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Neutral and Cationic Zirconium Complexes Bearing Multidentate Aminophenolato Ligands for Hydrophosphination Reactions of Alkenes and Heterocumulenes

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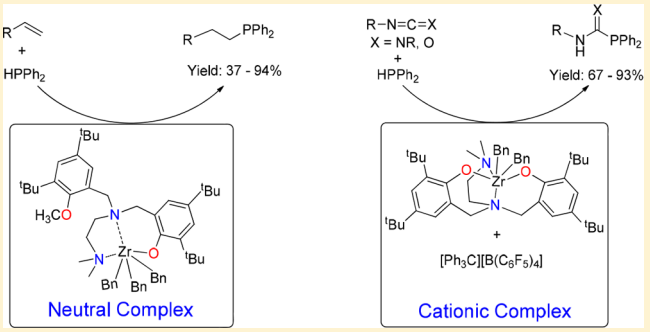
Supporting Information

ABSTRACT: Zirconium complexes supported by multidentate aminophenolato ligands were synthesized and characterized. The catalytic activities of neutral zirconium complexes and their cationic derivatives in the hydrophosphination of alkenes as well as heterocumulenes have been investigated and compared. Neutral complex **1** bearing a multidentate amino mono(phenolato) ligand exhibited high activity in hydrophosphination of simple alkenes, and anti-Markovnikov products were obtained in 37−94% yields at room temperature. Cationic species generated in situ from complex **3** stabilized by a bis(phenolato) ligand were found to be more active for hydrophosphination of heterocumulenes, i.e., carbodiimides and isocyanates, and gave phosphaguanidines and phosphaureas in 67−93% yields. The Lewis acidity and coordination space of metal centers are modified through changes in the ligand structure, which is found to significantly influence catalytic activity. These complexes are among the most active group 4 metal-based catalysts for hydrophosphination reactions.



INTRODUCTION

Phosphorus-containing compounds are widely used in the chemical and biological industries.[1] The hydrophosphination reaction, i.e., the addition of a P−H bond to C−C unsaturated bonds, is a 100% atom-economical route to construct C−P bonds and has gained great attention in the past few decades.[2] Since the first metal catalysts for hydrophosphination reported in 1990,[3] various catalytic systems involving late-transition-metal,[2i,h] lanthanide,[2b] and main-group[2k] elements have been designed and studied. Some of them suffer from certain limitations, such as low tolerance to functional groups (e.g., lanthanide complexes),[4] high cost (e.g., late-transition-metal complexes),[2f,3,5] and requirement of excess phosphine (e.g., Cu complexes).[6] Although group 4 metal complexes have shown good activity in hydroelementation reactions, e.g., hydroamination, studies on their application in hydrophosphination are limited.[7] Waterman et al. reported triamidoamine-supported zirconium complexes which catalyzed hydrophosphination of primary phosphines with alkenes with high activity[7d,e] and hydrophosphination of secondary phosphines with alkynes and carbodiimides with moderate activity.[7c] Le Gendre et al. reported Ti(II)-catalyzed 1,4-hydrophosphination of 1,3-dienes, which however showed no activity for alkynes.[7b] Zwitterionic titanium complexes reported by Mindiola et al. catalyzed hydrophosphination of diphenylacetylene and gave a mixture of *E* and *Z* isomers in 73% yield.[7a]

Our group has reported that cationic zirconium complexes are more active than their neutral analogues in inter- and intramolecular hydroamination reactions.[8] As a continuation of our interest in group 4 metal catalyzed hydroelementation reactions, a study of neutral and cationic zirconium complexes in catalyzing hydrophosphination reactions was conducted and compared. Neutral zirconium trialkyl complexes were found to be more active in catalyzing hydrophosphination of simple alkenes, while cationic species showed superior activity in hydrophosphination of heterocumulenes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Zirconium Complexes. Amine-bridged bis(phenolato) ligands are a promising class of ancillary ligands that well stabilize metal centers.[9] Moreover, ligand modifications can be easily achieved through changes in substituents on the nitrogen atom and/or aromatic rings, which influences complex structures and catalytic activities. In this study, one of the phenolate groups was etherified, giving rise to mono(phenolato) ligands bearing multiple coordination sites. Ligand precursors were prepared via modified literature procedures.[10] Zirconium trialkyl complexes **1** and **2** were synthesized through a straightforward metathesis method by treating ligand precursors L^1H and L^2H with $ZrBn_4$, which were isolated in 72% and 45% yields, respectively (Scheme 1). Zirconium dialkyl complexes **3**−**6**

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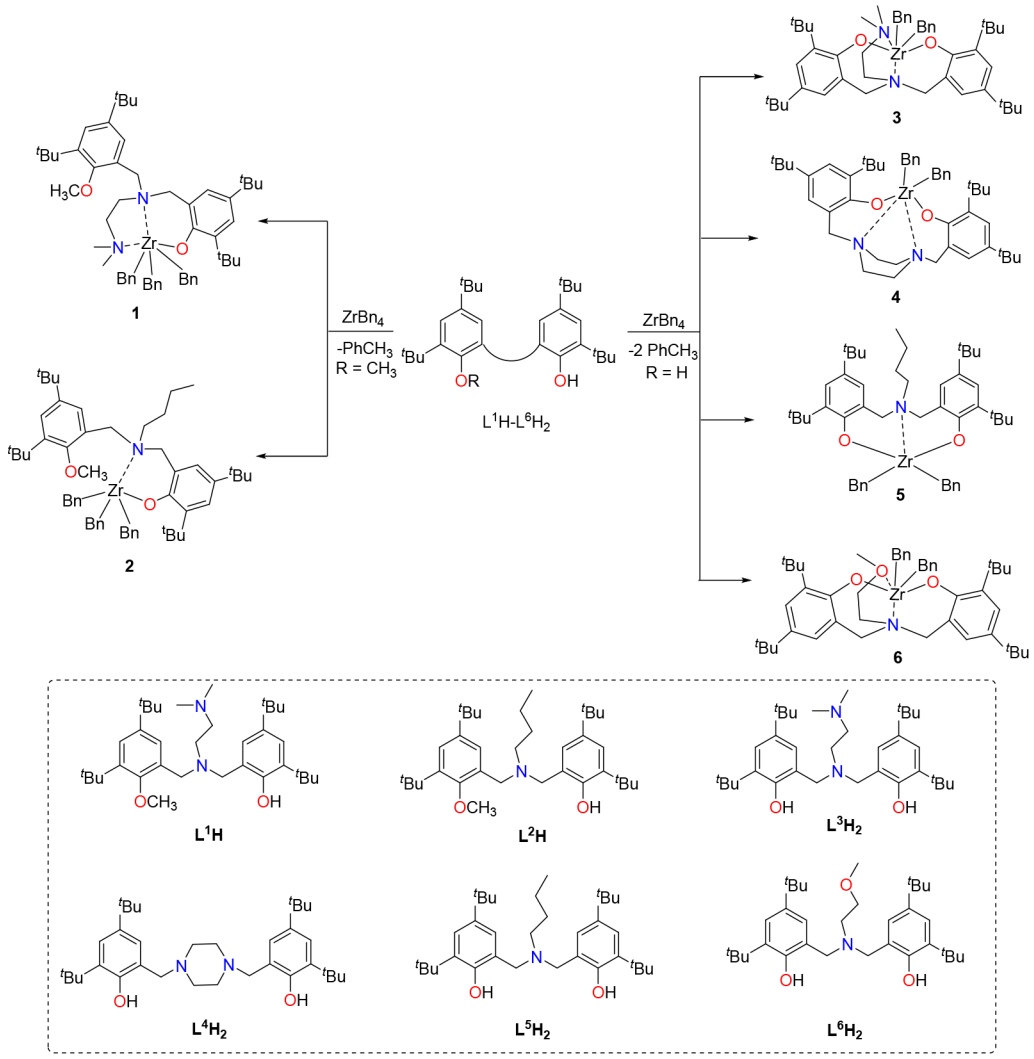
Scheme 1. Synthesis of Zirconium Complexes Bearing Multidentate Phenolato Ligands



were prepared according to literature methods for comparison purposes.[8,11]

The identity of complex **1** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analyses and X-ray diffraction analysis. In the ^{1}H NMR spectrum, all methylene protons become diastereotopic and give rise to doublets/multiplets in the range of 4.8−2.4 ppm. Signals of the $N(CH_3)_2$ group appear as two singlets at 2.17 and 1.59 ppm, in contrast to the singlet in ligand L^1, suggesting coordination of the $N(CH_3)_2$ group to the metal center. The OCH_3 group was found resonating at 3.39 ppm as a sharp singlet. Moreover, in addition to the major set of signals, a smaller set of signals with an integration consistent with the stoichiometric structure of complex **1** was observed, which indicates that two isomers, i.e., cis and trans configurations, may exist in solution (Figure 1).[10a] Variable-temperature ^{1}H NMR spectra of complex **1** were recorded over the range of 10−60 °C in C_6D_6 to elucidate whether there is fluxional behavior (Supporting Information). As temperature changes, the proportion of trans−cis configurations changes only slightly, while all signals remain sharp. This finding implies that there is limited fluxionality of complex **1** in solution. A more fluxional solution behavior of complex **2** was observed, as methylene protons give rise to broad signals. In addition to cis−trans isomerization, a coordination−dissociation process involving the OMe group as a result of one less donor in ligand L^2 may occur in solution.

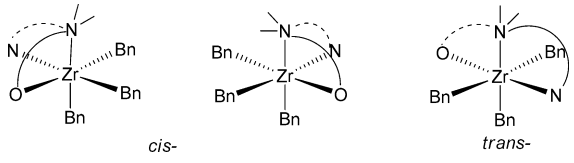


Figure 1. Possible cis and trans configurations of complex **1**.

The solid-state structure of complex **1** (depicted in Figure 2) shows that the zirconium center is six-coordinate, ligated by three benzyl groups and two N atoms and one O atoms from ligand L^1. The coordination geometry is distorted octahedral with atoms N2 and C50 occupying the axial positions (N2−Zr1−C50 175.85°), and atoms Zr1, N1, O1, C43, and C36 (the sum of angles N1−Zr1−O1, O1−Zr1−C43, C43−Zr1−C36, and C36−Zr1−N1 is 359.06°) are nearly coplanar. A cis-chelating mode of L^1 is observed, as supported by the N1−Zr1−O1 angle of 76.08° and N2−Zr1−O1 angle of 92.57°. The OCH_3 group does not coordinate to the metal center, as evidenced by the longer distance between Zr1 and O2 (5.5893(2) Å) in comparison to the sum of atomic radii (r_{Zr}

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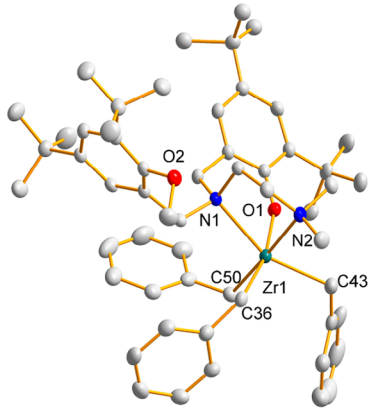
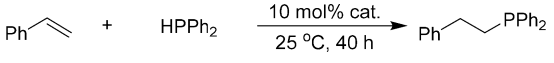


Figure 2. Molecular structure of **1**·C_7H_8 showing 30% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Zr1−O1 1.995(2), Zr1−N1 2.535(3), Zr1−N2 2.573(3), Zr1−C36 2.326(4), Zr1−C43 2.295(4), Zr1−C50 2.296(4); O1−Zr1−N1 76.07(9), O1−Zr1−N2 92.58(10), O1−Zr1−C36 165.10(12), O1−Zr1−C43 98.15(14), O1−Zr1−C50 90.03(13), N1−Zr1−N2 70.74(9), N1−Zr1−C36 89.12(11), N1−Zr1−C43 151.69(13), N1−Zr1−C50 106.82(12), N2−Zr1−C36 83.96(13), N2−Zr1−C43 82.02(14), N2−Zr1−C50 175.85(12), C36−Zr1−C43 95.72(15), C36−Zr1−C50 92.70(15), C43−Zr1−C50 100.81(16).

= 2.16 Å, r_O = 1.520 Å), which is consistent with Zn, Mg, and Ti complexes of similar ligands.[10]

Catalytic Hydrophosphination Reactions of Alkenes. To study the catalytic activities of complexes **1**−**6**, a hydrophosphination reaction of styrene (**7a**) and diphenylphosphine (**8**) was first tested (Table 1). Under mild conditions (neat, 25 °C, 40 h), reactions catalyzed by 10 mol % of zirconium tribenzyl complexes **1** and **2** gave the anti-Markovnikov product **9a** in 94% and 90% yields (entries 1 and 2), respectively, which are in general higher than those of dibenzyl zirconium complexes **3**−**6** (61−65% yields) (entries 3, 4, and 6), with the exception of complex **5** (90% yield) (entry 5). Lowering the catalyst loading to 5 mol % resulted in a lower yield of 60% (entry 1). The activity difference between zirconium tribenzyl and dibenzyl complexes may be due to the fact that more alkyl groups per zirconium center in the former will participate in a metathesis reaction with $HPPh_2$ (vide infra). The fact that 15 mol % of complex **3** led to a higher yield of 96% supported this hypothesis (entry 3). It is noteworthy that 7.5 mol % of $ZrBn_4$ bearing the same number of benzyl groups resulted in only 72% yield, proving that the multidentate phenolato ligand contributes to catalytic activity improvement through adjustment of electronic and steric properties. The higher catalytic activity of complex **5** carrying an [ONO] tridentate bis(phenolato) ligand may be ascribed to more coordination sites for substrates as a result of one less donor in ligand L^5, which is consistent with previous findings from Zr-catalyzed hydroamination reactions.[8]

Table 1. Intermolecular Hydrophosphination of Styrene (7a) with Diphenylphosphine (8) Catalyzed by Complexes 1−6[a]



7a **8** **9a**

entry	cat.	solvent	conversn (%)[b]
1	**1**	none	94 (90,[c] 60[d])
2	**2**	none	90
3	**3**	none	64 (96)[e]
4	**4**	none	65
5	**5**	none	90
6	**6**	none	61
7	**1** + TB	none	56
8	**3** + TB	none	60
9	**1**	toluene	40
10	**1**	PhCl	65
11	none	none	48

[a]Conditions unless specified otherwise: styrene (**7a**; 114 μL, 1 mmol), diphenylphosphine (**8**; 174 μL, 1 mmol) precatalyst **1**−**6** (0.1 mmol, 10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.092 g, 0.1 mmol) if necessary, solvent (2 mL) if necessary, 25 °C, 40 h. [b]Determined by ^{1}H NMR spectroscopy. [c]Isolated yield. [d]5 mol % catalyst loading. [e]15 mol % catalyst loading.

Addition of $[Ph_3C][B(C_6F_5)_4]$ (TB) led to decreased yields of 56% and 60%, respectively (Table 1, entries 7 and 8), which is different from observations that cationic complexes are more active than their neutral counterparts in hydroamination reactions.[8] This may be due to the fact that the Zr−P bond formed from the Zr-alkyl complex and PPh_2H is stronger for cationic species, which inhibits the subsequent insertion of alkene into Zr−P bonds (vide infra). Similar phenomena have been reported for cationic group 3 metal catalysts.[12] With the neutral complex **1**, different solvents were also screened (entries 9 and 10), and neat conditions were found to be optimal. In the absence of Zr complex, a low yield of 48% was obtained (entry 11).

Under optimal conditions, a series of alkenes were studied and tertiary phosphines formed as anti-Markovnikov addition products in 37−94% yields (Table 2). Styrene derivatives bearing either electron-donating or -withdrawing groups at ortho, meta, or para positions reacted smoothly at room temperature and gave tertiary phosphines in 82−93% yields (entries 1−6), indicating good functional group tolerance of this catalytic system. 2- and 4-vinylpyridine were converted to tertiary phosphines in 92 and 87% yields, respectively (entries 7 and 8). A low yield of 37% was obtained with 2-methylstyrene due to steric reasons (entry 9). The transformation of phenylacetylene was less efficient, which resulted in 40% yield, albeit in good *Z*/*E* selectivity of 96/4 (entry 10). In comparison, a much lower yield of 6% was obtained with $ZrBn_4$ (entry 10). Although many catalytic systems have been reported to catalyze this reaction,[13] examples operative at room temperature are rare, which involve iron complexes reported by Webster et al. and ytterbium and calcium complexes by Cui et al.[4c,14] A comparison of Zr complex **1** with literature reports showed higher activity for heterocycle-containing alkenes, i.e., 2-vinylpyridine (**7p**) and 4-vinylpyridine (**7q**), which generally required higher reaction temperature and/or prolonged reaction time.[4c,14] For some substrates, i.e., 1-methoxy-4-vinylbenzene (**7n**) and 1-chloro-4-vinylbenzene (**7j**), higher yields were also obtained in the presence of zirconium complex **1**. Trialkyl zirconium complexes represent the first group 4 metal based catalysts capable of promoting hydrophosphination reactions of secondary phosphines at room temperature.

In addition to aromatic alkenes, hydrophosphination reactions of aliphatic alkenes were also explored, including dienes and acrylates (Table 3). 1,4-Addition reactions of dienes occurred exclusively, which were less efficient than that of

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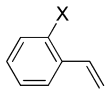
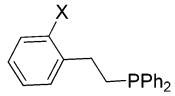
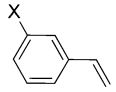
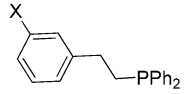
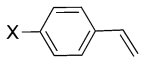
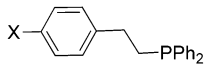
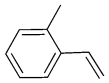
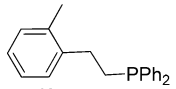
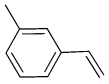
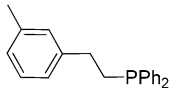
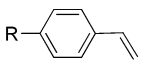
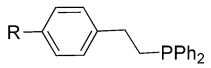
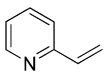
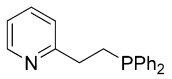
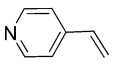
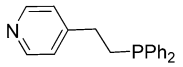
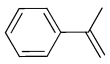
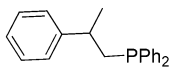
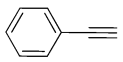
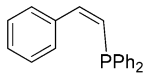
Table 2. Intermolecular Hydrophosphination Reactions of Aromatic Alkenes and Alkynes with Diphenylphosphine Catalyzed by Complex 1[a]

Entry	Subtrate	Product	Yield (%)[b]
1	 **7b-d**	 **9b-d**	X = F (**9b**), 79; X = Cl (**9c**), 82; X = Br (**9d**), 81
2	 **7e-g**	 **9e-g**	X = F (**9e**), 84; X = Cl (**9f**), 94; X = Br (**9g**), 83
3	 **7h-j**	 **9h-j**	X = F (**9h**), 82; X = Cl (**9i**), 93; X = Br (**9j**), 90
4	 **7k**	 **9k**	90
5	 **7l**	 **9l**	86
6	 **7m-o**	 **9m-o**	R = Me (**9m**), 88; R = OMe (**9n**), 93; R = Ph (**9o**), 80
7	 **7p**	 **9p**	92
8	 **7q**	 **9q**	87
9	 **7r**	 **9r**	37
10	 **7s**	 **9s**	40[c] (6[d])

[a]Conditions: alkene **7** (0.5 mmol), diphenylphosphine (**8**; 87 μL, 0.5 mmol), complex **1** (0.045 g, 0.05 mmol), neat, 25 °C, 40 h. [b]Isolated yield. [c]*Z*/*E* ratio 96/4, determined by ^{31}P NMR spectroscopy. [d]7.5 mol % of $ZrBn_4$.

styrene, as temperature elevation was required (entries 1 and 2). Moreover, a steric effect was obvious, as reaction time extension was needed for substrate **7u** bearing a bulky hexyl substituent. Methyl acrylate (**7v**) reacted smoothly with $HPPh_2$ at room temperature, and the reaction was complete within 12 h with 85% isolated yield (entry 3). In comparison, slightly lower yields were obtained with complexes **2**−**6** (entry 3). Reactions of other aliphatic alkenes, e.g. hexene, 1,3-cyclohexadiene, and norbornene, did not proceed; however, these reactions worked in the presence of a triamidoamine Zr complex or Ca complex.[7d,15]

Catalytic Hydrophosphination Reactions of Carbodiimides. Metal catalyst systems,[16] involving alkali-metal,[16a] and alkaline-earth-metal,[16b,h] rare-earth,[16c,f,g,17] and actinide complexes,[16d,e,i] have been developed to catalyze hydrophosphination reactions of carbodiimides. The only example of a zirconium catalyst was reported by Waterman et al., which led to phosphaguanidine formation in moderate yields of 53−75%.[7c] Reaction of *N*,*N*′-diisopropylcarbodiimide (**10a**) and

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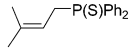
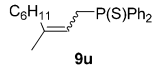
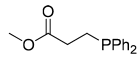
Table 3. Intermolecular Hydrophosphination Reactions of Aliphatic Alkenes with Diphenylphosphine Catalyzed by Complex 1[a]

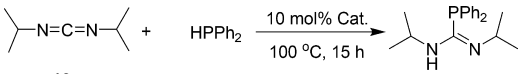
Entry	Subtrate	Conditions	Product	Yield (%)[b]
1	 **7t**	60 °C 26 h	 **9t**	80
2	 **7u**	60 °C 42 h	 **9u**	83[c]
3	 **7v**	25 °C 12 h	 9v	85 (complex **1**) 83 (complex **2**) 79 (complex **3**) 80 (complex **4**) 82 (complex **5**) 80 (complex **6**)

[a]Conditions: alkene **7** (0.5 mmol), diphenylphosphine (**8**; 87 μL, 0.5 mmol), complex **1** (0.045 g, 0.05 mmol), neat. [b]Isolated yield. S_8 (0.018 g, 0.07 mmol) was added to facilitate the purification on silica gel. [c]*Z*/*E* ratio 3/1 determined by ^{31}P NMR spectroscopy.

diphenylphosphine (**8**) was examined with complexes **1**–**6** (Table 4). A trace amount of the product formed in the reaction and generated product **11a** in a low yield of 23% (entry 10). Nearly no conversion was detected in the absence of any catalyst (entry 11).

Aliphatic and aromatic carbodiimides were converted into the corresponding phosphaguanidines in 85% and 82% yields (Table 5), respectively. A higher temperature was required for the reaction of dicyclohexylcarbodiimide (entry 1) in comparison to that for diphenylcarbodiimide (entry 2). No reaction took place at room temperature, making zirconium complexes less active than alkali-metal and alkaline-earth-metal complexes.[16a,b,h]

Table 4. Intermolecular Hydrophosphination of Diisopropylmethanediimine (10a) with Diphenylphosphine (8) Catalyzed by Complexes 1–6[a]



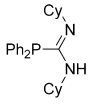
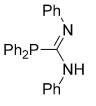
10a **8** **11a**

entry	cat.	solvent	conversn (%)[b]
1	**1**	PhCl	11
2	**3**	PhCl	trace
3	**1** + TB	PhCl	85
4	**2** + TB	PhCl	85
5	**3** + TB	PhCl	90 (88)[c]
6	**3** + TB	none	52
7	**4** + TB	PhCl	82
8	**5** + TB	PhCl	75
9	**6** + TB	PhCl	77
10	TB	PhCl	23
11	none	PhCl	3

[a]Conditions: diisopropylmethanediimine (**10a**; 154 μL, 1 mmol), diphenylphosphine (**8**; 174 μL, 1 mmol), precatalyst **1**–**6** (0.1 mmol, 10 mol %), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.092 g, 0.1 mmol) if necessary, PhCl (2 mL) if necessary, 100 °C, 15 h. [b]Determined by ^{31}P NMR spectroscopy. [c]Isolated yield.

presence of either neutral zirconium tribenzyl complex **1** or dibenzyl complex **3** (entries 1 and 2). However, cationic species generated in situ from neutral complexes and TB efficiently catalyzed the hydrophosphination of carbodiimide (entries 3 and 5). Although the Zr–P bond is stronger for cationic species, the insertion of heterocumulenes is feasible, possibly due to the formation of a chelating phosphaguanidine ligand. The interplay between suitable Lewis acidity and coordination space of metal centers influences catalytic activities. On comparison of complexes **1**–**6**, cationic complexes derived from zirconium dibenzyl complex **3** bearing an [ONNO]-type tetradentate bis(phenolato) ligand showed the highest activity in PhCl (entries 3–9). $[Ph_3C][B(C_6F_5)_4]$ alone catalyzed the

Table 5. Intermolecular Hydrophosphination Reactions of Carbodiimides with Diphenylphosphine Catalyzed by Complex 3[a]

Entry	Subtrate	Conditions	Product	Yield (%)[b]
1	Cy–N=C=N–Cy **10b**	100 °C 15 h	 **11b**	86
2	Ph–N=C=N–Ph **10c**	60 °C 15 h	 **11c**	82

[a]Conditions: **10** (0.5 mmol), diphenylphosphine (87 μL, 0.5 mmol), **3** (0.040 g, 0.05 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.046 g, 0.05 mmol), PhCl (2 mL). [b]Isolated yield.

Catalytic Hydrophosphination Reactions of Isocyanates. Studies on hydrophosphinaton reactions of isocyanates are relatively rare in comparison to those of alkenes and carbodiimides, as only a few catalysts based on actinide,[16d,e,i] iron,[18] and rare-earth metals[16] have been reported. No Zr-catalyzed hydrophosphinaton of isocyanates have been reported. Phenyl isocyanate (**12a**) was treated with diphenylphosphine (**8**) in the presence of zirconium trialkyl complex **1** and dialkyl complex **3** at 60 °C, respectively, and moderate yields of 70% and 58% were obtained (Table 6, entries 1 and 2). Addition of TB led to increased yields of 81% and 93%, respectively (entries 3 and 4). Similar to reactions of carbodiimides, cationic species showed higher activity, and the combination of complex **3** and TB gave the best result (entries 3 and 8–11). A mixture of complex **1** and $[Ph_3C][B(C_6F_5)_4]$ (2 equiv) was employed to catalyze the hydrophosphination of phenyl isocyanate, and a lower yield of 73% yield was obtained (entry 3). This may be due to the fact that strong Lewis acidities of dicationic species lead to strong binding of substrates, which inhibits the subsequent insertion of alkene into Zr–P bonds. Different conditions (neat, 5 mol % catalyst loading, or room temperature) were screened, and the optimal result was obtained in PhCl at 60 °C in the presence of 10 mol % of catalyst (entry 3). It is noteworthy that, at room temperature, a good yield of 82% (entry 7) was obtained, revealing that zirconium complexes are more active than actinide and rare-earth-metal catalysts.[16d,e,17] Low yields were detected with either TB alone or no catalyst (entries 12 and 13).

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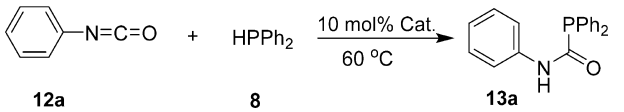
Inorg. Chem. XXXX, XXX, XXX–XXX

Table 6. Intermolecular Hydrophosphination Reactions of Phenyl Isocyanate (12a) with Diphenylphosphine (8) Catalyzed by Zirconium Complexes[a]



12a 8 13a

entry	cat.	solvent	yield (%)[b]
1	**1**	PhCl	70
2	**3**	PhCl	58
3	**1** + TB	PhCl	81 (73)[c]
4	**3** + TB	PhCl	93 (90)[d]
5	**3** + TB	none	69
6	**3** + TB	PhCl	79[e]
7	**3** + TB	PhCl	82[f]
8	**2** + TB	PhCl	74
9	**4** + TB	PhCl	71
10	**5** + TB	PhCl	74
11	**6** + TB	PhCl	88
12	TB	PhCl	40
13	none	PhCl	48[f]

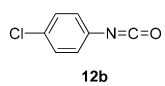
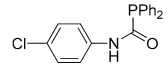
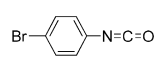
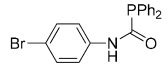
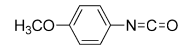
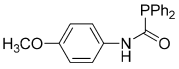
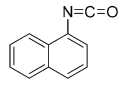
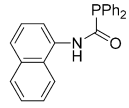
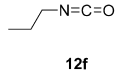
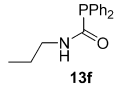
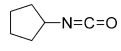
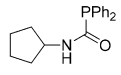
[a]Conditions unless specified otherwise: phenyl isocyanate (**12a**; 54 μL, 0.5 mmol), diphenylphosphine (**8**; 87 μL, 0.5 mmol), **3** (0.05 mmol, 0.040 g), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.046 g, 0.05 mmol) if necessary, PhCl (2 mL), 60 °C, 24 h. [b]Determined by ^{31}P NMR spectroscopy. [c]0.2 mmol of TB. [d]Isolated yield. [e]5 mol % catalyst loading. [f]Room temperature.

Aryl isocyanates bearing different substituents were tested under optimized conditions (Table 7). Both electron-withdrawing and -donating groups were tolerated in this catalytic system, and good yields of 83−93% were obtained (entries 1−3). Reaction of 1-naphthyl isocyanate (**12e**) afforded the desired product phosphaurea **13e** in a moderate yield of 71%, possibly due to steric reasons (entry 4). Aliphatic isocyanates, i.e., propyl isocyanate and cyclopentyl isocyanate, were also converted into the respective phosphaureas **13f,g** in 87 and 67% yields, respectively (entries 5 and 6), showing a broad substrate scope of this Zr-based catalytic system.

CONCLUSION

In summary, zirconium complexes bearing multidentate aminophenolato ligands have been prepared to catalyze hydrophosphination reaction of alkenes and heterocumulenes. Catalytic activities were significantly influenced by modification of ancillary ligands. For hydrophosphination of simple alkenes, trialkyl zirconium complex **1** bearing a multidentate amino mono(phenolato) ligand was found to be more active than dialkyl zirconium complexes **3**−**6** stabilized by bis(phenolato) ligands. Various alkenes with different substituents reacted with $HPPh_2$ and formed tertiary phosphines in 37−94% yields at room temperature. In comparison, cationic species generated in situ from complex **3** were found to be more active for the hydrophosphination of heterocumulenes, i.e., carbodiimides and isocyanates, and gave phosphaguanidines and phosphaureas in 67−93% yields. Through ligand structure modification, the Lewis acidity and coordination space of metal centers are adjusted, which is found to significantly influence catalytic activity. These complexes are among the most active group 4 metal based catalysts for hydrophosphination reactions. Further studies on the group 4 metal complexes and their catalytic activities are ongoing in our laboratory.

Table 7. Intermolecular Hydrophosphination Reactions of Isocyanates 12 with Diphenylphosphine 8 Catalyzed by Complex 3[a]

Entry	Subtrate	Conditions	Product	Yield (%)[b]
1	 **12b**	60 °C 24 h	 **13b**	90
2	 **12c**	60 °C 24 h	 **13c**	93
3	 **12d**	60 °C 24 h	 **13d**	83
4	 **12e**	60 °C 24 h	 **13e**	71
5	 **12f**	60 °C 24 h	 **13f**	87[c]
6	 **12g**	60 °C 24 h	 **13g**	67[c]

[a]Conditions unless specified otherwise: **12** (0.5 mmol), diphenylphosphine (**8**; 87 μL, 0.5 mmol), **3** (0.040 g, 0.05 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.046 g, 0.05 mmol), PhCl (2 mL). [b]Isolated yield. [c]In PhBr-d_5 (0.7 mL), determined by ^1H NMR spectroscopy.

EXPERIMENTAL SECTION

General Considerations. All operations of air- or moisture-sensitive reactions were carried out under a nitrogen atmosphere using standard Schlenk glassware or glovebox techniques. Toluene and hexane were dried by refluxing over Na wire and distilled prior to use. PhCl, PhBr-d_5, and $CDCl_3$ were distilled from CaH_2 and stored under argon. $ZrBn_4$[19] and complexes **3**−**6** were synthesized according to methods reported in the literature.[8,11] ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AVANCE III HD-400 spectrometer. X-ray crystallographic data were acquired using an AXS D8 X-ray diffractometer. Elemental analysis data were obtained with an EA-1110 instrument.

Preparation of Complex 1. A flame-dried 50 mL Schlenk tube was charged with $ZrBn_4$ (0.91 g, 2 mmol) and toluene (10 mL). A solution of L^1H_1 (1.08 g, 2 mmol) in toluene (20 mL) was added dropwise at room temperature. A yellow solid precipitated out during this period. After the mixture was stirred overnight, it was heated until the solid was mostly dissolved and centrifuged. The saturated solution was left in the Schlenk flask, and after a few days, yellow crystals formed from the solution at room temperature. Crystals were collected, washed with toluene (3 × 2 mL), and dried (1.30 g, 1.4 mmol, 72%). Complex **1** is sensitive to both air and moisture and can be stored under inert conditions for months. ^1H NMR (400 MHz, C_6D_6): δ 7.51 (d, 1H, J = 2.35 Hz, ArH), 7.49 (d, 1H, J = 2.51 Hz, ArH), 7.33 (m, 8H, ArH), 7.12 (m, 2H, ArH), 6.94 (m, 3H, ArH), 6.82 (m, 3H, ArH), 6.60 (d, 1H, J = 2.28 Hz, ArH), 4.83 (d, 1H, J = 13.13 Hz, CH_2N), 3.71 (d, 1H, J = 13.13 Hz, CH_2N), 3.37 (s, 3H, OCH_3), 3.25−3.22 (m, 1H, CH_2N), 3.13 (t, 1H, CH_2N), 3.03−2.96 (m, 1H, CH_2N), 2.93 (s, 2H, CH_2Ar), 2.84 (s, 2H, CH_2Ar), 2.80−2.73 (m, 2H, CH_2N), 2.43 (t, 1H, CH_2N), 2.17 (s, 3H, NCH_3), 1.90 (s,

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Inorg. Chem. XXXX, XXX, XXX−XXX

2H, CH_2Ar), 1.75 (s, 9H, $C(CH_3)_3$), 1.59 (s, 3H, NCH_3), 1.37 (s, 9H, $C(CH_3)_3$), 1.35 (s, 9H, $C(CH_3)_3$), 1.11 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 157.8, 155.8, 152.9, 148.1, 145.3, 142.6, 141.9, 136.5, 131.2, 128.3, 126.7, 125.9, 125.8, 125.2, 125.1, 123.8, 123.6, 121.4, 120.3, 120.1 (Ar-C), 63.5 (Ar-CH_2N), 59.9 (Ar-CH_2N), 58.7 (OCH_3), 54.3 (NCH_2), 50.2 (NCH_2), 47.3 (NCH_3), 45.4 (NCH_3), 35.4 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$). Anal. Calcd for $C_{56}H_{78}N_2O_2Zr$: C, 74.53; H, 8.71; N, 3.10. Found: C, 75.44; H, 8.39; N, 2.77.

Preparation of Complex 2. A flame-dried 50 mL Schlenk tube was charged with $ZrBn_4$ (0.91 g, 2 mmol) and toluene (10 mL), and a solution of L^2H_1 (1.05 g, 2 mmol) in toluene (20 mL) was added dropwise at room temperature. The solution turned from orange to yellow during this period. After the mixture was stirred overnight, it was concentrated to around 5 mL and centrifuged. The saturated solution was left in the Schlenk flask, and after a few days, yellow crystals formed from the solution at −30 °C. Crystals were collected, washed with toluene (3 × 2 mL), and dried (0.80 g, 0.9 mmol, 45%). Complex **2** is sensitive to both air and moisture and can be stored under inert conditions for months. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H, J = 2.60 Hz, ArH), 7.32−7.37 (m, 2H, ArH), 6.97−6.95 (m, 7H, ArH), 6.85−6.76 (m, 3H, ArH), 6.78−6.68 (m, 9H, ArH), 3.76 (s, 3H, OCH_3), 2.95 (s, 4H, CCH_2N), 2.68 (s, 6H, $ArCH_2$), 2.29 (d, 3H, NCH_2C), 1.68 (s, 9H, o-$C(CH_3)_3$), 1.58 (s, 9H, o-$C(CH_3)_3$), 1.54(s, 1H, CCH_2C), 1.50(s, 1H, CCH_2C), 1.32 (s, 9H, p-$C(CH_3)_3$) 1.29 (s, 9H, p-$C(CH_3)_3$), 1.26 (m, 2H, CCH_2C), 0.70 (s, 3H, CCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, $CDCl_3$): 156.5, 153.8, 148.7, 141.9, 141.6, 138.0, 136.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.1, 126.3, 125.8, 125.1, 124.1, 120.7 (Ar-C), 66.4 (Ar-CH_2N), 58.8 (Ar-CH_2N), 55.8 (OCH_3), 53.1 (NCH_2C), 36.3 ($C(CH_3)_3$), 35.4 ($C(CH_3)_3$), 34.7 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 33.3 ($C(CH_3)_3$), 31.9 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 23.2 (CCH_2C), 20.2 (CCH_2C), 14.5 (CH_3). Anal. Calcd for $C_{56}H_{77}NO_2Zr$: C, 75.79; H, 8.75; N, 1.58. Found: C, 73.73; H, 8.07; N, 0.969.

General Procedure for Hydrophosphination Reactions. For hydrophosphination of alkenes, a flame-dried 5 mL Schlenk tube was charged with complex **1** (0.045 g, 0.05 mmol), diphenylphosphine (87 μL, 0.5 mmol), and alkene **7** (0.5 mmol). The resulting mixture was stirred neat at 25 °C for 40 h unless otherwise specified. After the reaction, the crude products were purified by column chromatography (petroleum ether/ethyl acetate 200/1, silica gel). S_8 (0.018 g, 0.7 mmol) was added in the case of products **9w−y** before column chromatography to facilitate purification. Isolated products were characterized by ^1H and ^{31}P NMR spectroscopy.

For hydrophosphination of heterocumulenes, a flame-dried 5 mL Schlenk tube was charged with complex **3** (0.040 g, 0.05 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB; 0.046 g, 0.05 mmol), and PhCl (2 mL). The solution was stirred for 5 min, and a color change from orange to yellow was observed. Subsequently diphenylphosphine (87 μL, 0.5 mmol) and carbodiimide **10** (0.5 mmol) or isocyanate **12** (0.5 mmol) were added. The resulting mixture was stirred at 100 °C for 15 h (for carbodiimide unless otherwise specified) or 60 °C for 24 h (for isocyanate). After the reaction, products were extracted by pentane and dried under vacuum (**11a−c**) or purified by column chromatography (petroleum ether/ethyl acetate 50/1, silica gel, **13a−e**). Isolated products were characterized by ^1H and ^{31}P NMR spectroscopy.

*Phenethyldiphenylphosphane (**9a**).*[4c] **9a** was prepared from **7a** (57 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 90% yield (0.131 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47−7.43 (m, 4H, ArH), 7.35−7.33 (m, 6H, ArH), 7.29−7.25 (m, 2H, ArH), 7.19−7.16 (m, 3H, ArH), 2.75−2.69 (m, 2H, CCH_2C), 2.38−2.34 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.87.

*(2-Fluorophenethyl)diphenylphosphane (**9b**).* **9b** was prepared from **7b** (60 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 79% yield (0.122 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49−7.45 (m, 4H, ArH), 7.35−7.34 (m, 6H, ArH), 7.19−7.14 (m, 2H, ArH), 7.05−6.97 (m, 2H, ArH), 2.80−2.74 (m, 2H, CCH_2C), 2.39−2.35 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.84. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 162.4, 160.0, 138.6, 138.5, 133.0, 132.8, 130.6, 130.5, 128.8, 128.7, 128.6, 128.0, 127.9, 124.2, 115.6, 115.3 (Ar-C), 29.0, 28.9 (PCH_2), 25.9 (CH_2). MS: calcd m/z 309.1208 for $C_{20}H_{19}FP$ $[M + H]^+$, found 309.1197.

*(2-Chlorophenethyl)diphenylphosphane (**9c**).*[20b] **9c** was prepared from **7c** (64 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 82% yield (0.133 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40−7.36 (m, 4H, ArH), 7.25−7.21 (m, 7H, ArH), 7.09−7.00 (m, 3H, ArH), 2.78−2.71 (m, 2H, CCH_2C), 2.29−2.25 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.54.

*(2-Bromophenethyl)diphenylphosphane (**9d**).* **9d** was prepared from **7d** (63 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 81% yield (0.149 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.37 (m, 5H, ArH), 7.25−7.24 (m, 6H, ArH), 7.10−7.09 (m, 2H, ArH), 6.92−6.96 (m, 1H, ArH), 2.78−2.72 (m, 2H, CCH_2C), 2.29−2.25 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.43. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 142.2, 142.0, 138.6, 138.4, 133.1, 132.0, 132.9, 130.5, 128.9, 128.7, 128.6, 128.0, 127.7, 124.3 (Ar-C), 33.1, 32.9 (PCH_2), 28.8, 28.7 (CH_2). MS: calcd m/z 369.0408 for $C_{20}H_{19}BrP$ $[M + H]^+$, found 369.0406.

*(3-Fluorophenethyl)diphenylphosphane (**9e**).* **9e** was prepared from **7e** (60 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 84% yield (0.129 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38−7.34 (m, 5H, ArH), 7.27−7.26 (m, 5H, ArH), 7.15−7.09 (m, 1H, ArH), 6.86−6.76 (m, 3H, ArH), 2.66−2.60 (m, 2H, CCH_2C), 2.28−2.24 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.1. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 164.3, 161.9, 145.4, 145.3, 145.1, 138.5, 138.4, 133.0, 132.8, 130.0, 128.9, 128.7, 124.0, 115.3, 115.1, 113.2, 113.0 (Ar-C), 32.2, 32.0 (PCH_2), 30.2, 30.0 (CH_2). MS: calcd m/z 309.1208 for $C_{20}H_{19}FP$ $[M + H]^+$, found 309.1198.

*(3-Chlorophenethyl)diphenylphosphane (**9f**).*[20b] **9f** was prepared from **7f** (64 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 82% yield (0.133 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.33 (m, 4H, ArH), 7.25−7.24 (m, 6H, ArH), 7.07−7.06 (m, 3H, ArH), 6.95−6.93 (m, 1H, ArH), 2.63−2.57 (m, 2H, CCH_2C), 2.27−2.23 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.05.

*(3-Bromophenethyl)diphenylphosphane (**9g**).*[20b] **9g** was prepared from **7g** (65 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 81% yield (0.153 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.32 (m, 4H, ArH), 7.25−7.20 (m, 8H, ArH), 7.04−6.97 (m, 2H, ArH), 2.62−2.56 (m, 2H, CCH_2C), 2.26−2.26 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.89.

*(4-Fluorophenethyl)diphenylphosphane (**9h**).*[4c] **9h** was prepared from **7h** (60 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 82% yield (0.126 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46−7.42 (m, 4H, ArH), 7.34−7.33 (m, 6H, ArH), 7.13−7.09 (m, 2H, ArH), 6.96−6.92 (m, 2H, ArH), 2.73−2.66 (m, 2H, CCH_2C), 2.36−2.32 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.26.

*(4-Chlorophenethyl)diphenylphosphane (**9i**).*[20b] **9i** was prepared from **7i** (60 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 82% yield (0.133 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37−7.33 (m, 4H, ArH), 7.25−7.24 (m, 6H, ArH), 7.14−7.12 (m, 2H, ArH), 7.00−6.98 (m, 2H, ArH), 2.63−2.57 (m, 2H, CCH_2C), 2.26−2.22 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.22.

*(4-Bromophenethyl)diphenylphosphane (**9j**).*[20b] **9j** was prepared from **7j** (65 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 90% yield (0.166 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.45−7.41 (m, 4H, ArH), 7.34−7.28 (m, 8H, ArH), 7.13−7.06 (m, 2H, ArH), 2.71−2.64 (m, 2H, CCH_2C), 2.35−2.30 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.01.

*(2-Methylphenethyl)diphenylphosphane (**9k**).*[20a] **9k** was prepared from **7k** (65 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 90% yield (0.137 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.44 (m, 4H, ArH), 7.34−7.33 (m, 6H, ArH), 7.13−7.09 (m, 4H, ArH), 2.71−2.65 (m, 2H, CCH_2C), 2.31−2.27 (m, 2H, CCH_2P), 2.17 (s, 3H, CH_3) $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.40.

*(3-Methylphenethyl)diphenylphosphane (**9l**).*[20b] **9l** was prepared from **7l** (66 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 86% yield (0.131 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.35 (m, 4H, ArH), 7.26−7.24 (m, 6H, ArH), 7.10−7.06 (m, 1H, ArH), 6.90 (t,

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Inorg. Chem. XXXX, XXX, XXX−XXX

3H, ArH), 2.64−2.58 (m, 2H, CCH_2C), 2.30−2.26 (m, 2H, CCH_2P), 2.23 (s, 3H, CH_3) $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.70.

*(4-Methylphenethyl)diphenylphosphane (**9m**).*[4c] **9m** was prepared from **7m** (66 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 88% yield (0.134 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.45−7.43 (m, 4H, ArH), 7.32−7.31 (m, 6H, ArH), 7.08−7.03 (m, 4H, ArH), 7.19−7.16 (m, 3H, ArH), 2.70−2.64 (m, 2H, CCH_2C), 2.35−2.29 (m, 5H, CCH_2P, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.00.

*(4-Methoxyphenethyl)diphenylphosphane (**9n**).*[4b] **9n** was prepared from **7n** (67 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 93% yield (0.149 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48−7.43 (m, 4H, ArH), 7.35−7.33 (m, 6H, ArH), 7.11−7.08 (d, 2H, J = 8.86 Hz, ArH), 6.83−6.81 (d, 2H, J = 8.44 Hz, ArH), 3.78 (s, 3H, OCH_3), 2.71−2.65 (m, 2H, CCH_2C), 2.37−2.33 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −16.16.

*(2-([1,1′-Biphenyl]-4-yl)ethyl)diphenylphosphane (**9o**).*[20b] **9o** was prepared from **7o** (0.090 g, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 80% yield (0.146 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56−7.54 (m, 2H, ArH), 7.50−7.38 (m, 8H, ArH), 7.34−7.28 (m, 7H, ArH), 7.24−7.21 (d, 2H, J = 8.25 Hz, ArH), 2.79−2.73 (m, 2H, CCH_2C), 2.41−2.37 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.83.

*2-(2-(Diphenylphosphanyl)ethyl)pyridine (**9p**).*[20b] **9s** was prepared from **7s** (53 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 92% yield (0.134 g). ^1H NMR (400 MHz, $CDCl_3$): δ 8.51−8.50 (d, 1H, J = 4.65 Hz, ArH), 7.56−7.51 (m, 1H, ArH), 7.46−7.42 (m, 4H, ArH), 7.32−7.30 (m, 6H, ArH), 7.09−7.06 (m, 2H, ArH), 2.92−2.85 (m, 2H, CCH_2C), 2.51−2.47 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.43.

*4-(2-(Diphenylphosphanyl)ethyl)pyridine (**9q**).*[20b] **9t** was prepared from **7t** (54 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 87% yield (0.127 g). ^1H NMR (400 MHz, $CDCl_3$): δ 8.46−8.44 (dd, 2H, J = 3.10 Hz, J = 6.40 Hz, ArH), 7.44−7.40 (m, 4H, ArH), 7.35−7.32 (m, 6H, ArH), 7.06−7.08 (d, 2H, J = 5.96 Hz, ArH), 7.09−7.06 (m, 2H, ArH), 2.72−2.65 (m, 2H, CCH_2C), 2.35−2.31 (m, 2H, CCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −15.99.

*Diphenyl(2-phenylpropyl)phosphane (**9r**).*[13e] **9r** was prepared from **7r** (66 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 37% yield (0.056 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.31 (m, 4H, ArH), 7.24−7.22 (m, 5H, ArH), 7.20−7.18 (m, 2H, ArH), 7.13−7.08 (m, 3H, ArH), 2.73−2.66 (m, 1H, CH), 2.40−2.34 (m, 1H, CH_2), 2.25−2.19 (m, 1H, CH_2), 1.33(d, 3H, J = 7.2 Hz, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −20.05.

*(Z)-Diphenyl(styryl)phosphane (**9s**).*[20b] **9v** was prepared from **7v** (55 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 40% yield (0.058 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.49 (d, 2H, J = 7.80 Hz, ArH), 7.44−7.43 (m, 4H, ArH), 7.35−7.23 (m, 10H, ArH, CH), 6.47−6.44 (dd, 1H, J = 2.17 Hz, J = 2.35 Hz, PCH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −24.80.

*(3-Methylbut-2-en-1-yl)diphenylphosphine Sulfide (**9t**).*[20a] **9w** was prepared from **7w** (50 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 85% yield (0.122 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82−7.76 (m, 4H, J = 7.80 Hz, ArH), 7.50−7.40 (m, 6H, ArH), 5.25−5.19 (m, 1H, CH), 3.29−3.21 (m, 2H, PCH_2), 1.66−1.64 (d, 3H, J = 4.78 Hz, CH_3), 1.40−1.39 (d, 3H, J = 3.62 Hz, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 41.46.

*(Z)-(3,7-Dimethylocta-2,6-dien-1-yl)diphenylphosphine Sulfide (**9u**).*[20a] **9x** was prepared from **7x** (86 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 83% yield (0.147 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94−7.86 (m, 4H, J = 7.80 Hz, ArH), 7.52−7.47 (m, 6H, ArH), 5.22−5.16 (m, 1H, C═CH), 5.05−5.02 (m, 1H, Me_2C═CH), 3.36−3.33 (d, 2H, J = 13.92 Hz, CH_2), 2.12−2.02 (m, 4H, CH_2), 1.70 (s, 3H, CH_3), 1.63−1.55 (m, 6H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 40.27.

*Methyl 3-(Diphenylphosphanyl)propanoate (**9v**).*[20b] **9y** was prepared from **7y** (45 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 85% yield (0.037 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.31 (m, 4H, ArH), 7.24−7.23 (m, 6H, ArH), 3.54 (s, 3H, CH_3), 2.35−2.24 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −0.23.

*N,N′-Diisopropyl-1,1-diphenylphosphanecarboximidamide (**11a**).*[7c] **11a** was prepared from **10a** (45 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a colorless oil in 88% yield (0.137 g). ^1H NMR (400 MHz, C_6D_6): δ 7.49−7.44 (m, 4H, ArH), 7.07−7.02 (m, 6H, ArH), 4.47−4.40 (m, 1H, CH), 4.36−4.30 (m, 1H, CH), 3.67−3.65 (d, 1H, NH J = 6.50 Hz), 1.27−1.25 (d, 6H, J = 6.19 Hz, CH_3), 0.97−0.95 (d, 6H, J = 6.58 Hz, CH_3). $^1P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −18.70.

*N,N′-Dicyclohexyl-1,1-diphenylphosphanecarboximidamide (**11b**).*[7c] **11b** was prepared from **10b** (0.103 g, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 86% yield (0.169 g). ^1H NMR (400 MHz, C_6D_6): δ 7.51−7.47 (m, 4H, ArH), 7.08−7.02 (m, 6H, ArH), 4.14−4.06 (m, 2H, CH), 3.81−3.79 (d, 1H, NH J = 6.13 Hz), 1.90−1.81 (m, 4H, CH_2), 1.72−1.57 (m, 5H, CH_2), 1.43−1.21 (m, 11H, CH_2), 0.99−0.94 (m, 2H, CH_2). $^1P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −18.31.

*N,N′,1,1-Tetraphenylphosphanecarboximidamide (**11c**).*[7c] **11c** was prepared from **10c** (0.097 g, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 82% yield (0.156 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77−7.75 (d, 1H, J = 7.91 Hz, ArH), 7.43−7.39 (m, 4H, ArH), 7.32−7.30 (m, 1H, ArH), 7.18−7.14 (t, 4H, ArH), 7.11−7.04 (m, 8H, ArH), 6.94−6.91 (q, 2H, ArH), 6.52 (s, 1H, NH). $^1P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −11.31.

*N,1,1-Triphenylphosphanecarboxamide (**13a**).*[17] **13a** was prepared from **12a** (54 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 90% yield (0.137 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53−7.49 (m, 4H, ArH), 7.35−7.34 (m, 6H, ArH), 7.30 (s, 1H, NH), 7.28 (s, 2H, ArH), 7.19−7.15 (t, 2H, ArH), 7.01−6.98 (t, 1H, ArH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −0.23.

*N-(4-Chlorophenyl)-1,1-diphenylphosphanecarboxamide (**13b**).*[17] **13b** was prepared from **12b** (0.077 g, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 90% yield (0.152 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.47 (m, 4H, ArH), 7.35−7.32 (m, 7H, ArH, NH), 7.25−7.23 (d, 2H, J = 8.95 Hz, ArH), 7.13−7.11 (d, 2H, J = 8.76 Hz, ArH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 0.14.

*N-(4-Bromophenyl)-1,1-diphenylphosphanecarboxamide (**13c**).*[17] **13c** was prepared from **12c** (0.099 g, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 90% yield (0.178 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.52−7.47 (m, 4H, ArH), 7.36−7.34 (m, 6H, ArH), 7.32 (brs, 1H, NH), 7.29−7.26 (d, 2H, J = 8.74 Hz, ArH), 7.20−7.18 (d, 2H, J = 8.87 Hz, ArH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 0.22.

*N-(4-Methoxyphenyl)-1,1-diphenylphosphanecarboxamide (**13d**).*[17] **13d** was prepared from **12d** (65 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 83% yield (0.139 g). ^1H NMR (400 MHz, $CDCl_3$): δ 7.52−7.48 (m, 4H, ArH), 7.33−7.32 (m, 6H, ArH), 7.24 (brs, 1H, NH), 7.23−7.20 (d, 2H, J = 9.32 Hz, ArH), 6.71−6.69 (d, 2H, J = 8.95 Hz, ArH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −0.78.

*N-(Naphthalen-1-yl)-1,1-diphenylphosphanecarboxamide (**13e**).*[17] **13e** was prepared from **12e** (72 μL, 0.5 mmol) and **8** (87 μL, 0.5 mmol) as a white solid in 71% yield (0.126 g). ^1H NMR (400 MHz, $CDCl_3$): δ 8.09−8.07 (d, 1H, J = 7.43 Hz, ArH), 7.75 (brs, 1H, NH), 7.69−7.67 (d, 1H, J = 8.10 Hz, ArH), 7.60 (brs, 4H, ArH), 7.52−7.50 (d, 1H, J = 8.24 Hz, ArH), 7.37−7.28 (m, 8H, ArH), 7.22−7.19 (t, 1H, ArH), 6.88−6.86 (d, 1H, J = 8.37 Hz, ArH). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −1.08.

*1,1-Diphenyl-N-propylphosphanecarboxamide (**13f**).* **13f** was prepared from **12f** (19 μL, 0.2 mmol) and **8** (35 μL, 0.2 mmol) in 87% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52−7.47 (m, 4H, ArH), 7.16−7.14 (m, 7H, ArH, NH), 3.03−2.98 (q, 2H, CH_2), 1.18−1.13 (q, 2H CH_2), 0.59−0.55 (t, 3H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −3.88. MS: calcd m/z 272.1204 for $C_{16}H_{19}NOP$ $[M + H]^+$, found 272.1200.

*N-Cyclopentyl-1,1-diphenylphosphanecarboxamide (**13g**).* **13g** was prepared from **12g** (23 μL, 0.2 mmol) and **8** (35 μL, 0.2 mmol) in 67% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52−7.47 (m, 4H, ArH), 7.16−7.14 (m, 7H, ArH, NH), 3.03−2.98 (q, 2H, CH_2), 1.18−1.13 (q, 2H CH_2), 0.59−0.55 (t, 3H, CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): −3.88. MS: calcd m/z 298.1361 for $C_{18}H_{21}NOP$ $[M + H]^+$, found 298.1368.

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■ ASSOCIATED CONTENT

Supporting Information

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NMR spectra of complexes **1** and **2** and hydrophosphination products (PDF)

Accession Codes

CCDC 1572024 contains 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) Allen, D. W. Phosphines and Related P−C-Bonded Compounds. *Organophosphorus Chem.* **2012**, *41*, 1−55. (b) Westheimer, F. H. The Role of Phosphorus in Chemistry and Biochemistry. *Phosphorus Chemistry* **1992**, *486*, 1−17.

(2) For recent reviews, see: (a) Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. Hydrophosphination with Cationic Primary Phosphine Iron Complexes: Synthesis of P-Chiral Functionalized Phosphines. *J. Organomet. Chem.* **2002**, *661*, 95−110. (b) Molander, G. A.; Romero, J. A. C. Lanthanocene Catalysts in Selective Organic Synthesis. *Chem. Rev.* **2002**, *102*, 2161−2185. (c) Coudray, L.; Montchamp, J.-L. Recent Developments in the Addition of Phosphinylidene-Containing Compounds to Unactivated Unsaturated Hydrocarbons: Phosphorus−Carbon Bond Formation by Hydrophosphinylation and Related Processes. *Eur. J. Org. Chem.* **2008**, *2008*, 3601−3613. (d) Glueck, D. S. Catalytic Asymmetric Synthesis of Chiral Phosphanes. *Chem. - Eur. J.* **2008**, *14*, 7108−7117. (e) Ananikov, V. P.; Beletskaya, I. P. Mechanisms of Metal-Catalyzed Hydrophosphination of Alkenes and Alkynes. *Top. Organomet. Chem.* **2012**, *43*, 1−20. (f) Rosenberg, L. Mechanisms of Metal-Catalyzed Hydrophosphination of Alkenes and Alkynes. *ACS Catal.* **2013**, *3*, 2845−2855. (g) Koshti, V.; Gaikwad, S.; Chikkali, S. H. Contemporary Avenues in Catalytic P-H Bond Addition Reaction: A Case Atudy of Hydrophosphination. *Coord. Chem. Rev.* **2014**, *265*, 52−73. (h) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. Iron-Catalysed Hydrofunctionalisation of Alkenes and Alkynes. *ChemCatChem* **2015**, *7*, 190−222. (i) Pullarkat, S. A. Recent Progress in Palladium-Catalyzed Asymmetric Hydrophosphination. *Synthesis* **2016**, *48*, 493−593. (j) Wathier, M.; Love, J. A. Hydroelementation of Unsaturated C−C Bonds Catalyzed by Metal Scorpionate Complexes. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2391−2402. (k) Hill, M. S.; Liptrot, D. J.; Weetman, C. Alkaline Earths as Main Group Reagents in Molecular Catalysis. *Chem. Soc. Rev.* **2016**, *45*, 972−988. (l) Bange, C. A.; Waterman, R. Challenges in Catalytic Hydrophosphination. *Chem. - Eur. J.* **2016**, *22*, 12598−12605.

(3) Pringle, P. G.; Smith, M. B. Platinum(0)-Catalysed Hydrophosphination of Acrylonitrile. *J. Chem. Soc., Chem. Commun.* **1990**, 1701−1702.

(4) (a) Basalov, I. V.; Yurova, O. S.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A. Amido Ln(II) Complexes Coordinated by Bi- and Tridentate Amidinate Ligands: Nonconventional Coordination Modes of Amidinate Ligands and Catalytic Activity in Intermolecular Hydrophosphination of Styrenes and Tolane. *Inorg. Chem.* **2016**, *55*, 1236−1244. (b) Liu, B.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. Heteroleptic Alkyl and Amide Iminoanilide Alkaline Earth and Divalent Rare Earth Complexes for the Catalysis of Hydrophosphination and (Cyclo)Hydroamination Reactions. *Chem. - Eur. J.* **2013**, *19*, 13445−13462. (c) Yuan, J.; Hu, H.; Cui, C. N-Heterocyclic Carbene−Ytterbium Amide as a Recyclable Homogeneous Precatalyst for Hydrophosphination of Alkenes and Alkynes. *Chem. - Eur. J.* **2016**, *22*, 5778−5785.

(5) (a) Scriban, C.; Kovacik, I.; Glueck, D. S. A Protic Additive Suppresses Formation of Byproducts in Platinum-Catalyzed Hydrophosphination of Activated Olefins. Evidence for P-C and C-C Bond Formation by Michael Addition. *Organometallics* **2005**, *24*, 4871−4874. (b) Glueck, D. S. Metal-Catalyzed Asymmetric Synthesis of P-Stereogenic Phosphines. *Synlett* **2007**, *2007*, 2627−2634. (c) Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. Hydrophosphination of Formaldehyde Catalysed by Tris-(hydroxymethyl)phosphine Complexes of Platinum, Palladium or Nickel. *J. Chem. Soc., Dalton Trans.* **1993**, *0*, 269−274. (d) Wicht, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. Platinum-Catalyzed Acrylonitrile Hydrophosphination via Olefin Insertion into a Pt-P Bond. *J. Am. Chem. Soc.* **1997**, *119*, 5039−5040. (e) Wicht, D. K.; Kourkine, I. V.; Kovacik, I.; Glueck, D. S. Platinum-Catalyzed Acrylonitrile Hydrophosphination. P-C Bond Formation via Olefin Insertion into a Pt-P Bond. *Organometallics* **1999**, *18*, 5381−5394. (f) Costa, E.; Pringle, P. G.; Worboys, K. Chemoselective Platinum(0)-Catalysed Hydrophosphination of Ethyl Acrylate. *Chem. Commun.* **1998**, *1*, 49−50. (g) Belli, R. G.; Burton, K. M. E.; Rufh, S. A.; McDonald, R.; Rosenberg, L. Inner- and Outer-Sphere Roles of Ruthenium Phosphido Complexes in the Hydrophosphination of Alkenes. *Organometallics* **2015**, *34*, 5637−5646. (h) Jérome, F.; Monnier, F.; Lawicka, H.; Dérien, S.; Dixneuf, P. H. Ruthenium Catalyzed Regioselective Hydrophosphination of Propargyl Alcohols. *Chem. Commun.* **2003**, 696−697.

(6) Isley, N. A.; Linstadt, R. T. H.; Slack, E. D.; Lipshutz, B. H. Copper-Catalyzed Hydrophosphinations of Styrenes in Water at Room Temperature. *Dalton Trans.* **2014**, *43*, 13196−13200.

(7) (a) Zhao, G.; Basuli, F.; Kilgore, U. J.; Fan, H.; Aneetha, H.; Huffman, J. C.; Wu, G.; Mindiola, D. J. Neutral and Zwitterionic Low-Coordinate Titanium Complexes Bearing the Terminal Phosphinidene Functionality. Structural, Spectroscopic, Theoretical, and Catalytic Studies Addressing the Ti−P Multiple Bond. *J. Am. Chem. Soc.* **2006**, *128*, 13575−13585. (b) Perrier, A.; Comte, V.; Moïse, C.; Le Gendre, P. L. First Titanium-Catalyzed 1,4-Hydrophosphination of 1,3-Dienes. *Chem. - Eur. J.* **2010**, *16*, 64−67. (c) Roering, A. J.; Leshinski, S. E.; Chan, S. M.; Shalumova, T.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. Insertion Reactions and Catalytic Hydrophosphination by Triamidoamine-Supported Zirconium Complexes. *Organometallics* **2010**, *29*, 2557−2565. (d) Ghebreab, M. B.; Bange, C. A.; Waterman, R. Intermolecular Zirconium-Catalyzed Hydrophosphination of Alkenes and Dienes with Primary Phosphines. *J. Am. Chem. Soc.* **2014**, *136*, 9240−9243. (e) Bange, C. A.; Ghebreab, M. B.; Ficks, A.; Mucha, N. T.; Higham, L.; Waterman, R. Zirconium-Catalyzed Intermolecular Hydrophosphination Using a Chiral, Air-Stable Primary Phosphine. *Dalton Trans.* **2016**, *45*, 1863−1867.

(8) (a) Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Synthesis of Group 4 Metal Complexes Stabilized by an AmineBridged Bis(phenolato) Ligand and Their Catalytic Behavior in Intermolecular Hydroamination Reactions. *Organometallics* **2014**, *33*, 994−1001. (b) Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Zirconium Catalysed Intermolecular Hydroamination Reactions of Secondary Amines with Alkynes. *Chem. Commun.* **2015**, *51*, 7633−7636. (c) Sun,

DOI: 10.1021/acs.inorgchem.7b02248
Inorg. Chem. XXXX, XXX, XXX−XXX

Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Zirconium Complexes Stabilized by Amine-Bridged Bis(phenolato) Ligands as Precatalysts for Intermolecular Hydroamination Reactions. *Dalton Trans.* **2015**, *44*, 20352−20360. (d) Zhang, Y.; Sun, Q.; Wang, Y.; Yuan, D.; Yao, Y.; Shen, Q. Intramolecular Hydroamination Reactions Catalyzed by Zirconium Complexes Bearing Bridged Bis(Phenolato) Ligands. *RSC Adv.* **2016**, *6*, 10541−10548.

(9) For selected reports, see: (a) Groysman, S.; Goldberg, I.; Kol, M. Pentabenzyltantalum: Straightforward Synthesis, X-ray Structure, and Application in the Synthesis of $[O_2N]TaBn_3$-Type and $[O_3N]TaBn_2$-Type Complexes. *Organometallics* **2003**, *22*, 3793−3795. (b) Mondal, A.; Sarkar, S.; Chopra, D.; Row, T. N. G.; Rajak, K. K. A Family of Oxorhenium(V) Complexes Incorporating Chelated Monoanionic ONN Reduced Schiff Base and Dianionic ONNO Tetradentate Ligands: Synthesis, Spectroscopic and Electrochemical Studies. *Dalton Trans.* **2004**, 3244−3250. (c) Allan, L. E. N.; MacDonald, J. P.; Nichol, G. S.; Shaver, M. P. Single Component Iron Catalysts for Atom Transfer and Organometallic Mediated Radical Polymerizations: Mechanistic Studies and Reaction Scope. *Macromolecules* **2014**, *47*, 1249−1257. (d) Dugah, D. T.; Skelton, B. W.; Delbridge, E. E. Synthesis and Characterization of New Divalent Lanthanide Complexes Supported by Amine Bis(Phenolate) Ligands and Their Applications in the Ring Opening Polymerization of Cyclic Esters. *Dalton Trans.* **2009**, 1436−1445. (e) Phomphrai, K.; Chumsaeng, P.; Sangtrirutnugul, P.; Kongsaeree, P.; Pohmakotr, M. Reverse Orders of Reactivities in the Polymerization of Cyclic Esters using N_2O_2 Aluminium Alkoxide Complexes. *Dalton Trans.* **2010**, *39*, 1865−1871. (f) Carpentier, J.-F. Rare-Earth Complexes Supported by Tripodal Tetradentate Bis(phenolate) Ligands: A Privileged Class of Catalysts for Ring-Opening Polymerization of Cyclic Esters. *Organometallics* **2015**, *34*, 4175−4189. (g) Jaffredo, C. G.; Chapurina, Y.; Guillaume, S. M.; Carpentier, J.-F. From Syndiotactic Homopolymers to Chemically Tunable Alternating Copolymers: Highly Active Yttrium Complexes for Stereoselective Ring-Opening Polymerization of β-Malolactonates. *Angew. Chem., Int. Ed.* **2014**, *53*, 2687−2691. (h) Guerin, W.; Diallo, A. K.; Kirilov, E.; Helou, M.; Slawinski, M.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. Enantiopure Isotactic PCHC Synthesized by Ring-Opening Polymerization of Cyclohexene Carbonate. *Macromolecules* **2014**, *47*, 4230−4235. (i) Zeng, T.; Wang, Y.; Shen, Q.; Yao, Y.; Luo, Y.; Cui, D. Synthesis and Characterization of Amine-Bridged Bis(phenolate) Yttrium Guanidinates and Their Application in the Ring-Opening Polymerization of 1,4-Dioxan-2-one. *Organometallics* **2014**, *33*, 6803−6811. (j) Klitzke, J. S.; Roisnel, T.; Kirillov, L.; Casagrande, J. O.; Carpentier, J.-F. Yttrium− and Aluminum Bis(phenolate)pyridine Complexes: Catalysts and Model Compounds of the Intermediates for the Stereoselective Ring-Opening Polymerization of Racemic Lactide and β-Butyrolactone. *Organometallics* **2014**, *33*, 309−321. (k) Chapurina, Y.; Klitzke, J.; Casagrande, O. J.; Awada, M.; Dorcet, V.; Kirillov, E.; Carpentier, J.-F. Scandium Versus Ytrium{Amino-Alkoxy-Bis-(Phenolate)} Complexes for the Stereoselective Ring-Opening Polymerization of Racemic Lactide and β-butyrolactone. *Dalton Trans.* **2014**, *43*, 14322−14333. (l) Nie, K.; Feng, T.; Song, F.; Zhang, Y.; Sun, H.; Yuan, D.; Yao, Y.; Shen, Q. Bimetallic Amine-Bridged Bis(Phenolate) Lanthanide Aryloxides and Alkoxides: Synthesis, Characterization, and Application in the Ring-Opening Polymerization of Rac-Lactide and Rac-β-Butyrolactone. *Sci. China: Chem.* **2014**, *57*, 1106−1116. (m) Zeng, T.; Qian, Q.; Zhao, B.; Yuan, D.; Yao, Y.; Shen, Q. Synthesis and Characterization of Rare-Earth Metal Guanidinates Stabilized by Amine-Bridged Bis(Phenolate) Ligands and Their Application in the Controlled Polymerization of Rac-Lactide and Rac-β-Butyrolactone. *RSC Adv.* **2015**, *5*, 53161−53171.

(10) (a) Zhao, R.; Liu, T.; Wang, L.; Ma, H. High Temperature Ethylene Polymerization Catalyzed by Titanium(IV) Complexes with Tetradentate Aminophenolate Ligands in cis-O, N, N Chelating Mode. *Dalton Trans.* **2014**, *43*, 12663−12677. (b) Song, S.; Zhang, X.; Ma, H.; Yang, Y. Zinc Complexes Supported by Claw-Type Aminophenolate Ligands: Synthesis, Characterization and Catalysis in the Ring-Opening Polymerization of Rac-Lactide. *Dalton Trans.* **2012**, *41*, 3266−3277. (c) Wang, L.; Ma, H. Highly Active Magnesium Initiators for Ring-Opening Polymerization of rac-Lactide. *Macromolecules* **2010**, *43*, 6535−6537. (d) Wang, L.; Ma, H. Zinc Complexes Supported by Multidentate Aminophenolate Ligands: Synthesis, Structure and Catalysis in Ring-Opening Polymerization of Rac-Lactide. *Dalton Trans.* **2010**, *39*, 7897−7910.

(11) (a) Tshuva, E. Y.; Goldberg, I.; Kol, M. Isospecific Living Polymerization of 1-Hexene by a Readily Available Nonmetallocene C2-Symmetrical Zirconium Catalyst. *J. Am. Chem. Soc.* **2000**, *122*, 10706−10707. (b) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M. [ONXO]-Type Amine Bis(phenolate) Zirconium and Hafnium Complexes as Extremely Active 1-Hexene Polymerization Catalysts. *Organometallics* **2002**, *21*, 662−670. (c) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. Novel Zirconium Complexes of Amine Bis(Phenolate) Ligands. Remarkable Reactivity in Polymerization of Hex-1-ene due to an Extra Donor Arm. *Chem. Commun.* **2000**, 379−380. (d) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. Zirconium Complexes of Amine-Bis(phenolate) Ligands as Catalysts for 1-Hexene Polymerization: Peripheral Structural Parameters Strongly Affect Reactivity. *Organometallics* **2001**, *20*, 3017−3028.

(12) Bambirra, S.; Tsurugi, H.; van Leusen, D.; Hessen, B. Neutral Versus Cationic Group 3 Metal Alkyl Catalysts: Performance in Intramolecular Hydroamination/Cyclisation. *Dalton Trans.* **2006**, 1157−1161.

(13) (a) Kissel, A. A.; Mahrova, T. V.; Lyubov, D. M.; Georgy, A. V. C.; Fukin, K.; Trifonov, A. A.; Rosald, I. D.; Marond, L. Metallacyclic Yttrium Alkyl and Hydrido Complexes: Synthesis, Structures and Catalytic Activity in Intermolecular Olefin Hydrophosphination and Hydroamination. *Dalton Trans.* **2015**, *44*, 12137−12148. (b) Shulyupin, M. O.; Kazankova, M. A.; Beletskaya, I. P. Catalytic Hydrophosphination of Styrenes. *Org. Lett.* **2002**, *4*, 761−763. (c) Moglie, Y.; González-Soria, M. J.; Martín-García, I.; Radivoy, G.; Alonso, F. Catalyst- and Solvent-Free Hydrophosphination and Multicomponent Hydrothiophosphination of Alkenes and Alkynes. *Green Chem.* **2016**, *18*, 4896−4907. (d) Leyva-Pérez, A.; Vidal-Moya, J. A.; Cabrero-Antonino, J. R.; Al-Deyab, S. S.; Al-Resayes, S. I.; Corma, A. Copper(I)-Catalyzed Hydrophosphination of Styrenes. *J. Organomet. Chem.* **2011**, *696*, 362−367. (e) He, M.; Gamer, M. T.; Roesky, P. W. Homoleptic Chiral Benzamidinate Complexes of the Heavier Alkaline Earth Metals and the Divalent Lanthanides. *Organometallics* **2016**, *35*, 2638−2644. (f) Rosca, S.-C.; Roisnel, T.; Dorcet, V.; Carpentier, J.-F.; Sarazin, Y. Potassium and Well-Defined Neutral and Cationic Calcium Fluoroalkoxide Complexes: Structural Features and Reactivity. *Organometallics* **2014**, *33*, 5630−5642. (g) Liu, B.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. When Bigger Is Better: Intermolecular Hydrofunctionalizations of Activated Alkenes Catalyzed by Heteroleptic Alkaline Earth Complexes. *Angew. Chem., Int. Ed.* **2012**, *51*, 4943−4946.

(14) (a) Gallagher, K. J.; Espinal-Viguri, M.; Mahon, M. F.; Webster, R. L. A Study of Two Highly Active, Air-Stable Iron(III)-m-Oxo Precatalysts: Synthetic Scope of Hydrophosphination Using Phenyl- and Diphenylphosphine. *Adv. Synth. Catal.* **2016**, *358*, 2460. (b) Gallagher, K. J.; Webster, R. L. Room Temperature Hydrophosphination Using a Simple Iron Salen Pre-Catalyst. *Chem. Commun.* **2014**, *50*, 12109−12111. (c) Hu, H.; Cui, C. Synthesis of Calcium and Ytterbium Complexes Supported by a Tridentate Imino-Amidinate Ligand and Their Application in the Intermolecular Hydrophosphination of Alkenes and Alkynes. *Organometallics* **2012**, *31*, 1208−1211.

(15) (a) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. Calcium-Catalyzed Intermolecular Hydrophosphination. *Organometallics* **2007**, *26*, 2953−2956. (b) Perrier, A.; Comte, V.; Moïse, C.; Richard, P.; Le Gendre, P. L. *n*BuLi-Mediated Hydrophosphination: A Simple Route to Valuable Organophosphorus Compounds. *Eur. J. Org. Chem.* **2010**, *2010*, 1562−1568.

(16) (a) Zhang, W.-X.; Nishiura, M.; Hou, Z. Alkali-Metal-Catalyzed Addition of Primary and Secondary Phosphines to Carbodiimides. A General and Efficient Route to Substituted Phosphaguanidines. *Chem.*

DOI: 10.1021/acs.inorgchem.7b02248
Inorg. Chem. XXXX, XXX, XXX−XXX

Commun. **2006**, 3812−3814. (b) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. Heavier Group 2 Element Catalyzed Hydrophosphination of Carbodiimides. *Organometallics* **2008**, *27*, 497−499. (c) Zhang, W.-X.; 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) Batrice, R. J.; Eisen, M. S. Catalytic Insertion of E-H Bonds (E═C, N, P, S) into Heterocumulenes by Amido-Actinide Complexes. *Chem. Sci.* **2016**, *7*, 939−944. (e) Karmel, I. S. R.; Tamm, M.; Eisen, M. S. Actinide-Mediated Catalytic Addition of E-HBonds (E═N, P, S) to Carbodiimides, Isocyanates, and Isothiocyanates. *Angew. Chem., Int. Ed.* **2015**, *54*, 12422−12425. (f) Ma, W.; Xu, L.; Zhang, W.-X.; Xi, Z. Half-Sandwich Rare-Earth Metal Tris(Alkyl) ate Complexes Catalyzed Phosphaguanylation Reaction of Phosphines with Carbodiimides: an Efficient Synthesis of Phosphaguanidines. *New J. Chem.* **2015**, *39*, 7649−7655. (g) 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. (h) De Tullio, M.; Hernán-Gómez, A.; Livingstone, Z.; Clegg, W.; Kennedy, A. R.; Harrington, R. W.; Antiñolo, A.; Martínez, A.; Carrillo-Hermosilla, F.; Hevia, E. Structural and Mechanistic Insights into s-Block Bimetallic Catalysis: Sodium Magnesiate-Catalyzed Guanylation of Amines. *Chem. - Eur. J.* **2016**, *22*, 17646−17656. (i) Liu, H.; Fridman, N.; Tamm, M.; Eisen, M. S. Addition of E−H (E═N, P, C, O, S) Bonds to Heterocumulenes Catalyzed by Benzimidazolin-2-iminato Actinide Complexes. *Organometallics* **2017**, *36*, 3896−3903.

(17) 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.

(18) Sharpe, H. R.; Geer, A. M.; Lewis, W.; Blake, A. J.; Kays, D. L. Iron(II)-Catalyzed Hydrophosphination of Isocyanates. *Angew. Chem., Int. Ed.* **2017**, *56*, 4845−4848.

(19) (a) Zucchini, U.; Albizzati, E.; Giannini, U. Synthesis and Properties of Some Titanium and Zirconium Benzyl Derivatives. *J. Organomet. Chem.* **1971**, *26*, 357−372. (b) Rong, Y.; Al-Harbi, A.; Parkin, G. Highly Variable Zr−CH_2−Ph Bond Angles in Tetrabenzylzirconium: Analysis of Benzyl Ligand Coordination Modes. *Organometallics* **2012**, *31*, 8208−8217. (c) Radlauer, M. R.; Agapie, T. Bimetallic Zirconium Amine Bis(phenolate) Polymerization Catalysts: Enhanced Activity and Tacticity Control for Polyolefin Synthesis. *Organometallics* **2014**, *33*, 3247−3250.

(20) (a) Leyva-Pérez, A.; Vidal-Moya, J. A.; Cabrero-Antonino, J. R.; Al-Deyab, S. S.; Al-Resayes, S. I.; Corma, A. Copper-Catalyzed Hydrophosphiantion of Styrenes. *J. Organomet. Chem.* **2011**, *696*, 362−367. (b) Liu, Q.; Wang, C.; Zhang, X.; Xue, M.; Yao, Y.; Zhang, Y.; Shen, Q. Synthesis and Molecular Structures of Divalent Bridged Bis(Guanidinate) Europium Complexes and Their Application in Intermolecular Hydrophosphination of Alkenes and Alkynes. *New J. Chem.* **2016**, *40*, 10447−10454.

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Inorg. Chem. XXXX, XXX, XXX−XXX