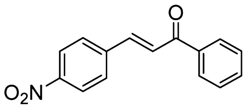
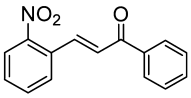
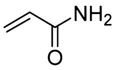
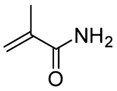
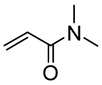
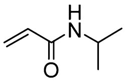
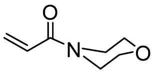
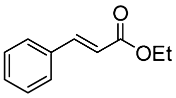
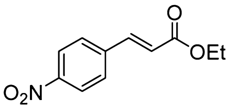
Entry	Substrate	Solvent	Time(min)	Product	Yield[b] (%)
19		toluene	120	**10n**	88 (75)
20		toluene	120	**10o**	87
21		toluene	120	**10p**	80
22		THF	720	**10q**	50
23		none	5	**10r**	99
24		none	5	**10s**	98
25		none	20	**10t**	98
26		none	20	**10u**	96
27		none	20	**10v**	95
28		toluene	120	**10w**	92
29		THF	120	**10x**	85

Table 3. continued

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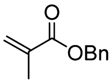
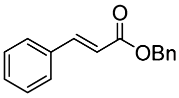
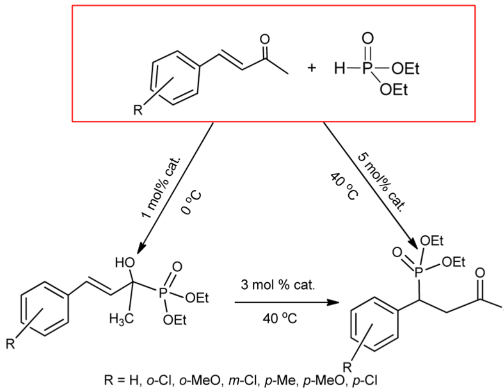
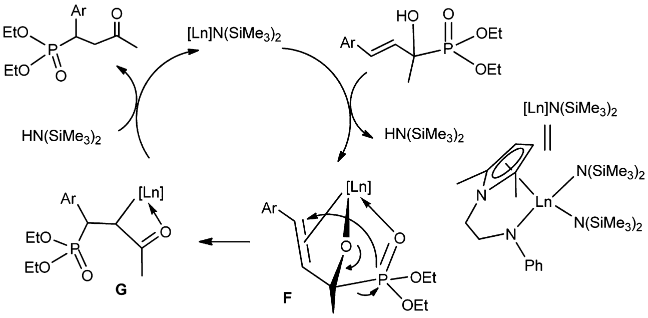
30		toluene	120	**10y**	90
31		toluene	120	**10z**	82

[a]Reaction conditions: substrate (2.0 mmol), diethyl phosphite (2.4 mmol), catalyst loading (1 mol %), toluene (2 mL) or solvent free, room temperature or 0 °C. [b]Isolated yields and the number in the parentheses refers to the yields of the reaction catalyzed by $[(Me_3Si)_2N]_3Nd(\mu\text{-}Cl)Li(THF)_3$ under the same conditions. [c]Temperature: 40 °C, catalyst (5 mol %)

Scheme 5. Catalytic Addition of Diethyl Phosphite to Benzylideneacetones and Transformation of 1,2-Addition Products to 1,4-Addition Products



Scheme 6. Proposed Mechanism for the Transformation of the 1,2-Addition Products to the 1,4-Addition Products



Preparation of [η^5:η^1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)]{η^1-[1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$]}$SmN(SiMe_3)_2$ (4). The compound $[(Me_3Si)_2N]_3Sm(\mu\text{-}Cl)Li(THF)_3$ was treated with 2 equiv of **1** following procedures similar to those used for preparation of **2** to give the product **4** in 50% yield. Mp: 168−170 °C. IR (KBr pellets, cm^{-1}): ν 2974 (s), 2908 (s), 2850 (s), 2360 (s), 1602 (m), 1510 (m), 1406 (m), 1327 (s), 1271 (s), 1178 (s), 1124 (s), 1018 (s), 775 (s), 752 (s), 690 (m). Anal. Calcd for $C_{34}H_{52}N_5Si_2Sm$: C, 55.38; H, 7.11; N, 9.50. Found: C, 55.68; H, 7.41; N, 9.30.

Preparation of [η^5:η^1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)]$_2$Nd-[η^1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)] (5). The complex **3** was treated with 2 equiv of **1** following procedures similar to those used for preparation of **2** to give the product **5** as blue crystals in 45% yield. Mp: 182−184 °C. IR (KBr pellets, cm^{-1}): ν 3356 (s), 2974 (m), 2852 (m), 1600 (s), 1510 (s), 1444 (m), 1325 (s), 1178 (m), 1124 (m), 1018 (m), 989 (w), 775 (m), 690 (m). Anal. Calcd for $C_{42}H_{51}N_6Nd$: C, 64.33; H, 6.56; N, 10.72. Found: C, 64.42; H, 6.46; N, 10.94.

Preparation of [η^5:η^1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)]La{η^1-2-[(2,6-^{i}$Pr_2C_6H_3$)NCH]C_4H_3N}$N(SiMe_3)_2$ (6). To a toluene (20.0 mL) solution of complex **2** (0.410 g, 0.61 mmol) was added a toluene (10.0 mL) solution of 2-[(2,6-^{i}$Pr_2C_6H_3$)NCH]C_4H_3NH (0.155 g, 0.61 mmol) at room temperature. After the reaction mixture was stirred for 24 h at 75 °C, the solvent was evaporated under reduced pressure. The residue was extracted with hexane (2 × 10.0 mL). The extraction was combined and dried under vacuum to afford complex **6** in 80% yield (0.729 g). Yellow crystals for X-ray analysis were obtained from hexane at 0 °C for several days. Mp: 184−187 °C. ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 7.83 (d, J = 13.6, CH═N, 1H), 7.17−7.05 (m, 6H, C_6H_5), 6.89 (s, 1H, Pyr), 6.60−6.53 (m, 2H, C_6H_5), 6.29 (d, J = 7.9 Hz, 1H, Pyr), 6.05 (s, 1H, Pyr), 5.69 (s, 2H, Pyr), 3.42 (s, 2H, CH_2), 3.35 (t, J = 6.3 Hz, 1H, $CHMe_2$), 2.97 (s, 1H, CH_2), 2.83 (t, J = 6.3 Hz, 1H, $CHMe_2$), 1.64 (s, 6H, CH_3), 1.05 (d, J = 6.5 Hz, 12H, 4CH_3), 0.34 (s, 18H, 6CH_3). ^{13}C NMR (75.0 MHz, C_6D_6, ppm): δ 162.3, 153.7, 149.4, 140.4, 139.8, 135.2, 129.2, 124.7, 122.6, 121.4, 116.6, 114.5, 111.5, 107.1, 50.3, 42.8, 27.5, 25.1, 20.9, 11.6, 4.1. IR (KBr pellets, cm^{-1}): ν 2960 (m), 2866 (m), 1622 (m), 1602 (m), 1510 (s), 1406 (s), 1300 (s), 1255 (s), 1180 (s), 1134 (s), 1091 (m), 1033 (m), 933 (m), 860 (s), 746 (m). Anal. Calcd for $C_{37}H_{56}LaN_5Si_2$: C, 58.02; H, 7.37; N, 9.14. Found: C, 58.15; H, 7.70; N, 9.52.

Preparation of [η^5:η^1-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)]La-[(η^1-2-^{t}BuNCH)C_4H_3N]$_2$ (7). To a toluene (20.0 mL) solution of complex **2** (0.376 g, 0.56 mmol) was added a toluene (10.0 mL) solution of 2-(^{t}$BuNCH_2$)C_4H_3NH (0.170 g, 1.12 mmol) at room temperature. After the reaction mixture was stirred for 24 h at 90 °C, the solvent was evaporated under reduced pressure. The residue was extracted with hexane (2 × 10.0 mL). The extraction was combined and dried under vacuum to afford complex 7 in 65% yield (0.237 g). Yellow crystals for X-ray analyses were obtained from hexane at 0 °C for several days. Mp: 184−185 °C. ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 8.10 (s, CH═N, 1H), 8.01 (s, CH═N, 1H), 7.42 (s, 1H, Pyr), 7.35 (s, 1H, Pyr), 7.25−7.19 (m, 2H, C_6H_5), 7.03 (s, 1H, Pyr), 6.93 (s, 1H, Pyr), 6.73−6.69 (m, 3H, C_6H_5), 6.67 (s, 1H, Pyr), 6.42 (s, 1H, Pyr), 6.18 (s, 1H, Pyr), 5.69 (s, 1H, Pyr), 3.93−3.85 (m, 1H, CH_2), 3.59−3.55 (m, 1H, CH_2), 3.14−3.09 (m, 1H, CH_2), 2.95−2.91 (m, 1H, CH_2), 1.89 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 0.95 (d, J = 13.2 Hz, 18H, ^{t}Bu). ^{13}C NMR (75.0 MHz, C_6D_6, ppm): δ 155.2, 154.3, 136.4, 134.9, 133.1, 132.6, 128.9, 119.2, 118.4, 113.8, 112.5, 110.4, 108.0, 107.3, 48.7, 42.9, 28.8 (d, J = 53 Hz), 11.9, 9.35. IR (KBr pellets, cm^{-1}): ν 2966 (m), 2910 (w), 1633 (s), 1510 (s), 1406 (m), 1363 (s), 1325 (m), 1209 (s), 1095 (s), 1031 (s), 912 (s), 804 (m), 775 (m), 752 (m), 692 (s). Anal. Calcd for $C_{32}H_{43}LaN_6$: C, 59.07; H, 6.66; N, 12.92. Found: C, 58.33; H, 6.74; N, 12.77.

Preparation of $[\eta^5:\eta^1$-(N-$C_6H_5NCH_2CH_2$)(2,5-$Me_2C_4H_2N$)]Nd[(η^1-2-^{t}BuNCH)$C_4H_3N]_2$ (8). Complex **8** was prepared as blue crystals in 70% yield from the reaction of compound **3** (0.352 g, 0.52 mmol) with 2 equiv of 2-(^{t}BuNCH$_2$)C_4H_3NH (0.158 g, 1.04 mmol) by employing procedures similar to those used for the preparation of **7**. Mp: 180−182 °C. IR (KBr pellets, cm^{-1}): ν 2742 (w), 2576 (m), 1936 (m), 1822 (s), 1631 (w), 1602 (w), 1510 (w), 1421 (w), 1363 (w), 1273 (m), 1209 (m), 1124 (m), 1095 (m), 958 (s), 912 (m), 866 (m). Anal. Calcd for $C_{32}H_{43}NdN_6$: C, 58.59; H, 6.61; N, 12.81. Found: C, 57.91; H, 6.72; N, 12.50.

General Procedure for Hydrophosphonylation of α,β-Unsaturated Carbonyl Derivatives (9c as an Example). A 30.0 mL Schlenk tube under dried argon was charged with complex **3** (13.5 mg, 0.02 mmol), diethyl phosphite (1.657 g, 2.4 mmol), and either no solvent or 2.0 mL of solvent, and then cinnamaldehyde (1.061 g, 2.0 mmol) was added to the mixture. The mixture was stirred at room temperature for 20 min. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with ethyl ether, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed under reduced pressure, the final products were further purified by recrystallization from ethyl acetate and hexane. Compound **9c** was isolated as white crystals (0.530 g, 98%).

Experiments for Probing the Transformation of 1,2-Addition Products to 1,4-Addition Products Using NMR Technique. In a glovebox, diethyl 2-hydroxy-4-phenylbut-3-en-2-ylphosphonate (**9e**) (20.0 mg, 14.5 μmol) and the catalyst of complex **2** (1.4 mg, 2.0 μmol) were loaded to an NMR tube, the mixture was dissolved with C_6D_6, and then the mixture was heated to 40 °C and monitored by ^{1}H NMR. ^{1}H NMR spectra were recorded with fixed interval. The transformation can be finished in 2 h by comparison of the ^{1}H NMR spectra of the purified **9e** and **10a** (see Supporting Information).

Crystal Structure Determinations. Suitable crystals of complexes **2**−**8** were 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. 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. All hydrogen atoms were refined using a riding model. CCDC numbers 905078−905084 for complexes **2**−**8** 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data and spectra for compounds, tables of crystallographic data and structure refinement for **2**−**8**, theoretical calculation of energy differences between HOMO and LUMO of Cp* and N-methyl-2,5-dimethylpyrrole, and X-ray crystallographic files, in CIF format, for structure determination of complexes **2**−**8**. 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.

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