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Article

Synthesis of Carbamoylphosphates from Isocyanates Catalyzed by Rare-Earth-Metal Alkyl Complexes with a Silicon-Linked Diarylamido Ligand

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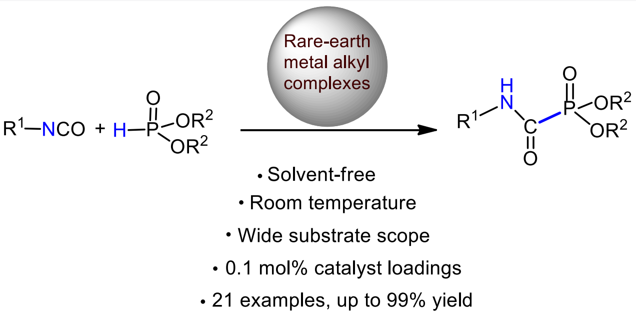
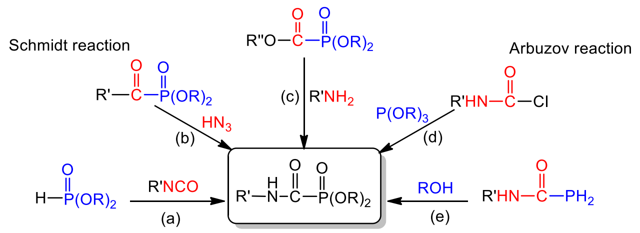
ABSTRACT: Neutral rare-earth-metal monoalkyl complexes and anionic rare-earth-metal dialkyl complexes with a silicon-linked diarylamido ligand were synthesized and characterized, and their catalytic activities toward the additions of dialkyl phosphites to isocyanates were developed. Reactions of rare-earth-metal trialkyl complexes RE(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with a silicon-linked diarylamine ligand in *n*-hexane afforded the neutral rare-earth-metal monoalkyl complexes LRE(CH$_2$SiMe$_3$)(THF)$_2$ (RE = Y (**1**), Er (**2**); L = (Me$_2$Si)(2,6-^{i}Pr$_2$C$_6$H$_3$N)$_2$) in good yields. The dinuclear rare-earth-metal chlorides [LRE(μ-Cl)(THF)$_2$]$_2$ (RE = Y (**3**), Er (**4**)) were synthesized by the salt metathesis reaction of H$_2$**L**, ^{n}BuLi, and anhydrous RECl$_3$. Treatment of the rare-earth-metal chlorides with 4 equiv of LiCH$_2$SiMe$_3$ in toluene generated the corresponding discrete heterobimetallic rare-earth-metal dialkyl complexes LRE(CH$_2$SiMe$_3$)$_2$(THF)Li(THF)$_4$ (RE = Y (**5**), Er (**6**)). Further investigation showed that a wide variety of carbamoylphosphates were efficiently synthesized in high to excellent yields (up to 99%) via the additions of dialkyl phosphites to various alkyl- and aryl-substituted isocyanates in the presence of 0.1 mol % rare-earth-metal monoalkyl or dialkyl complexes as catalysts under solvent-free conditions at room temperature within 5 min, which provided a green and highly efficient method for the rapid construction of C−P bonds to afford various carbamoylphosphate derivatives.



■ INTRODUCTION

The formation of C−P bonds to construct organophosphorus compounds, such as hydroxyphosphonates, aminophosphonates, phosphaguanidines, and phosphaureas, is of great importance and significance due to their wide application in industrial, agricultural, and medicinal areas.[1] In contrast to the α-functional phosphonic acid derivatives, carbamoylphosphonates (CPOs) are important scaffolds and synthons and have attracted wide attention in biomedical and clinical research.[2] Further investigation showed that CPOs have an important antiviral activity by controlling tumor cell proliferation and dissemination, and they also serve as inhibitors of matrix metalloproteinases (MMP) associated with a variety of diseases.[3] However, the efficient synthesis of CPOs has remained largely unexplored. It is well-known that common methods for the preparation of CPO derivatives involve the Schmidt reaction,[4] the Arbuzov reaction,[5] and the substitution reaction between phosphonoformates and amines (Scheme 1b−d).[6] Very recently, the reactions of phosphoramides and alcohols can achieve CPOs via phosphorylation and oxygenation using I$_2$ as a catalyst or using ^{n}Bu$_4$NI as a catalyst through an electrochemical method (Scheme 1e).[7] Among the aforementioned methods, several reagents, such as acylphosphonates, phosphonoformates, carbamoyl chlorides, and phosphoramides, are required for synthesis according to the literature procedures. In contrast to the commercially available isocyanates, the addition of dialkyl phosphites to isocyanates is

Scheme 1. Synthetic Methods for Carbamoylphosphate Derivatives



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regarded as the most straightforward and 100% atom-economical route for the preparation of CPOs (Scheme 1a), however, only a limited number of catalytic systems have been used for this transformation so far.

Strong bases, such as sodium and triethylamine, can smoothly catalyze the addition reaction of dialkyl phosphites to isocyanates.[8] Kaboudin and co-workers found that 0.1 equiv of anhydrous calcium chloride as a Lewis base catalyst can promote the addition reaction to prepare CPOs in moderate yields (≤65%).[9] Raju et al. developed the silica-supported Lewis acid catalyst SiO_2-$CeCl_3·7H_2O$ to synthesize CPOs via the addition of diethyl phosphite to aromatic isocyanates under heating or ultrasonication conditions.[10] Challenges still exist despite these recent advances, such as high catalyst loading, low yields of the desired products, long reaction times, limited scope of isocyanates, and harsh conditions. Therefore, the development of highly efficient catalysts for the preparation of CPOs under mild conditions is still strongly required.

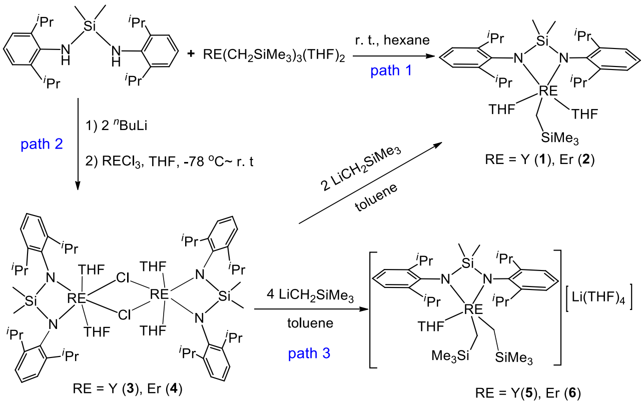
Bridged ancillary ligands have been widely used in rare-earth-metal complexes because such ligands have a powerful electronic and steric tuning capability to stabilize highly electrophilic rare-earth-metal ions, such as phenylene-bridged bis(*β*-diketiminate), carbon-bridged bis(thiol), piperazine-bridged bis (phenolate), pyridine-bridged bis(arylamido), and furan- and silylene-bridged ancillary ligands.[11] It is reported that group 4 complexes bearing silylene-bridged cyclopentadiene derivatives have good catalytic activities in propylene polymerization.[12] An yttrium complex with a chiral silicon-linked amido-indenyl ligand can catalyze the intramolecular hydroamination of olefins with high enantioselectivity.[13] We have found that rare-earth-metal amides with a silicon-bridged diamido ligand exhibit high catalytic properties for the cyclotrimerization or cyclodimerization of the isocyanates.[14] These results prompted us to explore the potential activity of these complexes as catalysts for C−P bond formation. Herein we will report newly synthesized neutral rare-earth-metal monoalkyl and anionic rare-earth-metal dialkyl complexes supported by a silicon-linked diarylamido ligand catalyze the additions of dialkyl phosphites to various isocyanates for the green synthesis of the CPO derivatives with a high efficiency.

■ RESULTS AND DISCUSSION

Synthesis and Structures of the Rare-Earth-Metal Alkyl Complexes and Chlorides. Neutral rare-earth-metal monoalkyl complexes $\mathbf{L}RE(CH_2SiMe_3)(THF)_2$ (RE = Y (**1**), Er (**2**); **L** = $(Me_2Si)(2,6\text{-}^iPr_2C_6H_3N)_2$) were synthesized in good yields (**1**, 82%; **2**, 80%) by the reactions of the rare-earth-metal trialkyl complexes $RE(CH_2SiMe_3)_3(THF)_2$ with an equimolar amount of the Me_2Si-linked diarylamine ligand $H_2\mathbf{L}$ via alkane elimination in *n*-hexane at room temperature (Scheme 2, path 1). Complexes **1** and **2** are sensitive to air and moisture and have a good solubility in *n*-hexane, toluene, and THF. The ^1H NMR (500 MHz, C_6D_6) spectrum of **1** clearly proves the presence of the $Y{-}CH_2SiMe_3$ moiety, exhibiting a doublet at −0.38 ppm ($^2J_{Y-H}$ = 3.5 Hz) due to coupling with the yttrium ion, which was further confirmed by a doublet at 28.3 ppm ($^1J_{Y-C}$ = 45.0 Hz) in the $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) spectrum (Figures S1 and S2 in the Supporting Information). The coupling constants are similar to those reported for yttrium alkyl complexes.[15]

Single-crystal X-ray analyses revealed that **1** and **2** adopt a distorted-square-pyramidal coordination geometry, with two nitrogen atoms of the ligand and two oxygen atoms of THF forming the basal plane and a carbon atom of the alkyl species occupying the apical position (Figure 1). It is interesting that the two Y−N(amido) bond lengths in **1** are not equivalent: one is 2.253(2) Å, while the other is 2.221(2) Å. The same phenomenon was also observed in the Y−O bond lengths (2.390(2) Å vs 2.3488(19) Å). The Y1−C35 bond length of 2.395(3) Å is comparable to those in a five-coordinate *β*-diketiminato yttrium alkyl complex (2.392(4), 2.394(3) Å),[15a] however, it is slightly shorter than that in an amidopyridinate-ligated yttrium alkyl complex (2.421(4) Å).[15c]

Scheme 2. Synthesis of the Rare-Earth-Metal Alkyl Complexes and Chlorides



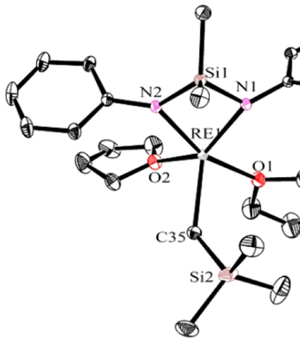


Figure 1. Representative molecular structure of complexes **1** and **2**. Hydrogen atoms and isopropyl groups on phenyl rings are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): for **1**, Y1−N1 2.253(2), Y1−N2 2.221(2), Y1−C35 2.395(3), Y1−O1 2.390(2), Y1−O2 2.3488(19), N(1)−Y(1)−N(2) 70.60(8), N(1)−Y(1)−C(35) 119.72(10), N(2)−Y(1)−C(35) 109.76(10), O(1)−Y(1)−C(35) 89.90(10), O(2)−Y(1)−C(35) 97.10(9); for **2**, Er1−N1 2.212(8), Er1−N2 2.175(9), Er1−C35 2.43(2), Er1−O1 2.396(8), Er1−O2 2.361(11), N(1)−Er(1)−N(2) 72.0(3), N(1)−Er(1)−C(35) 102.4(6), N(2)−Er(1)−C(35) 100.6(6), O(1)−Er(1)−C(35) 97.8(6), O(2)−Er(1)−C(35) 111.4(7).

The salt metathesis reactions of the ligand $H_2\mathbf{L}$ with ^{n}BuLi in THF at −78 °C, followed by treatment with 1 equiv of anhydrous $RECl_3$ at room temperature, after workup gave the centrosymmetric dinuclear rare-earth-metal chlorides $[\mathbf{L}RE(\mu\text{-}Cl)(THF)_2]_2$ (RE = Y (**3**), Er (**4**)) (Scheme 2, path 2). The structure of **4** was determined by single-crystal X-ray diffraction. Although the quality of the structural data of **3** is not satisfactory, the ^1H NMR (500 MHz, toluene-d_8) spectrum of **3** clearly proved the existence of the Me_2Si-linked dianiline group coordinated to the yttrium ions in a *N*,*N*-bidentate fashion (Figure S3). The molecular structure of **4** is shown in Figure 2. In the dinuclear rare-earth-metal chlorides, each metal ion is coordinated by two nitrogen atoms of the ligand, two oxygen atoms of THF, and two chlorides in a bridged form, displaying a distorted-octahedral geometry. Although **4** has a centrosymmetrical structure, the two Er−N(amido) bond lengths (2.220(4) Å vs 2.200(4) Å), Er−Cl bond lengths (2.7182(16) Å vs 2.7892(15) Å), and Er−O bond lengths (2.369(4) Å vs 2.424(4) Å) around the same metal center are not equal, which is similar to the case observed in **1** and **2**.

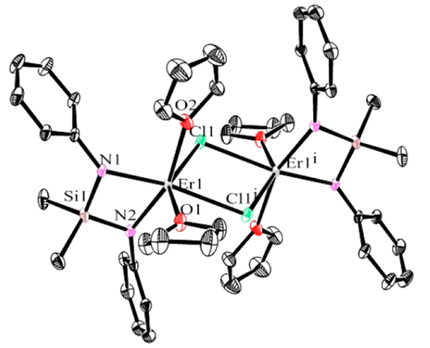


Figure 2. Molecular structure of complex **4**. Hydrogen atoms and isopropyl groups on phenyl rings are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Er1−N1 2.220(4), Er1−N2 2.200(4), Er1−Cl1 2.7182(16), Er1−Cl1^{i} 2.7892(15), Er1−O1 2.369(4), Er1−O2 2.424(4), N(1)−Er(1)−N(2) 73.05(14), Cl(1)−Y(1)−Cl^{i}(35) 73.47(5).

Treatment of dinuclear rare-earth-metal chlorides with 2 equiv of $LiCH_2SiMe_3$ in toluene at 0 °C afforded the rare-earth-metal monoalkyl complexes **1** and **2** in moderate yield (**1**, 57%; **2**, 59%). Due to the relatively low transformation efficiency in comparison to the alkane elimination, the preparation of **1** and **2** adopted path 1 in Scheme 2. When the amount of $LiCH_2SiMe_3$ was increased to 4 equiv, the reactions between the rare-earth-metal chlorides and organolithium $LiCH_2SiMe_3$ under the same conditions gave the discrete heterobimetallic rare-earth-metal dialkyl complexes $LRE(CH_2SiMe_3)_2(THF)Li(THF)_4$ (RE = Y (**5**), Er (**6**)) in 64% and 60% yields, respectively (Scheme 2, path 3). As shown in Figure 3, complexes **5** and **6** are discrete ion-pair rare-earth-metal dialkyl complexes, containing a bidentate diamido group $[(Me_2Si)(2,6\text{-}^{i}Pr_2C_6H_3N)_2]$, two alkyl groups CH_2SiMe_3, and a molecule of THF, forming a five-coordinate rare-earth-metal anionic species and four-THF-coordinated lithium cationic species. The coordination geometry of anionic rare-earth-metal complex **5** is not fundamentally different from that of its neutral counterpart **1**. The position of the molecule of THF in yttrium monoalkyl complex **1** is replaced by an alkyl group, forming the anionic yttrium dialkyl counterpart **5**. However, the bond lengths Y1−N1 2.288(3) Å and Y1−N2 2.282(3) Å in **5** are longer than those of 2.253(2) Å and 2.221(2) Å in **1**. Similarly, the bond lengths of Y−C(alkyl) 2.438(3) Å and 2.435(4) Å in **5** are much longer than that of 2.395(3) Å in **1**. The formation of **5** and **6** is similar to the reactions of $[Me_2Si(NLiPh)_2]$ with $RECl_3$, followed by treatment with CpNa to produce the anionic rare-earth-metal complexes $\{[Me_2Si(NPh)_2]LnCp_2\}\{Li(DME)_3\}$ (Ln = Yb, Sm).[16] The Y−N(amido) bond lengths in the range 2.288(3)−2.282(3) Å in **5** are comparable to those in the range 2.224(6)−2.318(6) Å in $[(Tp^{Me2})_2Y][((Me_3Si)_2N)_2Y(CH_2)SiMe_2N(SiMe_3)]$ (Tp = tris(pyrazolyl)borate).[17]

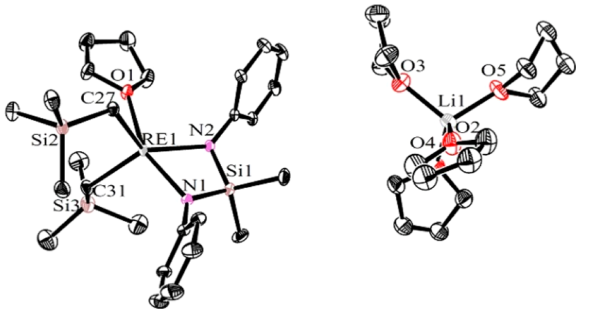
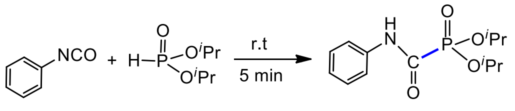


Figure 3. Representative molecular structure of complexes **5** and **6**. Hydrogen atoms and isopropyl groups on phenyl rings are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): for **5**, Y1−N1 2.288(3), Y1−N2 2.282(3), Y1−C27 2.438(3), Y1−C31 2.435(4), Y1−O1 2.438(3), N(1)−Y(1)−N(2) 69.51(10), N(1)−Y(1)−C(31) 108.54(13), N(2)−Y(1)−C(31) 122.88(12); for **6**, Er1−N1 2.279(6), Er1−N2 2.281(5), Er1−C27 2.411(7), Er1−C31 2.401(12), Er1−O1 2.432(5), N(1)−Er(1)−N(2) 70.0(2), N(1)−Er(1)−C(31) 109.1(11), N(2)−Er(1)−C(31) 121.3(6).

Catalytic Activity. The catalytic addition of diisopropyl phosphite to phenyl isocyanate for the preparation of diisopropyl anilinocarbonylphosphonate was employed as the model reaction in our initial screening of the newly synthesized catalysts, and the results are presented in Table 1. It is remarkable that, in the presence of 2 mol % of complex **1**, the addition product of **7a** could be quantitatively obtained in THF at room temperature within 5 min (entry 1). Decreasing the catalyst loading from 2 mol % to 0.1 mol % also afforded **7a** in excellent yields (entries 2−4). When the catalyst loading was decreased further to 0.05 mol %, the desired product was

Table 1. Optimization of the Reaction Conditions for the Addition of Diisopropyl Phosphite to Phenyl Isocyanate[a]



7a

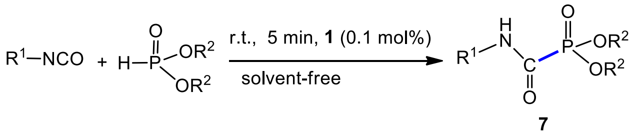
entry	cat. (mol %)	solvent	yield (%)[b]
1	**1** (2)	THF	99
2	**1** (1)	THF	99
3	**1** (0.5)	THF	99
4	**1** (0.1)	THF	98
5	**1** (0.05)	THF	47
6	**1** (0.1)	*n*-hexane	97
7	**1** (0.1)	toluene	98
8	**1** (0.1)	Et_2O	96
9[c]	**1** (0.1)	solvent-free	99
10	**2** (0.1)	solvent-free	95
11	**3** (0.1)	toluene	0
12	**4** (0.1)	toluene	0
13	**5** (0.1)	solvent-free	99
14	**6** (0.1)	solvent-free	94
15		solvent-free	0

[a] Reaction conditions: phenyl isocyanate (2.0 mmol), diisopropyl phosphite (2.0 mmol). [b] Isolated yields. [c] The addition sequence was isocyanate/diisopropyl phosphite/cat. with vigorous stirring under solvent-free conditions.

isolated in 47% yield (entry 5). It is worth noting that the catalytic system has a good compatibility with different solvents, such as *n*-hexane, toluene, and Et_2O (entries 6−8). To our delight, when the catalytic addition was carried out under solvent-free conditions, the carbamoylphosphonate product was isolated in 99% yield (entry 9). In sharp contrast to **1** and **2**, dinuclear rare-earth-metal chlorides **3** and **4** showed no activity in this catalytic reaction (entries 11 and 12). Anionic rare-earth-metal dialkyl complexes **5** and **6** can successfully promote the catalytic addition with the isolation of excellent yields of the product **7a**. In contrast to erbium catalysts, yttrium complexes **1** and **5** exhibited better catalytic efficiency (entries 9, 10, 13, and 14), suggesting that a rare-earth metal with a large ionic radius has a positive influence on the catalytic reaction. The addition of diisopropyl phosphite to phenyl isocyanate without the catalyst could not take place, and no product was observed under the same conditions (entry 15).

Next, the scopes of various isocyanates and dialkyl phosphites under the optimized conditions were investigated (Table 2). It is interesting to find that the isocyanates with either electron-donating or electron-withdrawing groups on the phenyl rings can smoothly react with diisopropyl phosphite to afford the corresponding carbamoylphosphates (**7b**−**k**) in good to high yields in the presence of 0.1 mol % of catalyst **1**. For example, the bulky 4-isopropyl and 2,6-diisopropyl phenylisocyanates could be used in the reaction, affording the products **7d**,**e** in 97% and 93% yields, respectively. Strongly electron withdrawing groups, such as nitro-, halogen (Cl, Br)-, and tosyl-substituted phenyl isocyanates, also worked well with diisopropyl phosphite, affording the products **7g**−**l** in 87−97% yields. Moreover, the catalyst **1** was also compatible with branched (isopropyl and *tert*-butyl), linear (ethyl), and cyclohexyl-substituted aliphatic isocyanates and the outputs of **7m**−**p** still remained in excellent efficiency (96−98% yields). In addition to diisopropyl phosphite, diethyl phosphite and dibenzyl phosphite were also suitable for the addition with alkyl- and aryl-substituted isocyanates, producing the corresponding carbamoylphosphate derivatives **7q**−**u** in 92−99% yields.

Table 2. Scope of the Isocyanates and Dialkyl Phosphites[a]

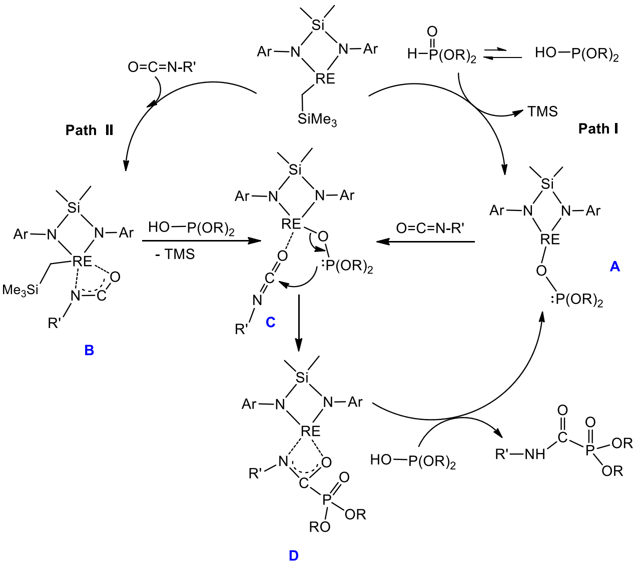


entry	R^1	R^2	product	yield (%)[a]
1	C_6H_5	^{i}Pr	**7a**	99
2	3-MeC_6H_4	^{i}Pr	**7b**	97
3	4-MeC_6H_4	^{i}Pr	**7c**	99
4	4-^{i}PrC_6H_4	^{i}Pr	**7d**	97
5	2,6-^{i}$Pr_2C_6H_3$	^{i}Pr	**7e**	93
6	4-$MeOC_6H_4$	^{i}Pr	**7f**	98
7	2-ClC_6H_4	^{i}Pr	**7g**	96
8	3-ClC_6H_4	^{i}Pr	**7h**	97
9	4-BrC_6H_4	^{i}Pr	**7i**	95
10[b]	4-$O_2NC_6H_4$	^{i}Pr	**7j**	87
11	3,4-$Cl_2C_6H_3$	^{i}Pr	**7k**	95
12	4-$MeC_6H_4SO_2$	^{i}Pr	**7l**	97
13	^{i}Pr	^{i}Pr	**7m**	97
14	^{t}Bu	^{i}Pr	**7n**	98
15	cyclohexyl	^{i}Pr	**7o**	98
16	$ClCH_2CH_2$	^{i}Pr	**7p**	96
17	C_6H_5	Et	**7q**	99
18	4-^{i}PrC_6H_4	Et	**7r**	97
19	3-ClC_6H_4	Et	**7s**	98
20	cyclohexyl	Bn	**7t**	92
21	4-$MeC_6H_4SO_2$	Bn	**7u**	94

[a] Reaction conditions unless specified otherwise: in a Schlenk reactor were placed isocyanates (2.0 mmol) and dialkyl phosphites (2.0 mmol) with vigorous stirring until dissolution before adding the catalyst **1** (2.0 μmol). Isolated yield. [b] Diisopropyl phosphites (2.4 mmol).

On the basis of the ^{1}H NMR monitoring control experiments (Figure S70) and previously reported mechanism studies of catalysis by rare-earth-metal complexes of the addition of dialkyl phosphites to C═N and C═O bonds[18] and cyclization of isocyanates,[14] a plausible catalytic mechanism was proposed (Scheme 3): the acid−base reaction between rare-earth-metal alkyl complexes and dialkyl phosphite (phosphonate as its tautomeric form) gave the intermediate **A**, which then formed isocyanate-coordinated intermediate **C** due to the strong oxytropism of the rare-earth-metal ions (path I). Meanwhile, the intermediate **C** can also be derived from the interaction of the intermediate **B** and dialkyl phosphite with the release of a molecule of TMS (path II). Electron deficiency on the carbon atom of isocyanate moiety in **C** led to the addition of the phosphorus atom of dialkyl phosphite, resulting in the formation of the intermediate **D**. Then the interaction between **D** and another dialkyl phosphite produced the final catalytic product CPOs and regenerated **A** to fulfill a catalytic cycle.

Scheme 3. Possible Mechanism for the Catalytic Addition



■ CONCLUSIONS

In summary, we have demonstrated that both neutral rare-earth-metal monoalkyl complexes and anionic rare-earth-metal dialkyl complexes supported by the silicon-linked diamido ligand can be synthesized through different pathways. Further studies show that these complexes displayed a high catalytic activity in the addition of dialkyl phosphites to a variety of isocyanates, providing a simple, mild, and highly efficient method for the formation of various carbamoylphosphate derivatives. Meanwhile, the rare-earth-metal alkyl complexes catalytic systems have the advantages of simple operation, high efficiency, low catalytic loadings, compatibility with a wide range of substrates, and proceeding under solvent-free conditions.

■ EXPERIMENTAL SECTION

Materials and Methods. All syntheses and manipulations of the air- and moisture-sensitive materials were performed under dry argon and an oxygen-free atmosphere, using standard Schlenk techniques or in a glovebox. All solvents (THF, *n*-hexane, and toluene) were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $RE(CH_2SiMe_3)_3(THF)_2$,[19] $RECl_3$,[20] $(Me_2Si)[(2,6\text{-}^iPr_2C_6H_3)NH]_2$,[21] and $LiCH_2SiMe_3$ (0.8 M solution in hexane) were prepared according to the reported methods. Solid isocyanates were used without further purification. Liquid isocyanates and diisopropyl, diethyl, and dibenzyl phosphites were purchased from Aldrich and distilled prior to use. Elemental analysis data were obtained on a PerkinElmer Model 2400 Series II elemental analyzer. HRMS measurements were conducted with an Agilent Model 6220 ESI-TOF mass spectrometer. ^1H, ^{13}C, and ^{31}P NMR data were obtained on a 300 MHz or a 500 MHz Bruker spectrometer. Chemical shifts (δ) are reported in ppm. The J values are reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400s spectrometer (measurements of KBr pellets were performed in a glovebox and protected by dry argon prior to IR determination). Melting points were measured with a SGWX-4 instrument.

Preparation of $LY(CH_2SiMe_3)(THF)_2$ (1). To a solution of $H_2\mathbf{L}$ (0.41 g, 1.00 mmol) in *n*-hexane (10.0 mL) was added a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.49 g, 1.00 mmol) in *n*-hexane (10.0 mL). The reaction mixture was stirred at room temperature for 4 h, and the solvent was evaporated under reduced pressure to about 8.0 mL. Colorless crystals were obtained after the solution was allowed to stand at 0 °C for several days (0.60 g, 82% yield). ^1H NMR (500 MHz, C_6D_6, ppm): δ 7.21 (d, 4H, J = 7.5 Hz, C_6H_3), 7.00 (t, J = 7.5 Hz, 2H, C_6H_3), 4.19 (br s, 4H, $CH(CH_3)_2$), 3.32 (t, J = 6.5 Hz, 8H, α-THF), 1.36 (br s, 24H, $CH(CH_3)_2$), 1.04−1.01 (m, 8H, β-THF), 0.38 (s, 6H, $Si(CH_3)_2$), 0.21 (s, 9H, $Si(CH_3)_3$), − 0.38 (d, $^2J_{Y-H}$ = 3.5 Hz, 2H, CH_2SiMe_3). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 150.1, 142.6, 123.4, 119.6, 69.9 (α-THF), 28.3 (d, $^1J_{Y-C}$ = 45.0 Hz), 27.6, 26.0, 25.1, 4.6 ($SiMe_2$). Anal. Calcd for $C_{38}H_{67}N_2O_2Si_2Y$: C, 62.60; H, 9.26; N, 3.84. Found: C, 62.96; H, 9.20; N, 3.84. IR (KBr pellets, cm^{-1}): ν 3061, 3026, 2963, 2871, 1917, 1859, 1796, 1620, 1586, 1461, 1439, 1383, 1358, 1325, 1255, 1195, 1110, 1054, 907, 882, 828, 786.

Preparation of $LEr(CH_2SiMe_3)(THF)_2$ (2). This complex was isolated as pink crystals in 80% yield by treatment of $Er(CH_2SiMe_3)_3(THF)_2$ (0.50 g, 0.87 mmol) with $H_2\mathbf{L}$ (0.36 g, 0.87 mmol) following a procedure similar to that for the preparation of **1**. Anal. Calcd for $C_{38}H_{67}N_2O_2Si_2Er$: C, 56.53; H, 8.36; N, 3.47. Found: C, 56.90; H, 8.37; N, 3.40. IR (KBr pellets, cm^{-1}): ν 3061, 3030, 2961, 2871, 1924, 1859, 1798, 1620, 1591, 1457, 1439, 1383, 1363, 1327, 1255, 1197, 1110, 1048, 907, 828, 786.

Preparation of $[LY(\mu\text{-}Cl)(THF)_2]_2$ (3). To a solution of $H_2\mathbf{L}$ (0.50 g, 1.22 mmol) in THF (10.0 mL) at −78 °C was added dropwise a solution of 1.6 M ^{n}BuLi (1.56 mL, 2.50 mmol) in *n*-hexane with rapid stirring. The mixture was slowly warmed to room temperature for 4 h; a THF suspension of YCl_3 (236 mg, 1.22 mmol) was then added to the mixture. The reaction mixture was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure to yield a pale yellow solid. Recrystallization from toluene afforded colorless crystals of **3** (0.71 g, 87% yield). ^1H NMR (500 MHz, toluene-d_8, ppm): δ 7.05 (s, 2H, C_6H_3), 7.01 (s, 4H, C_6H_3), 3.55 (s, 6H, α-THF), 3.49 (sept, J = 7.0 Hz, 4H, $CH(CH_3)_2$), 2.60 (s, 2H, α-THF), 1.44 (s, 8H, β-THF), 1.15 (d, J = 7.0 Hz, 24H, $CH(CH_3)_2$), 0.19 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (125 MHz, toluene-d_8, ppm): δ 144.6, 139.3, 124.5, 123.4, 67.8 (α-THF), 28.6, 25.7 (β-THF), 23.8, 0.03 ($SiMe_2$). Anal. Calcd for $C_{68}H_{112}N_4O_4Si_2Cl_2Y_2\cdot C_6H_{14}$: C, 61.69; H, 8.82; N, 3.89. Found: C, 61.78; H, 9.16; N, 3.76. IR (KBr pellets, cm^{-1}): ν 3075, 2963, 2874, 1852, 1622, 1461, 1439, 1383, 1360, 1351, 1331, 1262, 1193, 1088, 1043, 909, 804, 746.

Preparation of $[LEr(\mu\text{-}Cl)(THF)_2]_2$ (4). This complex was isolated as pink crystals in 77% yield by treatment of a solution of $H_2\mathbf{L}$ (0.50 g, 1.22 mmol) in THF with a solution of 1.6 M ^{n}BuLi (1.56 mL, 2.50 mmol) in *n*-hexane, followed by reaction with a THF suspension of $ErCl_3$ (333 mg, 1.22 mmol) following a procedure similar to that for the preparation of **3**. Anal. Calcd for $C_{68}H_{112}N_4O_4Si_2Cl_2Er_2\cdot C_6H_{14}$: C, 55.64; H, 7.95; N, 3.51. Found: C, 55.56; H, 8.18; N, 3.43. IR (KBr pellets, cm^{-1}): ν 3066, 2961, 2869, 2869, 1921, 1854, 1794, 1622, 1591, 1436, 1322, 1258, 1197, 1139, 1106, 1043, 911, 788.

Preparation of $LY(CH_2SiMe_3)_2(THF)Li(THF)_4$ (5). To a solution of **3** (0.50 g, 0.37 mmol) in toluene (5.0 mL) was added dropwise a solution of 0.8 M $LiCH_2SiMe_3$ (2.0 mL, 1.60 mmol) in hexane with rapid stirring at 0 °C. The mixture was stirred at room temperature for 8 h. The solvent was evaporated under reduced pressure to yield a viscous solid. Recrystallization from *n*-hexane afforded colorless crystals of **5** (0.48 g, 64% yield). ^1H NMR (500 MHz, C_6D_6, ppm): δ 7.35 (d, J = 7.5 Hz, 1H, C_6H_3), 7.06 (d, J = 7.5 Hz, 2H, $_6H_3$), 6.86 (t, J = 7.5 Hz, 2H, C_6H_3), 6.69 (t, J = 7.5 Hz, 1H, C_6H_3), 4.46 (br s, 2H, $CH(CH_3)_2$), 3.69 (br s, 2H, $CH(CH_3)_2$), 3.23 (s, 12H, α-THF), 1.49−1.04 (m, 36H, β-THF and $CH(CH_3)_2$), 0.42 (s, 6H, $Si(CH_3)_2$), 0.20 (s, 18H, $Si(CH_3)_3$), − 1.02 (s, 4H, CH_2SiMe_3). ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 152.2, 143.8, 123.8, 117.9, 68.5 (α-THF), 27.2, 26.7, 26.5 (β-THF), 25.1, 24.9, 4.1 ($SiMe_2$). Anal. Calcd for $C_{54}H_{102}LiN_2O_5Si_3Y\cdot(-2THF)$: C, 61.71; H, 9.68; N, 3.13. Found: C, 61.36; H, 9.29; N, 3.40. IR (KBr pellets, cm^{-1}): ν 2310, 1589, 1458, 1438, 1361, 1328, 1195, 1111, 1043, 906, 829, 786. The reaction of **3** with 2 equiv of $LiCH_2SiMe_3$ following a procedure similar to the preparation of **5** produced complex **1** in 57% yield.

Preparation of $LEr(CH_2SiMe_3)_2(THF)Li(THF)_4$ (6). This complex was isolated as pink crystals in 60% yield by treatment of **4** (0.50 g, 0.33 mmol) with 0.8 M $LiCH_2SiMe_3$ (1.8 mL, 1.44 mmol) following a procedure similar to that for the preparation of **5**. Anal. Calcd for $C_{54}H_{102}LiN_2O_5Si_3Er\cdot(-3THF)$: C, 55.95; H, 8.72; N, 3.11. Found: C, 56.25; H, 8.38; N, 3.45. IR (KBr pellets, cm^{-1}): ν 2345, 1589, 1456, 1438, 1358, 1328, 1253, 1195, 1111, 1043, 906, 829. The reaction of **4** with 2 equiv of $LiCH_2SiMe_3$ following a procedure similar to the preparation of **6** produced complex **2** in 59% yield.

General Procedure for the Addition of Dialkyl Phosphites to Isocyanates (7a as an Example). A mixture of phenyl isocyanate (2.0 mmol) and diisopropyl phosphite (2.0 mmol) was stirred for 1 min. Complex **1** (2.0 μmol) was then added, and the reaction mixture was rapidly stirred for 5 min. The clear liquid mixture changed slowly to a white solid during the reaction. Water was added, and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure after filtration. The product **7a** was recrystallized from a mixture of *n*-hexane and ethyl acetate (0.56 mg, 99% yield).

X-ray Crystallographic Analyses. Suitable crystals of complexes **1** and **4**−**6** were sealed in thin-walled glass capillaries under argon. 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.[22] 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.[23] All hydrogen atoms were refined using a riding model.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00627.

Characterization data of compounds **7a−u**, ^{1}H, ^{13}C, and ^{31}P NMR spectra for compounds **7a−u**, and crystallographic data for complexes **1**, **2**, and **4−6** (PDF)

Accession Codes

CCDC 1969143−1969144, 2030786−2030787, and 2047086 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Gu, X.; Zhang, L.; Zhu, X.; Wang, S.; Zhou, S.; Wei, Y.; Zhang, G.; Mu, X.; Huang, Z.; Hong, D.; Zhang, F. Synthesis of Bis(NHC)-Based CNC-Pincer Rare-Earth-Metal Amido Complexes and Their Application for the Hydrophosphination of Heterocumulenes. *Organometallics* **2015**, *34*, 4553−4559. (b) Behrle, A. C.; Schmidt, J. A. R. Insertion Reactions and Catalytic Hydrophosphination of Heterocumulenes using α-Metalated *N,N*-Dimethylbenzylamine Rare-Earth-Metal Complexes. *Organometallics* **2013**, *32*, 1141−1149. (c) Zhang, W.; Nishiura, M.; Mashiko, T.; Hou, Z. Half-Sandwich *o-N,N*-Dimethylaminobenzyl Complexes over the Full Size Range of Group 3 and Lanthanide Metals. Synthesis, Structural Characterization, and Catalysis of Phosphine P−H Bond Addition to Carbodiimides. *Chem. - Eur. J.* **2008**, *14*, 2167−2179. (d) Demmer, C. S.; Krogsgaard-Larsen, N.; Bunch, L. Review on Modern Advances of Chemical Methods for the Introduction of a Phosphonic Acid Group. *Chem. Rev.* **2011**, *111*, 7981−8006. (e) Zhao, D.; Wang, R. Recent developments in metal catalyzed asymmetric addition of phosphorus nucleophiles. *Chem. Soc. Rev.* **2012**, *41*, 2095−2108.

(2) (a) Reich, R.; Katz, Y.; Hadar, R.; Breuer, E. Carbarnoylphosphonate matrix metalloproteinase inhibitors 3: In vivo evaluation of cyclopentylcarbamoylphosphonic acid in experimental metastasis and angiogenesis. *Clin. Cancer Res.* **2005**, *11*, 3925−3929. (b) Frant, J.; Veerendhar, A.; Chernilovsky, T.; Nedvetzki, S.; Vaksman, O.; Hoffman, A.; Breuer, E.; Reich, R. Orally Active, Antimetastatic, Nontoxic Diphenyl Ether-Derived Carbamoylphosphonate Matrix Metalloproteinase Inhibitors. *ChemMedChem* **2011**, *6*, 1471−1477. (c) Salomon, C. J.; Breuer, E. Facile "one-pot" preparation of phosphonothiolformates. Useful reagents for the synthesis of carbamoylphosphonates. *Synlett.* **2000**, *6*, 815−816. (d) Hoffman, A.; Qadri, B.; Frant, J.; Katz, Y.; Bhusare, S. R.; Breuer, E.; Hadar, R.; Reich, R. Carbamoylphosphonate matrix metalloproteinase inhibitors 6: cis-2-aminocyclohexylcarbamoylphosphonic acid, a novel orally active antimetastatic matrix metalloproteinase-2 selective inhibitor - Synthesis and pharmacodynamic and pharmacokinetic analysis. *J. Med. Chem.* **2008**, *51*, 1406−1414.

(3) (a) Breuer, E.; Salomon, C. J.; Katz, Y.; Chen, W.; Lu, S.; Röschenthaler, G.-V.; Hadar, R.; Reich, R. Carbamoylphosphonates, a new class of in vivo active matrix metalloproteinase inhibitors. 1. Alkyl- and cycloalkylcarbamoylphosphonic acids. *J. Med. Chem.* **2004**, *47*, 2826−2832. (b) Farkas, E.; Katz, Y.; Bhusare, S.; Reich, R.; Röschenthaler, G.-V.; Königsmann, M.; Breuer, E. Carbamoylphosphonate-based matrix metalloproteinase inhibitor metal complexes: solution studies and stability constants. Towards a zinc-selective binding group. *JBIC, J. Biol. Inorg. Chem.* **2004**, *9*, 307−315. (c) Reich, R.; Hoffman, A.; Veerendhar, A.; Maresca, A.; Innocenti, A.; Supuran, C. T.; Breuer, E. Carbamoylphosphonates Control Tumor Cell Proliferation and Dissemination by Simultaneously Inhibiting Carbonic Anhydrase IX and Matrix Metalloproteinase-2. Toward

Nontoxic Chemotherapy Targeting Tumor Microenvironment. *J. Med. Chem.* **2012**, *55*, 7875−7882. (d) Li, N. G.; Shi, Z. H.; Tang, Y. P.; Lian, Y.; Duan, J. A. Discovery of Selective Small Molecular TACE Inhibitors for the Treatment of Rheumatoid Arthritis. *Curr. Med. Chem.* **2012**, *19*, 2924−2956.

(4) Sprecher, M.; Kost, D. The Schmidt Reaction of Dialkyl Acylphosphonates. *J. Am. Chem. Soc.* **1994**, *116*, 1016−1026.

(5) Reetz, T.; Chadwick, D. H.; Hardy, E. E.; Kaufman, S. Carbamoylphosphonates. *J. Am. Chem. Soc.* **1955**, *77*, 3813−3816.

(6) (a) Harel, E.; Rubinstein, A.; Chen, W.; Breuer, E.; Tirosh, B. Aminoalkylcarbamoylphosphonates reduce TNF alpha release from activated immune cells. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6518−6523. (b) Veerendhar, A.; Cohen, S.; Frant, J.; Supuran, C. T.; Reich, R.; Breuer, E. Synthesis of Enantiomeric Aminoalkylcarbamoylphosphonates and Their Evaluation as Dual-Action Anticancer MMP and Carbonic Anhydrase Inhibitors. *Heteroat. Chem.* **2015**, *26*, 257−269. (c) Beylis, I.; Frant, J.; Mussai, N.; Reich, R.; Breuer, E. Carbamoylphosphonates Part 7. An efficient method for the synthesis of hindered carbamoylphosphonates using 4-nitrophenoxycarbonylphosphonate diesters. *Tetrahedron Lett.* **2008**, *49*, 2875−2877.

(7) (a) Wu, Y. H.; Wu, Q. L.; Wang, W. P.; Wang, X. C.; Quan, Z. J. Iodine-Promoted Rapid Construction of Carbamoylphosphonates from Phosphinecarboxamides. *Adv. Synth. Catal.* **2018**, *360*, 2382−2388. (b) Wu, Q. L.; Chen, X. G.; Huo, C. D.; Wang, X. C.; Quan, Z. J. Electrochemically driven P−H oxidation and functionalization: synthesis of carbamoylphosphonates from phosphoramides and alcohols. *New J. Chem.* **2019**, *43*, 1531−1535.

(8) Fox, R. B.; Venezky, D. L. The Base-catalyzed Reaction of Dialkyl Phosphonates with Isocyanates. *J. Am. Chem. Soc.* **1956**, *78*, 1661−1663.

(9) Kaboudin, B.; Zahedi, H. A Novel and Convenient Method for Synthesis of Carbamoyl and Thiocarbamoyl Phosphonates. *Heteroat. Chem.* **2009**, *20*, 250−253.

(10) Rao, D. S.; Madhava, G.; Rasheed, S.; Basha, S. K. T.; Devamma, M. N. L.; Raju, C. N. $CeCl_3.7H_2O$-SiO_2 Catalyzed Ultrasonicated Solvent-free Synthesis of Carbamoyl/ Carbamothioyl phosphonates and Antimicrobial Activity Evaluation. *Phosphorus, Sulfur Silicon Relat. Elem.* **2015**, *190*, 574−584.

(11) (a) Yao, Y. M.; Xu, X. P.; Liu, B.; Zhang, Y.; Shen, Q. Carbon-bridged bis(phenolato)lanthanide alkoxides: Syntheses, structures, and their application in the controlled polymerization of epsilon-caprolactone. *Inorg. Chem.* **2005**, *44*, 5133−5140. (b) Konkol, M.; Kondracka, M.; Voth, P.; Spaniol, T. P.; Okuda, J. Rare-earth metal alkyl and hydrido complexes containing a thioether-functionalized bis(phenolato) ligand: Efficient catalysts for olefin hydrosilylation. *Organometallics* **2008**, *27*, 3774−3784. (c) Zhou, S.; Wang, S.; Yang, G.; Li, Q.; Zhang, L.; Yao, Z.; Zhou, Z.; Song, H. Synthesis, Structure, and Diverse Catalytic Activities of [Ethylenebis(indenyl)]lanthanide(III) Amides on N-H and C-H Addition to Carbodiimides and ε-Caprolactone Polymerization. *Organometallics* **2007**, *26*, 3755−3761. (d) Sun, S.; Sun, Q.; Zhao, B.; Zhang, Y.; Shen, Q.; Yao, Y. Unexpected C−H Bond Activation Promoted by Bimetallic Lanthanide Amido Complexes Bearing a META-Phenylene-Bridged Bis(β-diketiminate) Ligand. *Organometallics* **2013**, *32*, 1876−1881. (e) Zhang, Z. J.; Xu, X. P.; Sun, S.; Yao, Y. M.; Zhang, Y.; Shen, Q. Facile syntheses of bimetallic ytterbium bisamides stabilized by a flexible bridged bis(phenolato) ligand and the high activity for the polymerization of L-lactide. *Chem. Commun.* **2009**, *47*, 7414−7416. (f) Zimmermann, M.; Tönroos, K. W.; Anwander, R. Alkyl migration and an unusual tetramethylaluminate coordination mode: Unexpected reactivity of organolanthanide imino-amido-pyridine complexes. *Angew. Chem., Int. Ed.* **2007**, *46*, 3126−3130. (g) Qian, C.; Zhu, D. Studies on Organolanthanide Complexes.55. Synthesis of Furan-Bridged Bis(cyclopentadienyl) lanthanide and Yttrium Chlorides, and Ligand and Metal Tuning of Reactivity of Organolanthanide Hydrides (in-situ). *J. Chem. Soc., Dalton Trans.* **1994**, *10*, 1599−1603. (h) Dreier, T.; Unger, G.; Erker, G.; Wibbeling, B.; Fröhlich, R. Group 4 metallocenes containing hetaryl substituents at their pi-ligands: synthesis and characterization of the parent bis[2-(2-furyl)indenyl]zirconocene system. *J. Organomet. Chem.* **2001**, *622*, 143−148. (i) Wang, B.; Nishiura, M.; Cheng, J.; Hou, Z. Half-sandwich scandium boryl complexes bearing a silylene-linked cyclopentadienyl-amido ligand. *Dalton Trans.* **2014**, *43*, 14215−14218.

(12) Veghini, D.; Henling, L. M.; Burkhardt, T. J.; Bercaw, J. E. Mechanisms of Stereocontrol for Doubly Silylene-Bridged C_s- and C_1-Symmetric Zirconocene Catalysts for Propylene Polymerization. Synthesis and Molecular Structure of $Li_2[(1,2\text{-}Me_2Si)_2\{C_5H_2\text{-}4\text{-}(1R,2S,5R\text{-menthyl})\}\{C_5H\text{-}3,5\text{-}(CHMe_2)_2)\}]\cdot 3THF$ and $[(1,2\text{-}Me_2Si)_2\{\eta^5\text{-}C_5H_2\text{-}4\text{-}(1R,2S,5R\text{-menthyl})\}\{\eta^5\text{-}C_5H\text{-}3,5\text{-}(CHMe_2)_2\}]\text{-}ZrCl_2$. *J. Am. Chem. Soc.* **1999**, *121*, 564−573.

(13) Chai, Z.; Hua, D.; Li, K.; Chu, J.; Yang, G. A novel chiral yttrium complex with a tridentate linked amido-indenyl ligand for intramolecular hydroamination. *Chem. Commun.* **2014**, *50*, 177−179.

(14) (a) Wu, Y.; Wang, S.; Zhu, X.; Yang, G.; Wei, Y.; Zhang, L.; Song, H. Synthesis, Characterization, and Catalytic Activity of Rare Earth Metal Amides Supported by a Diamido Ligand with a CH_2SiMe_2 Link. *Inorg. Chem.* **2008**, *47*, 5503−5511. (b) Zhu, X.; Fan, J.; Wu, Y.; Wang, S.; Zhang, L.; Yang, G.; Wei, Y.; Yin, C.; Zhu, H.; Wu, S.; Zhang, H. Synthesis, Characterization, Selective Catalytic Activity, and Reactivity of Rare Earth Metal Amides with Different Metal-Nitrogen Bonds. *Organometallics* **2009**, *28*, 3882−3888.

(15) (a) Zhu, X.; Li, Y.; Guo, D.; Wang, S.; Wei, Y.; Zhou, S. Versatile reactivities of rare-earth metal dialkyl complexes supported by a neutral pyrrolylfunctionalized β-diketiminato ligand. *Dalton Trans.* **2018**, *47*, 3947−3957. (b) Guo, L. P.; Zhu, X. C.; Zhang, G. C.; Wei, Y.; Ning, L. X.; Zhou, S. L.; Feng, Z. J.; Wang, S. W.; Mu, X. L.; Chen, J.; Jiang, Y. Z. Synthesis and Characterization of Organo-Rare-Earth Metal Monoalkyl Complexes Supported by Carbon σ-Bonded Indolyl Ligands: High Specific Isoprene 1,4-*Cis* Polymerization Catalysts. *Inorg. Chem.* **2015**, *54*, 5725−5731. (c) Karpov, A. V.; Shavyrin, A. S.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A. Reactions of Bis(alkyl)yttrium Complexes Supported by Bulky *N,N* Ligands with 2,6-Diisopropylaniline and Phenylacetylene. *Organometallics* **2012**, *31*, 5349−5357.

(16) Zhou, L.; Yao, Y.; Li, C.; Zhang, Y.; Shen, Q. Synthesis and Characterization of a Series of New Lanthanide Derivatives Supported by Silylene-Bridged Diamide Ligands and Their Catalytic Activities for the Polymerization of Methyl Methacrylate. *Organometallics* **2006**, *25*, 2880−2885.

(17) Han, F.; Zhang, J.; Yi, W.; Zhang, Z.; Yu, J.; Weng, L.; Zhou, X. γ-Deprotonation of Anionic Bis(trimethylsilyl)amidolanthanide Complexes with a Countered $[(Tp^{Me2})_2Ln]^+$ Cation. *Inorg. Chem.* **2010**, *49*, 2793−2798.

(18) (a) Wu, Q. M.; Zhou, J.; Yao, Z. G.; Xu, F.; Shen, Q. Lanthanide Amides $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ Catalyzed Hydrophosphonylation of Aryl Aldehydes. *J. Org. Chem.* **2010**, *75*, 7498−7501. (b) Zhu, X.; Wang, S.; Zhou, S.; Wei, Y.; Zhang, L.; Wang, F.; Feng, Z.; Guo, L.; Mu, X. Lanthanide Amido Complexes Incorporating Amino-Coordinate-Lithium Bridged Bis(indolyl) Ligands: Synthesis, Characterization, and Catalysis for Hydrophosphonylation of Aldehydes and Aldimines. *Inorg. Chem.* **2012**, *51*, 7134−7143.

(19) Lappert, M. F.; Pearce, R. Stable silylmethyl and neopentyl complexes of scandium(III) and yttrium(III). *J. Chem. Soc., Chem. Commun.* **1973**, *4*, 126.

(20) Taylor, M. D.; Carter, C. P. Preparation of Anhydrous Lanthanide Halides, Especially Iodides. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387−391.

(21) (a) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. Synthesis and Structural Characterization of Manganese(II) Derivatives of the Bulky, Chelating Bis(amido) Ligands $[(NMes)_2SiMe_2]^{2-}$ and $[DippNCH_2CH_2NDipp]^{2-}$, Their Neutral Amine Precursors, and Their Lithium Salts (Mes = 2,4,6-$Me_3C_6H_2$;Dipp = 2,6-*i*-$Pr_2C_6H_3$). *Inorg. Chem.* **1991**, *30*, 2487−2494. (b) Day, B. M.; Pugh, T.; Hendriks, D.; Guerra, C. F.; Evans, D. J.; Bickelhaupt, F. M.; Layfield, R. A. Normal-to-Abnormal

Rearrangement and NHC Activation in Three-Coordinate Iron(II) Carbene Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 13338−13341.

(22) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(23) (a) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997. (b) Sheldrick, G. M. SHELXT-Integrated space-group and crystals-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3−8. (c) Dolomanov, O. V. L.; Bourhis, J. R.; Gildea, J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339−341.