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# Insertion Reactions and Catalytic Hydrophosphination of Heterocumulenes using α-Metalated *N,N*-Dimethylbenzylamine Rare-Earth-Metal Complexes

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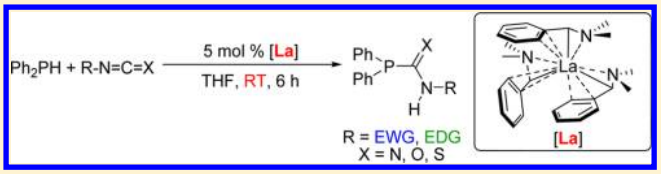
Supporting Information

**ABSTRACT:** The reactivity of homoleptic α-metalated dimethylbenzylamine lanthanide complexes (α-Ln(DMBA)$_3$; Ln = La, Y; DMBA = α-deprotonated dimethylbenzylamine) was probed through a series of stoichiometric insertion and catalytic hydrophosphination reactions. Both rare-earth-metal species inserted 3 equiv of various carbodiimides to form the corresponding homoleptic amidinates. α-La(DMBA)$_3$ was also found to be a useful precatalyst for the room-temperature hydrophosphination of heterocumulenes to form phosphaguanidines, phosphaureas, and phosphathioureas in moderate to excellent isolated yields. Furthermore, through a series of stepwise stoichiometric protonation and insertion reactions, a plausible mechanism for the hydrophosphination catalysis was investigated.




## INTRODUCTION

In the ever-growing discipline of catalysis, the improvement of carbon−heteroatom bond-forming reactions remains at the forefront. The effective catalysis of hydroamination,[1−3] hydrosilylation,[4−6] and hydrophosphination[7−10] is very attractive, due to the 100% atom economy involved in these reactions.[11] In contrast to the myriad reported catalysts for hydroamination and hydrosilylation reactions, the number of known hydrophosphination catalysts remains small, although they span the entire periodic table, with several reports involving late transition metals.[10,12−17] Early-metal catalysts, such as those of Waterman and Mindiola, have been utilized in the intermolecular hydrophosphination of alkynes.[18,19] Main-group metals can also be effective, as noted in Cui, Stephan, and Hill's reports on alkali-metal- and alkaline-earth-metal-catalyzed hydrophosphination reactions.[8,20,21] Furthermore, the Marks and Hou groups have shown that even f elements can be employed, as demonstrated in the hydrophosphination of olefins and carbodiimides using constrained-geometry lanthanide catalysts.[22,23] We were especially intrigued by the use of lanthanides, due to the various possible advantages available with these metals, such as their electrophilicities, the ability to tune the steric environment about these metal centers through a proper choice of supporting ligands, and their absence of unproductive oxidative addition/reductive elimination reaction pathways.

Catalytic hydrophosphination of an unsaturated species yields product phosphines with one more substituent than the related reactant (e.g., a secondary phosphine is converted to a tertiary phosphine). In addition to its atom efficiency, this reaction serves as a convenient way to make unsymmetrically substituted phosphines (e.g., $R_2PR'$; $R \neq R'$). The hydrophosphination products are valuable, due to their utility in various applications such as use as ligands for the stabilization of metals[24] and in medicine,[25] complex organic synthesis,[26] and materials chemistry.[27] The hydrophosphination of heterocumulenes has recently come under scrutiny as a convenient means to synthesize phosphorus analogues of guanidines, ureas, thioureas, and amidines.[28−33] Early investigations demonstrated that alkali-metal amides serve as catalysts for the hydrophosphination of carbodiimides,[34] while recent work has shown that constrained-geometry lanthanide catalysts also effect this transformation but require elevated temperatures (80 °C).[23] The product phosphaguanidines are known to be a versatile ligand class for Al, Y, La, Ti, Zr, Nb, Cu, and Zn species with broadly tunable properties.[35−38] Direct synthesis of phosphaguanidines from phosphines and carbodiimides does not work; therefore, metal-catalyzed hydrophosphination of carbodiimides, in which the P−H bond is added across the diimine, reducing the bond order by 1, represents a useful new method to produce these compounds.

Although Hou has shown that silyl-bridged cyclopentadienyl-amido lanthanide complexes efficiently catalyze the hydrophosphination of carbodiimides, these reactions required elevated temperatures for catalysis.[23] To date, there have been no reports of successful hydrophosphination of heterocumulenes at room temperature using a rare-earth-metal catalyst. As our recent efforts have focused on the production of new lanthanide complexes,[39] we set out to explore their possible utility in catalytic hydrophosphination reactions. Herein, we report the room-temperature hydro-

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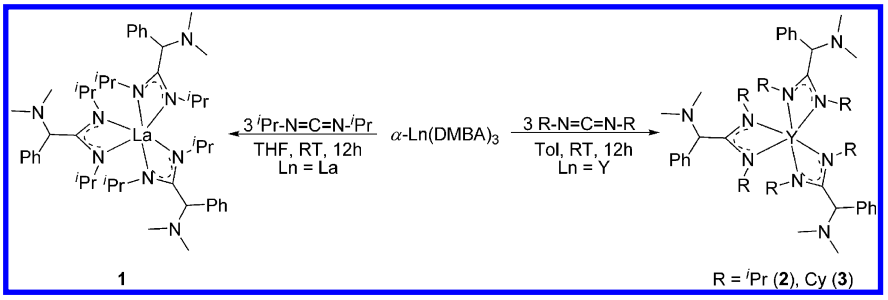
**Scheme 1. Stoichiometric Insertion of Carbodiimides**




phosphination of carbodiimides and isocyanates using homoleptic $\alpha$-metalated *N,N*-dimethylbenzylamine (DMBA) rare-earth complexes.

## RESULTS AND DISCUSSION

We recently reported the synthesis and preliminary protonolysis reactivity of a new class of non-cyclopentadienyl homoleptic rare-earth-metal complexes utilizing exclusively $\alpha$-metalated dimethylbenzylamine supporting ligands.[39] In our ongoing experiments, we sought to expand the reactivity scope of the $\alpha$-Ln(DMBA)$_3$ (Ln = La, Y) complexes by investigating stoichiometric insertion reactions, as well as the related catalytic processes utilizing both insertion and protonolysis reactions. As such, complex **1** was synthesized via the stoichiometric reaction of $\alpha$-La(DMBA)$_3$ with 3 equiv of *N,N′*-diisopropylcarbodiimide in THF at ambient temperature (Scheme 1). Over the course of 12 h, this reaction underwent a color change from orange-red to golden yellow. The product was isolated from a concentrated solution of diethyl ether as a microcrystalline powder. Its NMR spectrum at ambient temperature was broad and uninterpretable, indicating significant fluxionality. When the temperature was raised to 78 °C, the spectrum sharpened and was consistent with the insertion product **1**. We attribute the fluxional behavior at ambient temperature to slow intramolecular ligand exchange processes in which the $NMe_2$ unit is transiently coordinated to the metal center instead of one of the amidinate nitrogen donor atoms. The overall composition was further supported by elemental analysis data.

Two related yttrium complexes (**2** and **3**; Scheme 1) were prepared in a manner similar to that used for **1**. As in the previous case, each of these two complexes exhibited fluxional NMR spectra at room temperature that sharpened nicely at elevated temperatures. Thus, we assigned **2** and **3** structures analogous to that of **1**, with compositions that were confirmed by elemental analysis data. Furthermore, for the cyclohexyl derivative (**3**), we were able to obtain X-ray-quality crystals from a concentrated solution of pentane at room temperature. The X-ray structure of **3** revealed a homoleptic tris-amidinate complex (Figure 1). To accurately describe the geometry of **3**, the torsion angle N1−Q1−Q2−N2, where Q1 and Q2 are centroids formed by the $N_1N_4N_7$ and $N_2N_5N_8$ planes from Figure 1, was determined. A perfect trigonal prism and octahedron will have torsion angles of 0 and 60°, respectively. In the case of **3**, the torsion angle N1−Q1−Q2−N2 is 28.15° and compares well to those of other yttrium guanidinates: Y[(N$^i$Pr)$_2$CNMe$_2$]$_3$ (20.77°) and Y[(N$^i$Pr)$_2$CNEt$_2$]$_3$ (21.43°).[40] The Ln−N bond distances vary from 2.371(3) to 2.405(4) Å and are also quite comparable to those of other amidinate and guanidinate complexes: Y$_2$[Me$_3$SiNC(Ph)N-(CH$_2$)$_3$NC(Ph)NSiMe$_3$]$_2$ (2.307(2)−2.354(2) Å), Y[$^t$BuNC-(CH$_3$)N$^t$Bu]$_3$ (2.379(3)−2.389(3) Å), Y[(N$^i$Pr)$_2$CNMe$_2$]$_3$ (2.362(2)−2.373(2) Å), and (C$_5$H$_5$)$_2$Y[$^i$PrNC(N$^i$Pr$_2$)N$^i$Pr] (2.316(3)−2.321(3) Å).[40−43]

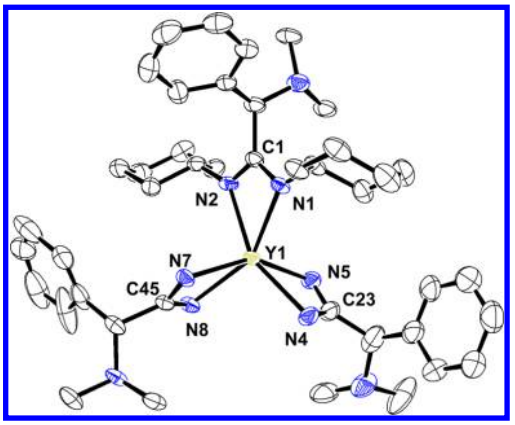
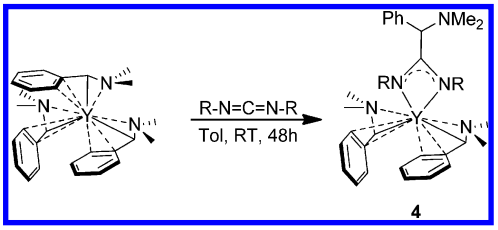



**Figure 1.** ORTEP diagram of **3**, with cyclohexyl groups from two ligands removed for clarity (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (deg): Y1−N1 = 2.393(3), Y1−N2 = 2.383(3); N1−Y1−N2 = 55.8(1).

Further derivatives of these insertion products were explored through two additional reactants: bis(trimethylsilyl)-carbodiimide and *N,N′*-di-*tert*-butylcarbodiimide. The latter showed no insertion into the Ln−C bond for either La or Y even at elevated temperatures, while the former inserted only 1 equiv of the carbodiimide, yielding complex **4** (Ln = Y) (Scheme 2). In the NMR spectrum of **4**, the benzyl amidinate

**Scheme 2. Synthesis of *N,N*-Dimethylbenzylamine Amidinate 4 (R = SiMe$_3$)**




contained three aryl resonances (7.47, 7.20, and 7.09 ppm) that were shifted significantly from those of the phenyl group of the dimethylbenzylamine ligand (7.24, 6.64, and 6.25 ppm). Also, the methine hydrogen of the newly formed amidinate ligand displayed a doublet with $^4J_{Y-H}$ = 1.9 Hz, while the methine of the DMBA ligand was a broad singlet. The $^{13}C\{^1H\}$ NMR of **4** displayed two doublets with a coupling constant of $^3J_{Y-C}$ = 4.8 Hz for the methine carbon of the amidinate ligand and $^1J_{Y-C}$ = 6.7 Hz for the methine carbon of the dimethylbenzylamine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ligand. These values are well within the wide range of coupling constants observed previously for yttrium nonmetallocene complexes.[44,45] The composition of **4** was also confirmed by X-ray crystallography, verifying the presence of one amidinate and two DMBA ligands bound to yttrium (Figure 2).

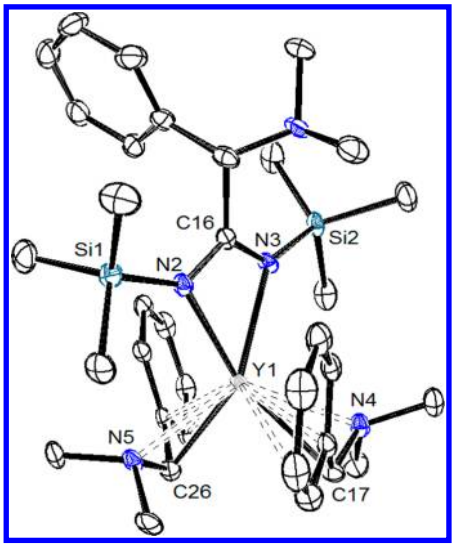


**Figure 2.** ORTEP diagram of **4** (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (deg): Y1−C17 = 2.490(3), Y1−C26 = 2.470(3), Y1−N2 = 2.377(2), Y1−N3 = 2.367(2), Y1−N4 = 2.487(3), Y1−N5 = 2.477(2), C16−N2 = 1.332(4), C16−N3 = 1.326(4); N2−Y1−N3 = 57.57(8), N2−C16−N3 = 118.5(3).

In a recent report, Hou and co-workers demonstrated that [{$Me_2Si(C_5Me_5)(NC_6H_2Me_3$-2,4,6)}La($CH_2C_6H_4NMe_2$-*o*)(thf)] functioned as a useful precatalyst for the hydrophosphination of a variety of carbodiimides at elevated temperatures (80 °C).[23] Given the results involving carbodiimide insertion reactions presented herein and our previous investigation into protonolysis reactions of *α*-Ln(DMBA)$_3$,[39] we felt that these new complexes were perfectly suited for use in catalytic hydrophosphination reactions. To test this hypothesis, we first added *N*,*N*′-diisopropylcarbodiimide to a solution of *α*-La(DMBA)$_3$ (5 mol %) and THF at room temperature, followed by the addition of 1 equiv of diphenylphosphine. While we did observe excellent conversion to the phosphaguanidine product, in accordance with the aforementioned results, this product was contaminated with the amidine $^{i}$PrN═C(NH$^{i}$Pr)CHPhNMe$_2$, which was likely formed by insertion of the carbodiimide into the La−DMBA bond, followed by subsequent protonolysis by $Ph_2PH$. Thus, this order of addition of reactants is limited to a maximum yield of 85% due to the initial formation of the insertion product **1**. Therefore, the order of addition was reversed in our subsequent experiments; that is, diphenylphosphine was added to *α*-La(DMBA)$_3$ followed by the *N*,*N*′-diisopropylcarbodiimide. Additionally, 1.15 equiv of $Ph_2PH$ was used to offset the amount consumed in activation of the precatalyst. Using this reversed order of addition, we found that DMBA-H was produced (via initial protonolysis of *α*-La(DMBA)$_3$ by $Ph_2PH$) instead of the amidine observed previously, and this byproduct was much more easily removed from the desired phosphaguanidines, improving isolated yields greatly. In order to confirm that this reaction required a catalyst to proceed, we investigated various control experiments. Attempted hydrophosphination with omission of *α*-La(DMBA)$_3$ resulted in no hydrophosphination product, even after the reaction mixture was heated to 90 °C for 48 h. To investigate the role of general Lewis or Brønsted acids, we substituted catalytic quantities of $LaCl_3$ or triflic acid, respectively. Use of $LaCl_3$ resulted in no change to the starting materials, while triflic acid yielded at least three uncharacterized products, none of which had NMR spectra corresponding to the desired hydrophosphination products.

Prior to full-scale catalytic screening, we additionally investigated a series of NMR-scale catalyses using [$D_8$]THF, in order to determine the optimal conditions for this reaction. There was a distinct color change upon addition of *N*,*N*′-diisopropylcarbodiimide to the mixture of *α*-La(DMBA)$_3$ and diphenylphosphine at room temperature. After 10 min, $^1$H NMR spectroscopy indicated that the reaction was >90% complete. For this and various other heterocumulenes, it was found that the reaction was essentially complete after 6 h at room temperature in THF. Noncoordinating reaction solvents such as $C_6D_6$ and $C_7D_8$ were screened, but no catalytic activity was observed. Alternate lanthanide complexes, such as *α*-Y(DMBA)$_3$ and *α*-Ce(DMBA)$_3$, demonstrated moderate catalytic activity (42% and 40% with diisopropylcarbodiimide, respectively), but both proved to be inferior to *α*-La(DMBA)$_3$. This was attributed to the decomposition of *α*-Y(DMBA)$_3$ and *α*-Ce(DMBA)$_3$ in THF, as noted in our previous report.[39]

To further develop the substrate scope of this catalytic reaction, hydrophosphination of a wide range of heterocumulenes was undertaken (Table 1). Additionally, a few commercially available phosphines were investigated. Hydrophosphination of unhindered carbodiimides was very efficient, and the resulting phosphaguanidines (**6a**,**b**) were isolated in excellent yields. In contrast, attempted hydrophosphination of *N*,*N*′-di-*tert*-butylcarbodiimide with diphenylphosphine did not result in production of the desired phosphaguanidine; instead, only starting materials were observed. This is consistent with the stoichiometric insertion results, where *N*,*N*′-di-*tert*-butylcarbodiimide was unable to insert because of the larger steric bulk of the *tert*-butyl groups. The hydrophosphination reaction also worked well with isocyanates and isothiocyanates, and it was tolerant of both electron-withdrawing and electron-donating nitrogen substituents on these heterocumulenes (**6c**−**l**). In fact, for most of the isocyanates, NMR spectroscopic observation of the crude reaction products indicated virtually quantitative conversion to the desired phosphaureas. The reduced overall yield is generally reflective of losses upon isolation and purification. A decrease in reaction yield with 1-adamantyl isocyanate can be attributed to the larger steric bulk of the adamantyl group, hindering insertion into the La−phosphide bond and consequently reducing conversion to the product. Hydrophosphination of the slightly larger *tert*-butyl isocyanate was even worse, with the desired phosphaurea compound afforded in very low yield (<20%), again demonstrating the deleterious effect of steric hindrance on this reaction. Furthermore, scale-up of this reaction with lower catalyst loading (1 mol %) was successful, giving gram-scale isolated yields of product **6i** (930 mg; 72% yield), although the reaction times were longer (7 days).

The acidity of the phosphine employed was also found to significantly affect the catalysis. Attempted hydrophosphination of *N*,*N*′-diisopropylcarbodiimide with di-*tert*-butylphosphine gave no product even on heating to 80 °C for 36 h. Small


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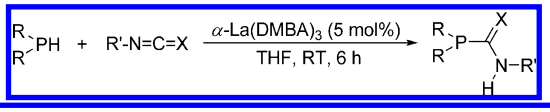
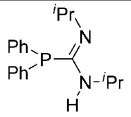
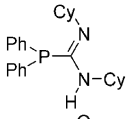
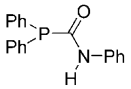
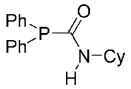
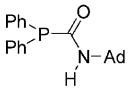
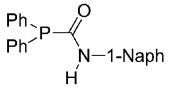
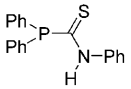
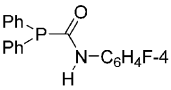
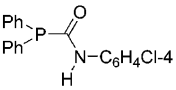
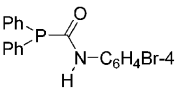
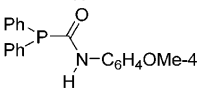
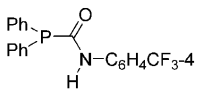
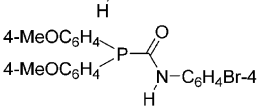
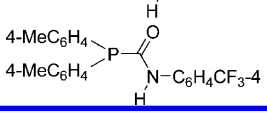
**Table 1. Catalytic Addition of Phosphines to Heterocumulenes**[a]




| Entry | $R_2PH$ | R'-N=C=X | Product | Yield[b] [%] |
|---|---|---|---|---|
| 1 | $Ph_2PH$ | $^i$PrN=C=N$^i$Pr |  | **6a** (93) |
| 2 | $Ph_2PH$ | CyN=C=NCy |  | **6b** (74) |
| 3 | $Ph_2PH$ | PhN=C=O |  | **6c** (60) |
| 4 | $Ph_2PH$ | CyN=C=O |  | **6d** (54) |
| 5 | $Ph_2PH$ | AdN=C=O |  | **6e** (38)[c] |
| 6 | $Ph_2PH$ | 1-NaphN=C=O |  | **6f** (76)[c] |
| 7 | $Ph_2PH$ | PhN=C=S |  | **6g** (91) |
| 8 | $Ph_2PH$ | (4-$FC_6H_4$)N=C=O |  | **6h** (83)[d] |
| 9 | $Ph_2PH$ | (4-$ClC_6H_4$)N=C=O |  | **6i** (83) |
| 10 | $Ph_2PH$ | (4-$BrC_6H_4$)N=C=O |  | **6j** (49) |
| 11 | $Ph_2PH$ | (4-$MeOC_6H_4$)N=C=O |  | **6k** (62) |
| 12 | $Ph_2PH$ | (4-$F_3CC_6H_4$)N=C=O |  | **6l** (88) |
| 13 | (4-$MeOC_6H_4$)$_2$PH | (4-$BrC_6H_4$)N=C=O |  | **6m** (45) |
| 14 | (4-$MeC_6H_4$)$_2$PH | (4-$F_3CC_6H_4$)N=C=O |  | **6n** (65) |

[a]Conditions: phosphine (1.15 mmol), heterocumulene (1.00 mmol), catalyst (0.05 mmol), THF (3 mL). [b]Isolated yield. [c]Reaction mixture stirred at 55 °C. [d]Product isolated as a 3:1 ratio of phosphaurea **6h** and trimerized isocyanate.

amounts of (4-$MeOC_6H_4$)$_2$PH and di-*p*-tolylphosphine were obtained from commercial sources for comparison. In both cases, the related phosphaureas (**6m**,**n**) were produced and isolated in yields very similar to those obtained with the unsubstituted diphenylphosphine, indicating little or no sensitivity to electronic effects at this position.

To gain insight into the possible catalysis mechanism, *α*-La(DMBA)$_3$ was treated with 3 equiv of diphenylphosphine in THF (15 mL), followed by 3 equiv of *N*,*N*′-diisopropylcarbodiimide (Scheme 3). After removal of THF under vacuum, the mixture was triturated with pentane (10 mL), washed twice with pentane (12 mL) at −78 °C, and dried under vacuum. The resulting product (**5**) was then recrystallized from a concentrated solution of toluene at room temperature. Its X-ray crystal structure revealed a homoleptic complex in which three phosphaguanidinate ligands are bound to the metal center through their chelating nitrogen atoms (Figure 3). The La−N bond distances of **5** (2.502(1)−2.566(1) Å) are slightly shorter than those found in [{$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)}La{$^i$PrNC($PPh_2$)N$^i$Pr}($OEt_2$)] (2.557(2) and 2.570(2) Å)[23] and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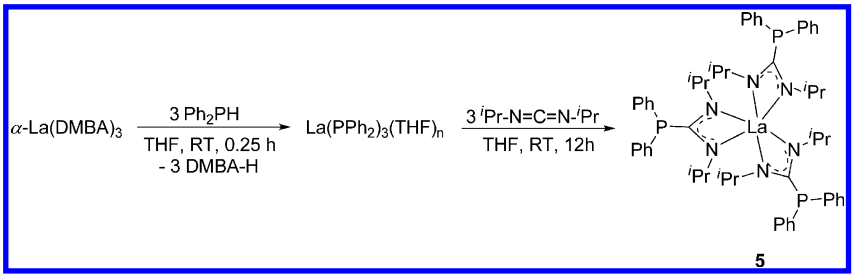
**Scheme 3. Synthesis of Homoleptic Lanthanum Phosphaguanidinate (5)**



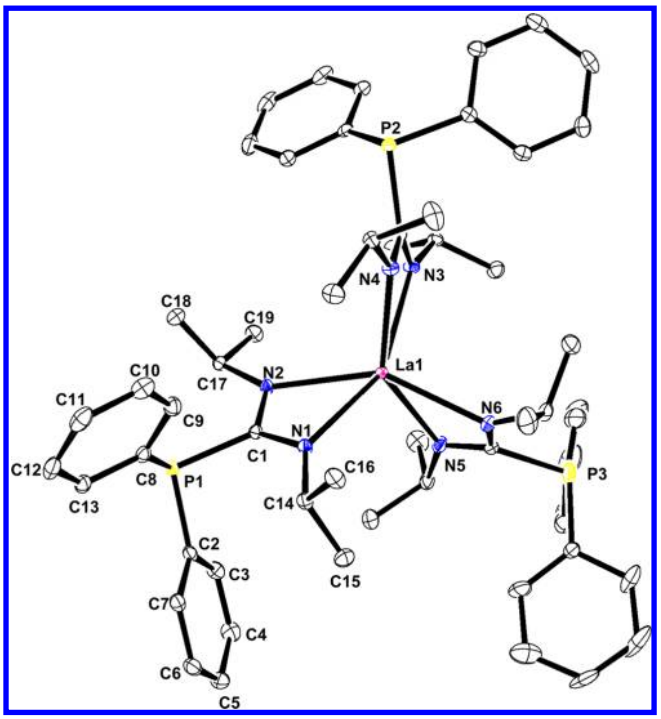
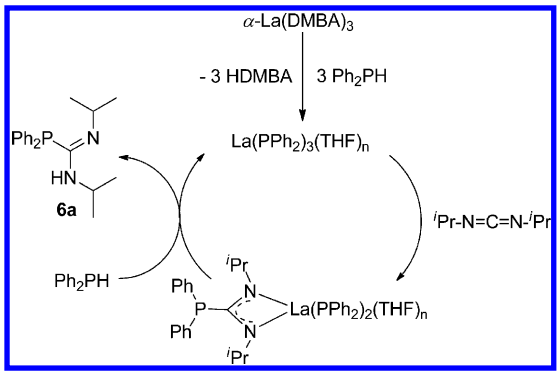




**Figure 3.** ORTEP diagram of **5** (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (deg): La1−N1 = 2.566(1), La1−N2 = 2.502(1), C1−N1 = 1.328(2), C1−N2 = 1.338(2), P1−C1 = 1.907(2), P1−C2 = 1.834(2), P1−C8 = 1.837(2), N1−C14 = 1.463(2), N2−C17 = 1.467(2); N1−La1−N2 = 52.87(4), N1−C1−N2 = 115.6(1), C2−P1−C8 = 106.63(7).

marginally longer than the amidinate bond distances of $[La\{MeC(NCy)_2\}_3]$ (2.493(4) and 2.501(4) Å).[23,46] Complex **5** proved to be a competent hydrophosphination catalyst. For example, the hydrophosphination of *N,N′*-diisopropylcarbodiimide with diphenylphosphine using a catalytic amount of **5** (5 mol %) yielded the phosphaguanidine **6a** (93%), supporting **5** as a possible catalytic intermediate.

Given the results discussed throughout this report, we propose the mechanism shown in Scheme 4 for this catalytic reaction. Transformation of the α-La(DMBA)$_3$ complex to the active catalyst is postulated to occur via protonolysis by the phosphine substrate, giving a THF-solvated lanthanum diphenylphosphide complex, most likely La(PPh$_2$)$_3$(THF)$_n$. The much higher catalytic efficiency observed in coordinating solvents is consistent with the formation of a catalytic species that requires donor ligands to inhibit catalyst decomposition pathways. Previous reports note that tris-phosphido lanthanide(III) complexes are notoriously difficult to isolate cleanly, often being formed as "ate" salts, a problem commonly experienced in early-transition-metal and lanthanide chemistry.[47] Our

**Scheme 4. Proposed Catalytic Cycle for the Hydrophosphination of *N,N′*-Diisopropylcarbodiimide**




attempts to isolate the putative catalyst via various synthetic routes have not been successful, and to our knowledge complexes of the form L$_n$La(PPh$_2$)$_3$ have not been reported (L = neutral donor ligand). The catalyst activation step produces either DMBA-H or the protonated product after heterocumulene insertion into the La−DMBA bond. In either case, the functional catalyst involves a La−PR$_2$ active moiety. Overall, the catalysis proceeds via insertion of the heterocumulene into a La−PR$_2$ bond, followed by protonolysis to yield the hydrophosphination product and regenerate the active species. As noted above, di-*tert*-butylphosphine was not a useful hydrophosphination reagent. Given its much lower acidity,[48] it is likely that the di-*tert*-butylphosphine is unable to protonate off the product phosphaguanidinate ligand, preventing catalytic turnover, while the other phosphine substrates tested were acidic enough to effect this step in the catalysis.

## ■ CONCLUSIONS

We have broadened the reactivity scope of the α-metalated *N,N*-dimethylbenzylamine rare-earth-metal complexes α-La(DMBA)$_3$ and α-Y(DMBA)$_3$. Both complexes have been shown to undergo triple-insertion reactions to form homoleptic amidinate and phosphaguanidinate complexes (**1**−**5**). Additionally, the La and Y homoleptic complexes serve as useful catalytic precursors for the addition of a P−H bond across the C═N bond of heterocumulenes. α-La(DMBA)$_3$ demonstrated excellent catalytic activity at room temperature for the hydrophosphination of a wide variety of heterocumulenes. It showed broad tolerance to electron-donating and electron-withdrawing substituents on aryl isocyanates. The catalytic effectiveness appeared to be dependent on both the acidity of the phosphine and the steric bulk of the heterocumulene. The catalytic mechanism likely begins with formation of a metal phosphide, followed by insertion of a heterocumulene, and subsequent protonation yields the hydrophosphination prod-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uct. The most important aspect of the results reported herein is the development of a new hydrophosphination catalyst with broad substrate tolerance that functions effectively at ambient temperature. Further catalytic studies involving catalytic hydrophosphination of $\alpha,\beta$-unsaturated ketones and allenes will be investigated in due course.

## EXPERIMENTAL SECTION

**General Considerations.** Compounds **1**−**5** and **6a**−**n** were prepared using standard Schlenk and drybox techniques. Lanthanum(III) chloride and yttrium(III) chloride were purchased from Strem and used without further purification. $\alpha$-La(DMBA)$_3$ and $\alpha$-Y(DMBA)$_3$ were synthesized as previously described.[39] Diphenylphosphine was synthesized according to the literature report for diisopropylphosphine, as previously described.[49] Diisopropylcarbodiimide, cyclohexyl isocyanate, phenyl isothiocyanate, and 1-naphthyl isocyanate were purchased from Acros, dried over 4 Å molecular sieves, freeze−pump−thawed three times, distilled, and stored under nitrogen. Dicyclohexylcarbodiimide was purchased from Acros and sublimed. Phenyl isocyanate was purchased from Aldrich, dried over 4 Å molecular sieves, freeze−pump−thawed three times, distilled, and stored under nitrogen. 1-Adamantyl isocyanate, 4-fluorophenyl isocyanate, 4-chlorophenyl isocyanate, 4-bromophenyl isocyanate, 4-(trifluoromethyl)phenyl isocyanate, 4-methoxyphenyl isocyanate, and di-*p*-methoxyphenyl phosphine were purchased from Aldrich, stored under nitrogen, and used without further purification. Di-*p*-tolylphosphine was purchased from Strem as a 10% by mass solution in hexane, and the hexane was removed in vacuo prior to use. $C_6D_6$ and $C_7D_8$ were purchased from Cambridge Isotope Laboratories and were vacuum-transferred from sodium/benzophenone ketyl and degassed with three freeze−evacuate−thaw cycles. $C_4D_8O$ was purchased from Cambridge Isotope Laboratories and was vacuum-transferred from 4 Å molecular sieves and degassed with three freeze−evacuate−thaw cycles. All other solvents were purchased from either VWR or Fisher. Pentane, methylene chloride, and toluene were purified by passage through columns of activated 4 Å molecular sieves and degassed prior to use. Diethyl ether was purified by passage through a column of activated alumina and degassed prior to use. Tetrahydrofuran was dried over sodium/benzophenone ketyl and distilled prior to use. All $^1$H, $^{13}$C, and $^{31}$P NMR data were obtained on a 400 MHz VXRS, 600 MHz Inova, or 600 MHz Avance III Bruker spectrometer. $^1$H NMR shifts given were referenced internally to the residual solvent peaks at $\delta$ 7.16 ppm ($C_6D_5H$), 2.08 ppm ($C_7D_7H$), and 3.58 ppm ($C_4D_7HO$). $^{13}$C NMR shifts given were referenced internally to the residual peaks at $\delta$ 128.0 ppm ($C_6D_6$) and 20.4 ppm ($C_7D_8$). Phosphorus NMR spectra were externally referenced to 0.00 ppm with 5% $H_3PO_4$ in $D_2O$. IR samples were prepared as Nujol mulls and taken between KBr plates on a Perkin-Elmer XTL FTIR spectrophotometer. Melting points were observed on a capillary Mel-Temp apparatus in sealed capillary tubes under nitrogen and are uncorrected. Elemental analyses were determined by Atlantic Microlabs, Inc., Norcross, GA. Single-crystal X-ray structure determinations were performed at The University of Toledo.

**La[$^i$PrNC(DMBA)N$^i$Pr]$_3$ (1).** An oven-dried Schlenk tube was charged with $\alpha$-La(DMBA)$_3$ (400 mg, 0.739 mmol). THF (15 mL) was added to the $\alpha$-La(DMBA)$_3$, followed by diisopropylcarbodiimide (355 $\mu$L, 0.288 g, 2.28 mmol). The mixture was stirred at room temperature for 12 h. The THF was removed under vacuum, the solid was extracted with diethyl ether, and the extract was filtered and concentrated. The flask was placed in a freezer at −20 °C to yield a white precipitate after 3 days (516 mg, 76%). $^1$H NMR ($C_7D_8$, 78 °C): $\delta$ 7.48−7.44 (m, 6H, *o*-H), 7.41 (t, $^3J_{H-H}$ = 6.4 Hz, 6H, *m*-H), 7.00 (t, $^3J_{H-H}$ = 6.4 Hz, 3H, *p*-H), 4.49 (s, 3H, C*H*(C$_6$H$_5$)(NMe$_2$)), 4.38 (bs, 6H, C*H*(CH$_3$)$_2$), 2.33 (s, 18H, CH(C$_6$H$_5$)(N*Me*$_2$)), 1.33−1.22 (m, 18H, CH(C*H*$_3$)$_2$), 0.93−0.85 (m, 18H, CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H} NMR ($C_7D_8$, 78 °C): $\delta$ 171.37, 140.96, 129.12, 128.29, 126.34, 68.85, 46.88, 45.15, 27.37. IR (Nujol, cm$^{-1}$): 2924 (s), 2767 (s), 2592 (m), 1645 (w), 1600 (m), 1471 (s), 1318 (s), 1254 (s), 1180 (s), 1120 (s), 1023 (s), 940 (m), 894 (s), 862 (m), 839 (m), 811 (m), 737 (s), 701 (s), 640 (m). Anal. Calcd for $C_{48}H_{78}LaN_9$: C, 62.66; H, 8.54; N, 13.70. Found: C, 61.60; H, 8.59; N, 13.35. Mp: 187 °C dec.

**Y[$^i$PrNC(DMBA)N$^i$Pr]$_3$ (2).** An oven-dried Schlenk tube was charged with $\alpha$-Y(DMBA)$_3$ (282 mg, 0.575 mmol). Toluene (15 mL) was added to the $\alpha$-Y(DMBA)$_3$, followed by diisopropylcarbodiimide (276 $\mu$L, 224 mg, 1.77 mmol). The mixture was stirred at room temperature for 12 h. The toluene was removed under vacuum, the solid was extracted with pentane, and the extract was filtered and concentrated. The flask was placed in a freezer at −20 °C to yield a white precipitate after 3 days (208 mg, 42%). $^1$H NMR ($C_7D_8$, 78 °C): $\delta$ 7.45 (d, $^3J_{H-H}$ = 7.2 Hz, 6H, *o*-H), 7.11 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, *m*-H), 7.01 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, *p*-H), 4.54 (bs, 3H, C*H*(C$_6$H$_5$)(NMe$_2$)), 4.50−4.30 (m, 6H, C*H*(CH$_3$)$_2$), 2.27 (s, 18H, CH(C$_6$H$_5$)(N*Me*$_2$)), 1.39−1.29 (m, 9H, CH(C*H*$_3$)$_2$), 1.09−1.00 (m, 18H, CH(C*H*$_3$)$_2$), 0.83−0.79 (m, 9H, CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H} NMR ($C_7D_8$, 78 °C): $\delta$ 173.33, 140.31, 129.53, 128.35, 126.58, 69.53, 46.55, 45.39, 27.67. IR (Nujol, cm$^{-1}$): 2896 (s), 2627 (s), 2352 (w), 1646 (w), 1595 (m), 1461 (s), 1337 (s), 1259 (s), 1189 (s), 1125 (s), 1093 (m), 1051 (s), 1018 (s), 940 (m), 917 (w), 894 (s), 867 (m), 839 (s), 816 (m), 738 (s), 701 (s), 650 (w). Anal. Calcd for $C_{48}H_{78}N_9Y$: C, 66.26; H, 9.04; N, 14.49. Found: C, 65.75; H, 9.13; N, 14.19. Mp: 180 °C dec.

**Y[CyNC(DMBA)NCy]$_3$ (3).** An oven-dried Schlenk tube was charged with $\alpha$-Y(DMBA)$_3$ (266 mg, 0.540 mmol). Toluene (15 mL) was added to the $\alpha$-Y(DMBA)$_3$, followed by dicyclohexylcarbodiimide (346 mg, 1.68 mmol). The mixture was stirred at room temperature for 36 h. The toluene was removed under vacuum, the solid was extracted with pentane, and the extract was filtered and concentrated. Colorless crystals grew from a concentrated pentane solution at room temperature (388 mg, 65%). $^1$H NMR ($C_7D_8$, 78 °C): $\delta$ 7.65−7.57 (m, 6H, *o*-H), 7.29−7.18 (m, 6H, *m*-H), 7.07−7.02 (m, 3H, *p*-H), 4.74−4.70 (m, 3H, C*H*(C$_6$H$_5$)(NMe$_2$)), 4.08 (bs, 6H, C*H*-cyclohexyl), 2.38−2.35 (m, 18H, CH(C$_6$H$_5$)(N*Me*$_2$)), 1.80−1.25 (m, 60H, C*H*$_2$-cyclohexyl). $^{13}$C{$^1$H} NMR ($C_7D_8$, 78 °C): $\delta$ 173.16, 140.53, 128.30, 126.63, 126.32, 68.23, 55.67, 45.44, 35.39, 32.40, 29.84. IR (Nujol, cm$^{-1}$): 2884 (s), 2758 (s), 2116 (s), 1598 (m), 1446 (s), 1344 (s), 1260 (s), 1176 (s), 1130 (s), 1024 (s), 990 (s), 957 (w), 923 (m), 889 (s), 843 (m), 830 (m), 805 (m), 741 (s), 699 (s), 623 (m). Anal. Calcd for $C_{66}H_{102}N_9Y$: C, 71.38; H, 9.26; N, 11.35. Found: C, 71.05; H, 9.40; N, 10.96. Mp: 178−181 °C.

**Y[Me$_3$SiNC(DMBA)NSiMe$_3$](DMBA)$_2$ (4).** An oven-dried Schlenk tube was charged with $\alpha$-Y(DMBA)$_3$ (368 mg, 0.749 mmol). Toluene (15 mL) was added, followed by bis(trimethylsilyl)carbodiimide (188 $\mu$L, 154 mg, 0.826 mmol). The mixture was stirred at room temperature for 48 h. The toluene was removed under vacuum, the solid was extracted with hot diethyl ether, and the extract was filtered and concentrated. The flask was placed in a freezer at −20 °C to yield a yellow precipitate after 3 days (429 mg, 84%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.47 (d, $^3J_{H-H}$ = 7.4 Hz, 2H, *o*-H(amidinate)), 7.24 (t, $^3J_{H-H}$ = 7.0 Hz, 4H, *m*-H(DMBA)), 7.20 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, *m*-H(amidinate)), 7.09 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, *p*-H(amidinate)), 6.64 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, *p*-H(DMBA)), 6.25 (d, $^3J_{H-H}$ = 7.0 Hz, 4H, *o*-H(DMBA)), 4.16 (d, $^4J_{Y-H}$ = 1.9 Hz, 1H, C*H*(amidinate)), 3.53 (s, 2H, C*H*(DMBA)), 2.20 (bs, 12H, N*Me*$_2$(DMBA)), 2.09 (s, 6H, N*Me*$_2$(amidinate)), 0.100 (s, 18H, Si*Me*$_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 177.89 (d, $^2J_{Y-C}$ = 4.4 Hz, amidinate), 139.98, 137.30, 131.99, 131.91, 128.45, 128.41, 114.73, 110.14, 80.08 (d, $^1J_{Y-C}$ = 6.7 Hz, DMBA), 77.61 (d, $^3J_{Y-C}$ = 4.8 Hz, amidinate), 46.11, 41.07, 3.48. IR (Nujol, cm$^{-1}$): 2928 (s), 2845 (s), 2129 (w), 1598 (m), 1535 (w), 1463 (s), 1374 (m), 1307 (w), 1245 (m), 1177 (w), 1151 (w), 1042 (w), 1011 (m), 975 (w), 868 (w), 835 (s), 731 (m), 695 (m), 674 (w), 638 (w), 607 (w). Anal. Calcd for $C_{34}H_{54}N_5Si_2Y$: C, 60.24; H, 8.03; N, 10.33. Found: C, 57.96; H, 7.84; N, 9.93. Mp: 149−153 °C.

**La[$^i$PrNC(PPh$_2$)N$^i$Pr]$_3$ (5).** An oven-dried Schlenk tube was charged with $\alpha$-La(DMBA)$_3$ (542 mg, 1.00 mmol). THF (15 mL) was added, followed by diphenylphosphine (568 mg, 3.05 mmol). The mixture was stirred until the solution was ruby red. A second oven-dried Schlenk tube was charged with diisopropylcarbodiimide (472 $\mu$L, 385 mg, 3.05 mmol) and THF (5 mL), which was then added to the initial reaction mixture. The reaction mixture was stirred at room temperature overnight to yield a yellow solution. The THF was


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removed under vacuum, and the mixture was triturated with pentane (10 mL) to yield a yellow precipitate. The precipitate was washed twice with pentane (12 mL) at −78 °C and dried under vacuum. The solid was dissolved in toluene (15 mL). Colorless X-ray-quality crystals were grown at room temperature from a concentrated solution of toluene (697 mg, 65%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.72 (t, $^3J_{H-H}$ = $^3J_{P-H}$ = 7.2 Hz, 12H, *o*-H), 7.14 (t, $^3J_{H-H}$ = 7.2 Hz, 12H, *m*-H), 7.06 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, *p*-H), 4.35 (sept, $^3J_{H-H}$ = 6.0 Hz, 6H, C*H*($CH_3$)$_2$), 1.17 (bs, 36H, CH($CH_3$)$_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 171.52 (d, $^1J_{P-C}$ = 54.6 Hz), 135.65 (d, $^1J_{P-C}$ = 28.6 Hz), 134.29 (d, $^2J_{P-C}$ = 19.8 Hz), 132.38 (d, $^3J_{P-C}$ = 17.8 Hz), 128.70 (d, $^4J_{P-C}$ = 5.5 Hz), 49.88 (d, $^3J_{P-C}$ = 21.1 Hz), 26.87. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ −18.86. IR (Nujol, cm$^{-1}$): 2918 (s), 2842 (s), 1948 (w), 1581 (s), 1433 (s), 1362 (s), 1311 (s), 1164 (s), 1117 (s), 1062 (m), 990 (s), 940 (w), 910 (w), 872 (w), 843 (w), 813 (w), 737 (s), 691 (s), 636 (s). Anal. Calcd for $C_{57}H_{72}LaN_6P_3$: C, 63.80; H, 6.76; N, 7.83. Found: C, 63.95; H, 6.72; N, 8.02. Mp: 201−204 °C.

**General Procedures for the Hydrophosphination of Heterocumulenes.** *Method A.* An oven-dried Schlenk tube was charged with $\alpha$-La(DMBA)$_3$ (27.0 mg, 0.0500 mmol) and THF (2 mL). Diphenylphosphine (214 mg, 1.15 mmol) and THF (1 mL) were added. The mixture was stirred until the solution turned ruby red. The carbodiimide (1.00 mmol) was then added. The mixture was stirred for 6 h at room temperature. The THF was removed under vacuum and triturated with 3 mL of pentane. The solid was extracted with pentane, filtered, and concentrated. The Schlenk tube was placed in a freezer at −20 °C to yield a white solid. Spectroscopic data for **6a,b** matched those of previously reported material.[23]

*Method B.* An oven-dried Schlenk tube was charged with $\alpha$-La(DMBA)$_3$ (27.0 mg, 0.0500 mmol) and THF (2 mL). The phosphine (1.15 mmol) and THF (1 mL) were added to the reaction mixture. The mixture was stirred until the solution turned ruby red. The heterocumulene (1.00 mmol) was then added. The mixture was stirred for 6 h at room temperature. The THF was removed under vacuum and triturated with 3 mL of pentane. The solid was washed with cold pentane (5 mL), filtered, and dried under vacuum, yielding a white or yellow precipitate.

*Method C.* An oven-dried Schlenk tube was charged with $\alpha$-La(DMBA)$_3$ (27.0 mg, 0.0500 mmol) and THF (2 mL). Diphenylphosphine (214 mg, 1.15 mmol) and THF (1 mL) were added to the reaction mixture. The mixture was stirred until the solution turned ruby red. The isocyanate (1.00 mmol) was then added. The mixture was stirred for 12 h at 55 °C. The THF was removed under vacuum and triturated with 3 mL of pentane. The solid was washed with pentane (5 mL), filtered, and dried under vacuum, yielding a white precipitate.

*$^i$PrN═C(PPh$_2$)(NH$^i$Pr) (**6a**).*[23] Method A. White solid (290 mg, 93%). Anal. Calcd for $C_{19}H_{25}N_2P$: C, 73.05; H, 8.07; N, 8.97. Found: C, 71.37; H, 7.98; N, 8.85. HRMS: calcd *m*/*z* 313.1834 for $C_{19}H_{26}N_2P$ [M + H]$^+$, measd 313.1825.

*CyN═C(PPh$_2$)(NHCy) (**6b**).*[23] Method A. White solid (290 mg, 74%). Anal. Calcd for $C_{25}H_{33}N_2P$: C, 76.50; H, 8.47; N, 7.14. Found: C, 74.81; H, 8.56; N, 6.93. HRMS: calcd *m*/*z* 393.2460 for $C_{25}H_{34}N_2P$ [M + H]$^+$, measd 393.2456.

*O═C(PPh$_2$)(NHPh) (**6c**).* Method B. White solid (184 mg, 60%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.57−7.55 (m, 4H, Ph-P), 7.34 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-H), 7.22 (d, $^3J_{P-H}$ = 8.4 Hz, 1H, N-*H*), 7.03−7.02 (m, 6H, Ph-P), 6.97 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, *m*-H), 6.81 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, *p*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 175.49 (d, $^1J_{P-C}$ = 15.4 Hz), 149.02, 135.06 (d, $^2J_{P-C}$ = 19.3 Hz), 134.64 (d, $^1J_{P-C}$ = 17.5 Hz), 130.20, 129.61, 129.51 (d, $^3J_{P-C}$ = 2.9 Hz), 124.87, 119.74. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 0.77. IR (Nujol, cm$^{-1}$): 3247 (m), 2941 (s), 2843 (s), 1701 (w), 1688 (w), 1590 (m), 1531 (m), 1455 (s), 1433 (s), 1348 (s), 1303 (m), 1236 (m), 1169 (w), 1088 (w), 1066 (w), 1026 (w), 990 (w), 914 (w), 887 (w), 757 (m), 735 (s), 690 (s), 650 (w), 587 (m). Anal. Calcd for $C_{19}H_{16}NOP$: C, 74.74; H, 5.28; N, 4.59. Found: C, 70.23; H, 4.89; N, 5.22. HRMS: calcd *m*/*z* 306.1048 for $C_{19}H_{17}NOP$ [M + H]$^+$, measd 306.1041.

*O═C(PPh$_2$)(NHCy) (**6d**).* Method B. White solid (167 mg, 54%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.67−7.65 (m, 4H, Ph-P), 7.10−7.06 (m, 6H, Ph-P), 5.49 (bd, $^3J_{H-H}$ = 6.0 Hz, 1H, N-*H*), 3.96−3.95 (m, 1H, C*H*), 1.65−1.62 (m, 2H, C$H_2$), 1.29−1.21 (m, 2H, C$H_2$), 1.04−0.98 (m, 2H, C$H_2$), 0.80−0.78 (m, 2H, C$H_2$), 0.71−0.69 (m, 2H, C$H_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 174.92 (d, $^1J_{P-C}$ = 12.3 Hz), 135.39 (d, $^1J_{P-C}$ = 12.7 Hz), 134.65 (d, $^2J_{P-C}$ = 18.8 Hz), 129.57, 129.00 (d, $^3J_{P-C}$ = 7.0 Hz), 48.69, 32.82, 25.58, 24.70. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ −3.35. IR (Nujol, cm$^{-1}$): 3251 (m), 2918 (s), 2285 (m), 1974 (w), 1957 (w), 1898 (w), 1883 (w), 1624 (s), 1497 (s), 1438 (s), 1370 (m), 1337 (m), 1303 (m), 1256 (m), 1218 (s), 1185 (m), 1151 (m), 1092 (m), 1024 (m), 999 (m), 919 (w), 885 (m), 839 (m), 805 (w), 739 (w), 746 (s), 695 (s). Anal. Calcd for $C_{19}H_{22}NOP$: C, 73.29; H, 7.12; N, 4.50. Found: C, 71.97; H, 7.12; N, 4.39. HRMS: calcd *m*/*z* 312.1517 for $C_{19}H_{23}NOP$ [M + H]$^+$, measd 312.1522.

*O═C(PPh$_2$)(NHAd) (**6e**).* Method C. White solid (138 mg, 38%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.69−7.66 (m, 4H, Ph-P), 7.11−7.08 (m, 4H, Ph-P), 7.06−7.04 (m, 2H, Ph-P), 5.35 (bs, 1H, N-*H*), 1.86 (bs, 6H, Ad-*H*), 1.79 (bs, 3H, Ad-*H*), 1.44−1.40 (m, 6H, Ad-*H*). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 174.86 (d, $^1J_{P-C}$ = 13.6 Hz), 135.69 (d, $^1J_{P-C}$ = 12.1 Hz), 134.53 (d, $^2J_{P-C}$ = 18.1 Hz), 129.34, 128.92 (d, $^3J_{P-C}$ = 6.0 Hz), 53.33, 41.66, 36.35, 29.74. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ −2.20. IR (Nujol, cm$^{-1}$): 3258 (m), 2933 (s), 2852 (s), 1625 (s), 1491 (s), 1455 (s), 1432 (s), 1375 (m), 1352 (m), 1308 (m), 1290 (m), 1276 (m), 1205 (s), 1182 (m), 1088 (m), 1026 (w), 999 (w), 941 (w), 887 (w), 856 (w), 802 (w), 748 (s), 722 (w), 695 (s). Anal. Calcd for $C_{23}H_{26}NOP$: C, 76.01; H, 7.21; N, 3.85. Found: C, 74.50; H, 7.41; N, 4.17. HRMS: calcd *m*/*z* 364.1830 for $C_{23}H_{27}NOP$ [M + H]$^+$, measd 364.1833.

*O═C(PPh$_2$)(NH-1-Naph) (**6f**).* Method C. White solid (271 mg, 76%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 8.70 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, 2-Naph), 7.83 (s, 1H, N-*H*), 7.61 (m, 4H, Ph-P), 7.52 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, 8-Naph), 7.34 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, 4-Naph), 7.21 (t, $^3J_{H-H}$ = 8.4 Hz, 1H, 3-Naph), 7.13 (t, $^3J_{H-H}$ = 8.4 Hz, 1H, 7-Naph), 7.06 (m, 7H, Ph-P and 6-Naph), 6.79 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, 5-Naph). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 175.46 (d, $^1J_{P-C}$ = 15.2 Hz), 134.82 (d, $^2J_{P-C}$ = 19.1 Hz), 134.39, 134.29 (d, $^1J_{P-C}$ = 12.8 Hz), 132.60 (d, $^3J_{P-C}$ = 2.1 Hz), 129.88, 129.29 (d, $^3J_{P-C}$ = 7.1 Hz), 129.14, 128.68, 126.29, 126.06, 125.80, 125.20, 119.54, 118.41. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ −0.36. IR (Nujol, cm$^{-1}$): 3257 (s), 2936 (s), 2849 (s), 1717 (w), 1630 (s), 1530 (s), 1469 (s), 1430 (s), 1400 (m), 1378 (m), 1339 (s), 1265 (m), 1248 (s), 1196 (s), 1161 (s), 1083 (w), 1026 (w), 952 (w), 909 (w), 888 (w), 856 (w), 793 (s), 771 (s), 740 (s), 692 (s), 644 (m). Anal. Calcd for $C_{23}H_{18}NOP$: C, 77.74; H, 5.11; N, 3.94. Found: C, 75.43; H, 5.08; N, 4.48. HRMS: calcd *m*/*z* 356.1204 for $C_{23}H_{19}NOP$ [M + H]$^+$, measd 356.1206.

*S═C(PPh$_2$)(NHPh) (**6g**).* Method B. Yellow solid (292 mg, 91%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 8.67 (bs, 1H, N-*H*), 7.67 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, *o*-H), 7.49−7.46 (m, 4H, Ph-P), 7.03−7.00 (m, 6H, Ph-P), 6.96 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, *m*-H), 6.86 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, *p*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 206.39 (d, $^1J_{P-C}$ = 39.3 Hz), 139.78, 135.80 (d, $^1J_{P-C}$ = 17.0 Hz), 134.74 (d, $^2J_{P-C}$ = 21.1 Hz), 130.07, 129.34 (d, $^3J_{P-C}$ = 6.0 Hz), 129.01, 126.60, 121.80. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 20.86. IR (Nujol, cm$^{-1}$): 3300 (m), 2953 (s), 2857 (s), 2284 (w), 1960 (w), 1886 (w), 1821 (w), 1660 (w), 1595 (m), 1521 (m), 1465 (s), 1443 (s), 1373 (s), 1204 (m), 1152 (m), 1083 (m), 1026 (m), 996 (m), 978 (m), 926 (w), 905 (m), 852 (w), 796 (m), 722 (s), 692 (s). Anal. Calcd for $C_{19}H_{16}NPS$: C, 71.01; H, 5.02; N, 4.36. Found: C, 68.58; H, 5.27; N, 3.99. HRMS: calcd *m*/*z* 322.0819 for $C_{19}H_{17}NPS$ [M + H]$^+$, measd 322.0811.

*O═C(PPh$_2$){N(H)C$_6$H$_4$F-4} (**6h**).* Method B. White solid in a 3:1 ratio of product and trimerized isocyanate (193 mg, 83%), purified by passing through a plug of silica gel. $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.57−7.54 (m, 4H, Ph-P), 7.12 (bs, 1H, N-*H*), 7.09−7.07 (m, 2H, *o*-H), 7.05−7.04 (m, 6H, Ph-P), 6.60 (t, $^3J_{F-H}$ = $^3J_{H-H}$ = 9.0 Hz, 2H, *m*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 174.94 (d, $^1J_{P-C}$ = 15.6 Hz), 159.57 (d, $^1J_{F-C}$ = 242.0 Hz), 134.66 (d, $^2J_{P-C}$ = 19.7 Hz), 134.39 (br), 134.09 (d, $^1J_{P-C}$ = 11.3 Hz), 129.89, 129.13 (d, $^3J_{P-C}$ = 7.1 Hz), 121.06 (d, $^3J_{F-C}$ = 7.7 Hz), 115.62 (d, $^2J_{F-C}$ = 22.2 Hz). $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 0.55. IR (Nujol, cm$^{-1}$): 3210 (m), 2929 (s), 2848 (s), 1881 (w), 1811 (w), 1630 (m), 1605 (m), 1529 (m), 1509 (m), 1464 (m),


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1434 (m), 1399 (m), 1379 (m), 1298 (m), 1253 (m), 1208 (m), 1168 (m), 1153 (m), 1097 (m), 1022 (w), 886 (w), 851 (w), 826 (m), 735 (m), 690 (m), 640 (m). HRMS: calcd $m/z$ 324.0954 for $C_{19}H_{16}FNOP$ $[M + H]^+$, measd 324.0948.

*O═C(PPh$_2$){N(H)C$_6$H$_4$Cl-4}* ***(6i)***. Method B. White solid (281 mg, 83%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.55−7.52 (m, 4H, Ph-P), 7.31 (s, 1H, N-*H*), 7.08 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *o*-H), 7.07−7.04 (m, 6H, Ph-P), 6.92 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *m*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 175.28 (d, $^1J_{P-C}$ = 16.1 Hz), 136.80 (d, $^3J_{P-C}$ = 4.2 Hz), 134.68 (d, $^2J_{P-C}$ = 19.6 Hz), 133.92 (d, $^1J_{P-C}$ = 10.9 Hz), 129.95, 129.49, 129.15 (d, $^3J_{P-C}$ = 7.6 Hz), 129.08, 120.68. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 1.00. IR (Nujol, cm$^{-1}$): 3239 (m), 2935 (s), 2857 (s), 1899 (w), 1690 (w), 1625 (m), 1591 (m), 1525 (m), 1460 (s), 1378 (s), 1300 (s), 1282 (m), 1235 (m), 1169 (m), 1091 (m), 1013 (m), 896 (w), 833 (m), 808 (m), 737 (m), 697 (m), 658 (m). HRMS: calcd $m/z$ 340.0658 for $C_{19}H_{16}ClNOP$ $[M + H]^+$, measd 340.0648.

*O═C(PPh$_2$){N(H)C$_6$H$_4$Br-4}* ***(6j)***. Method B. White solid (190 mg, 49%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.54−7.51 (m, 4H, Ph-P), 7.06 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, *o*-H), 7.05−7.03 (m, 6H, Ph-P), 7.00 (bs, 1H, N-*H*), 6.97 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, *m*-H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 175.68 (d, $^1J_{P-C}$ = 16.4 Hz), 137.63 (d, $^3J_{P-C}$ = 3.9 Hz), 135.06 (d, $^2J_{P-C}$ = 19.6 Hz), 134.27 (d, $^1J_{P-C}$ = 10.9 Hz), 132.43, 130.34, 129.53 (d, $^3J_{P-C}$ = 7.6 Hz), 121.38, 117.46. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 1.28. IR (Nujol, cm$^{-1}$): 3265 (m), 2927 (s), 2857 (s), 1630 (m), 1599 (m), 1534 (m), 1460 (s), 1378 (m), 1308 (m), 1243 (m), 1169 (w), 1070 (w), 1004 (m), 822 (m), 731 (m), 692 (m). HRMS: calcd $m/z$ 384.0153 for $C_{19}H_{16}BrNOP$ $[M + H]^+$, measd 384.0144.

*O═C(PPh$_2$){N(H)C$_6$H$_4$OMe-4}* ***(6k)***. Method B. Recrystallized from a $CH_2Cl_2$/pentane mixture. White solid (208 mg, 62%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.61−7.58 (m, 4H, Ph-P), 7.28 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *o*-H), 7.11 (s, 1H, N-*H*), 7.05−7.04 (m, 6H, Ph-P), 6.61 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *m*-H), 3.20 (s, 3H, OC$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 174.47 (d, $^1J_{P-C}$ = 14.4 Hz), 156.85, 134.70 (d, $^2J_{P-C}$ = 19.6 Hz), 134.52, 134.27 (d, $^1J_{P-C}$ = 17.7 Hz), 129.76, 129.09 (d, $^3J_{P-C}$ = 7.4 Hz), 121.01, 114.25, 54.82. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 0.18. IR (Nujol, cm$^{-1}$): 3257 (m), 2927 (s), 2831 (s), 1690 (s), 1607 (s), 1590 (s), 1507 (s), 1497 (s), 1377 (s), 1299 (s), 1251 (s), 1164 (s), 1104 (m), 1025 (s), 891 (w), 821 (s), 752 (m), 730 (m), 691 (m), 636 (m). HRMS: calcd $m/z$ 336.1153 for $C_{20}H_{19}NO_2P$ $[M + H]^+$, measd 336.1149.

*O═C(PPh$_2$){N(H)C$_6$H$_4$CF$_3$-4}* ***(6l)***. Method B. White solid (329 mg, 88%). $^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.55−7.52 (m, 4H, Ph-P), 7.16 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, *o*-H), 7.07 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, *m*-H), 7.06 (s, 1H, N-*H*), 7.06−7.04 (m, 6H, Ph-P). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 175.92 (d, $^1J_{P-C}$ = 17.5 Hz), 140.95 (d, $^3J_{P-C}$ = 3.6 Hz), 134.68 (d, $^2J_{P-C}$ = 19.1 Hz), 133.60 (d, $^1J_{P-C}$ = 10.5 Hz), 130.08, 129.21 (d, $^3J_{P-C}$ = 7.5 Hz), 126.32 (q, $^3J_{F-C}$ = 4.0 Hz), 126.08 (q, $^2J_{F-C}$ = 32.8 Hz), 124.76 (q, $^1J_{F-C}$ = 272.0 Hz), 119.09. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 1.63. IR (Nujol, cm$^{-1}$): 3220 (m), 2916 (s), 2838 (s), 1950 (w), 1898 (w), 1629 (s), 1525 (s), 1460 (s), 1403 (m), 1377 (m), 1316 (m), 1273 (m), 1208 (m), 930 (s), 856 (m), 761 (m), 708 (m), 665 (m), 635 (m), 600 (m). HRMS: calcd $m/z$ 374.0922 for $C_{20}H_{16}F_3NOP$ $[M + H]^+$, measd 374.0920.

*O═C[(4-MeOC$_6$H$_4$)$_2$P]{N(H)C$_6$H$_4$Br-4}* ***(6m)***. Method B. White solid (200 mg, 45%).$^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.54 (t, $^3J_{H-H}$ = $^3J_{P-H}$ = 8.6 Hz, 4H, *o*-H), 7.18 (s, 1H, N-*H*), 7.09 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *o*-H), 7.06 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, *m*-H), 6.72 (d, $^3J_{H-H}$ = 8.6 Hz, 4H, *m*-H), 3.21 (s, 6H, OC$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 177.12 (d, $^1J_{P-C}$ = 15.8 Hz), 161.92, 137.89 (d, $^3J_{P-C}$ = 3.9 Hz), 136.81 (d, $^2J_{P-C}$ = 21.1 Hz), 135.87 (d, $^1J_{P-C}$ = 18.6 Hz), 132.45, 125.29 (d, $^4J_{P-C}$ = 7.7 Hz), 121.34, 115.35 (d, $^3J_{P-C}$ = 8.1 Hz), 55.09. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ −1.97. IR (Nujol, cm$^{-1}$): 3299 (m), 2933 (s), 2838 (s), 2274 (w), 1894 (w), 1659 (s), 1594 (s), 1564 (s), 1520 (s), 1494 (s), 1455 (s), 1390 (s), 1282 (s), 1247 (s), 1182 (s), 1147 (m), 1099 (s), 1073 (m), 1012 (m), 960 (w), 943 (w), 891 (w), 821 (s), 791 (m), 717 (w), 630 (w). HRMS: calcd $m/z$ 444.0364 for $C_{21}H_{20}BrNO_3P$ $[M + H]^+$, measd 444.0355.

*O═C[(4-MeC$_6$H$_4$)$_2$P]{N(H)C$_6$H$_4$CF$_3$-4}* ***(6n)***. Method B. White solid (262 mg, 65%).$^1$H NMR ($C_6D_6$, 23 °C): $\delta$ 7.53 (t, $^3J_{H-H}$ = $^3J_{P-H}$ = 8.0 Hz, 4H, *o*-H), 7.31 (s, 1H, N-*H*), 7.17 (d, $^3J_{H-H}$ = 9.6 Hz, 2H, *o*-H), 7.15 (d, $^3J_{H-H}$ = 9.6 Hz, 2H, *m*-H), 6.94 (d, $^3J_{H-H}$ = 8.0 Hz, 4H, *m*-H), 2.01 (s, 6H, C$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 176.76 (d, $^1J_{P-C}$ = 17.3 Hz), 141.15 (d, $^3J_{P-C}$ = 3.2 Hz), 140.28, 134.82 (d, $^2J_{P-C}$ = 19.8 Hz), 130.39 (d, $^1J_{P-C}$ = 9.0 Hz), 130.01 (d, $^3J_{P-C}$ = 7.8 Hz), 126.30 (q, $^3J_{F-C}$ = 3.5 Hz), 125.94 (q, $^2J_{F-C}$ = 32.8 Hz), 124.80 (q, $^1J_{F-C}$ = 272.0 Hz), 119.11, 20.74. $^{31}$P{$^1$H} NMR ($C_6D_6$, 23 °C): $\delta$ 0.24. IR (Nujol, cm$^{-1}$): 3263 (s), 2925 (s), 2881 (s), 1906 (w), 1632 (s), 1602 (s), 1524 (s), 1459 (s), 1403 (s), 1372 (m), 1312 (s), 1246 (s), 1173 (s), 1147 (s), 1116 (s), 1064 (s), 1012 (m), 964 (w), 903 (m), 838 (m), 799 (m), 751 (w), 712 (m), 630 (m). HRMS: calcd $m/z$ 402.1235 for $C_{22}H_{20}F_3NOP$ $[M + H]^+$, measd 402.1237.

**Hydrophosphination Scale-Up Experiment.** Method B was employed with the following chemicals: $Ph_2PH$ (810 mg, 4.35 mmol), 4-chlorophenyl isocyanate (580 mg, 3.78 mmol), La(DMBA)$_3$ (22 mg, 0.041 mmol), and THF (7 mL). The reaction mixture was stirred at ambient temperature for 7 days. After workup product **6i** was isolated (930 mg, 72%), with spectroscopic properties matching those reported above.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, a table, and CIF files giving crystal data, including bond lengths and angles, and additional crystallographic experimental information for compounds **3**−**5**. 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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