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Carbene Ligands

N-Heterocyclic Carbene–Ytterbium Amide as a Recyclable Homogeneous Precatalyst for Hydrophosphination of Alkenes and Alkynes

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Abstract: The N-heterocyclic carbene–ytterbium(II) amides $(NHC)_2Yb[N(SiMe_3)_2]_2$ (**1**: NHC: 1,3,4,5-tetramethylimidazo-2-ylidene (IMe_4); **2**: NHC: 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr)) and the NHC-stabilized rare-earth phosphide $(IMe_4)_3Yb(PPh_2)_2$ (**3**) have been synthesized and fully characterized. Complexes **1**–**3** are active precatalysts for the hydrophosphination of alkenes, alkynes, and dienes and exhibited much superior catalytic activity to that of the NHC-free amide $(THF)_2Yb[N(SiMe)_2]_2$. Complex **1** is the most active precursor among the three complexes. In particular, complex **1** can be recycled and recovered from the reaction media after the catalytic reactions. Furthermore, it was found that complex **3** could catalyze the polymerization of styrene to yield atactic polystyrenes with low molecular weights. To the best of our knowledge, complex **1** represents the first rare-earth complex that can be recovered after catalytic reactions.

Introduction

Well-defined lanthanide complexes have received a great deal of attention as catalysts for catalytic polymerization and addition of heteroatom–hydrogen bonds to unsaturated organic substrates.[1–3] Among the various lanthanide catalysts, lanthanide amides are one of the most attractive classes because of their high stability. Thus, various lanthanide amides with different types of ligands have been designed for catalytic applications.[2] Recent studies have shown that homoleptic $Ln[N(SiMe_3)_2]_n$ ($n=2$ or 3) complexes can be directly used as catalysts for some transformations.[3] However, their efficiency and selectivity have to be modified through the development of simple strategies to extend the applications. We have recently shown that the efficiency and selectivity for the ytterbium silylamide catalyzed cross-coupling of amines with hydrosilanes were significantly improved by combination with N-heterocyclic carbenes (NHCs).[2i] As a large number of NHCs with different steric and electronic effects are available, it appeared that this strategy would open some new opportunities for rare-earth catalysis.[2i,4] Despite functionalized anionic NHC–lanthanide complexes that have been extensively studied,[5] the NHC–rare-earth amides are few in number, probably because of the incompatibility of the relatively soft NHC ligands with the hard Lewis acidity of the lanthanide ions.[2i,6]

Metal-catalyzed hydrophosphination of alkenes and alkynes represents one of the most atom-economic tools to construct C–P bonds.[7] However, transition-metal catalysts suffer from low efficiencies because the resultant phosphines may suppress catalytic processes.[7c,d] This drawback may be overcome by the employment of rare-earth catalysts because of the highly Lewis acidic metal ions. Therefore, a number of rare-earth catalysts have been developed in the past decades.[7,8] Herein, we report the synthesis of NHC–ytterbium amides $(NHC)_2Yb[N(SiMe_3)_2]_2$ (**1**: NHC: 1,3,4,5-tetramethylimidazol-2-ylidene (IMe_4); **2**: NHC: 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr)) and their catalytic applications for the hydrophosphination of styrene derivatives, alkynes, and dienes. The results indicate that the catalytic performance of $(THF)_2Yb[N(SiMe_3)_2]_2$ can be significantly improved by the replacement of the coordinated THF molecules with the NHCs. Remarkably, it was found that catalyst **1** could be recycled and recovered from the reaction medium. To the best of our knowledge, there are no recoverable and recyclable homogeneous lanthanide catalysts that have been reported so far. In addition, the isolation of the first NHC–lanthanide phosphide $(IMe_4)_3Yb(PPh_2)_2$ (**3**) provided convincing evidence to enable the understanding of the catalytic mechanism.

Results and Discussion

The NHC–ytterbium amides **1** and **2** can be easily obtained in high yields by the reactions of $(THF)_2Yb[N(SiMe_3)_2]_2$ with two equivalents of IMe_4 and I*i*Pr, respectively (Scheme 1). The reaction of complex **1** with two equivalents of $HPPh_2$ in toluene for several hours and subsequent workup resulted in the

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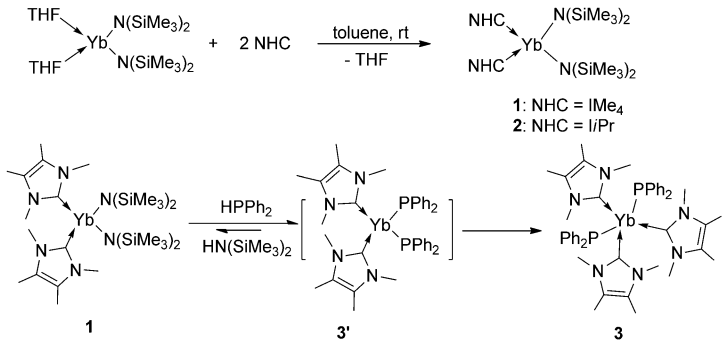


Scheme 1. Synthesis of **1**–**3**.

isolation of the first NHC–lanthanide phosphide complex $(IMe_4)_3Yb(PPh_2)_2$ (**3**) in 41% yield. Complex **3** is very likely to be formed by the ligand redistribution of the possible intermediate $(IMe_4)_2Yb(PPh_2)_2$ (**3′**; Scheme 1). Unfortunately, attempts to isolate the intermediate have been unsuccessful to date, probably as a result of its instability. Alternatively, the reaction of $(THF)_4Yb(PPh_2)_2$ with three equivalents of IMe_4 resulted in the isolation of complex **3** in 64% yield, whereas attempts to isolate complex **3′** by a similar reaction with two equivalents of IMe_4 failed. The isolation of **3** from the reaction of **1** with $HPPh_2$ indicated that an exchange of the NHC and phosphine molecules takes place.

Complexes **1**–**3** have been fully characterized by multiple NMR spectroscopy techniques and elemental analysis. The ^{13}C NMR spectrum of **3** displays the C_{NHC} resonance at $\delta = 201.3$ ppm, which is very similar to that found in complex **1**. The ^{31}P NMR spectrum of **3** exhibits a broad peak at $\delta = 10.7$ ppm at room temperature, which becomes a sharp one at $\delta = 12.8$ ppm at 80 °C. However, the ^{171}Yb satellite could not be observed in the ^{31}P NMR spectra.[9] Crystals of **1** and **3** suitable for X-ray single-crystal analysis were obtained from toluene at −40 °C. The structures are given in Figure 1, together with selected bond parameters. Complex **3** is monomeric with a five-coordinate ytterbium atom, with a largest P1–Yb1–P2 angle of 147.350(16)°. The three Yb–C_{NHC} bond lengths of 2.567(2), 2.5859(19), and 2.591(2) Å are slightly shorter than those observed in complex **1** (2.615(3) Å). The two Yb–P bond lengths of 2.8914(8) and 2.9645(7) Å are comparable to those found in $(THF)_4Yb(PPh_2)_2$ (2.991(2) Å).[9] Complex **3** represents the first example of an NHC–lanthanide phosphide.[10]

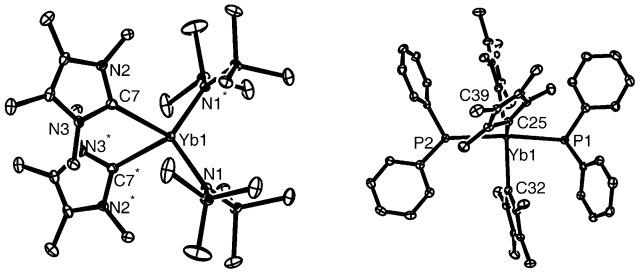
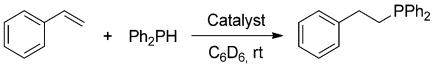


Figure 1. Ortep drawings of **1** (left) and **3** (right) with 30% ellipsoid probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **1**: Yb1–N1 2.736(3), Yb1–C7 2.615(3); N1–Yb1–N1* 118.58(12), C7–Yb1–C7* 79.28(13). **3**: Yb1–P1 2.9645(7), Yb1–P2 2.8914(8), Yb1–C25 2.5859(19), Yb1–C32 2.567(2), Yb1–C39 2.591(2); P1–Yb1–P2 147.350(16), C25–Yb1–C32 111.29(6), C25–Yb(1) –C39 104.63(6), C32–Yb1–C39 143.70(6).

NHC complexes **1**–**3** and (IMes)Yb[$N(SiMe_3)_2$]$_2$ (**4**: IMes:1,3-dimesitylimidazol-2-ylidene)[2l] have been examined as precatalysts for the hydrophosphination of styrene with $HPPh_2$ in C_6D_6 on the NMR scale, and the results are summarized in Table 1. All of the complexes (Table 1, entries 3–7) are active, and the best results were obtained with 5 mol% of **1** (Table 1, entry 3). In contrast, the THF adduct (Table 1, entry 2) only exhibited a very low activity. The catalytic reaction led almost exclusively to the formation of anti-Markovnikov products, with a trace amount of side products. Notably, amide **1** is more active than phosphide **3**, probably because more reactive intermediates, such as low-coordinate phosphide intermediates, were formed during the catalytic process.

Table 1. Hydrophosphination of styrene with different NHC–ytterbium amides.



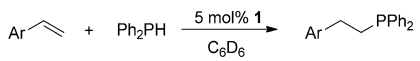
Entry[a]	Cat. (loading [mol%])	*t* [h]	Conv. [%][b]
1	none	10	4
2	$(THF)_2Yb[N(SiMe_3)_2]_2$ (5)	2	10
3	**1** (5)	2	98 (96[c])
4	**1** (3)	2	70
5	**2** (5)	2	65
6	**3** (5)	2	58
7	**4** (5)	2	33

[a] Reaction conditions: Ph_2PH (0.25 mmol, 46.6 mg), styrene (0.3 mmol, 31.2 mg), and catalyst in C_6D_6 (0.4 mL) at room temperature. [b] Based on ^1H and ^{31}P NMR spectroscopy. [c] Yield of isolated product [%].

The hydrophosphination of various styrene derivatives has been examined with 5 mol% of **1** as the precatalyst. Most of the styrenes yielded the corresponding hydrophosphination products in high yields (94–100%), but the substrates with pyridine (Table 2, entries 9 and 10) and MeO- and CN-substituted phenyl groups (Table 2, entries 2 and 7) gave modest conversions. Notably, the reaction is very efficient for the substrates with Me-, F-, Cl-, Br-, and ester-substituted phenyl groups (Table 2, entries 1, 3–6), as well as for napthalenyl ethylene (Table 2, entry 8). The tolerance to heteroatom-containing functional groups observed in the catalytic reactions may be attributed to the strong electron-donating property of the NHC ligands, which render the metal ion less Lewis acidic.[3b]

The catalytic system can also be applied for the hydrophosphination of diphenyl alkenes, alkynes, and dienes (Table 3). The reaction with 1,1-diphenyl alkene at room temperature yielded a single hydrophosphination product in almost quantitative yield (Table 3, entry 1). In contrast, *cis*- and *trans*-1,2-di-

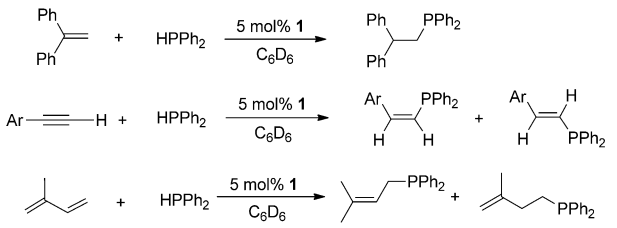
Table 2. Hydrophosphination of monoaryl-substituted ethylene with Ph_2PH in C_6D_6.

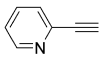
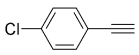
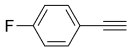


Entry[a]	Ar	T [°C]	t [h]	Conv. [%][b]	Yield [%][c]
1	*p*-MeC_6H_4	60	5	97	94
2	*p*-$MeOC_6H_4$	60	20	62	57
3	*p*-FC_6H_4	RT	6	94	93
4	*p*-ClC_6H_4	RT	1	96	94
5	*p*-BrC_6H_4	RT	1	96	94
6	*p*-$MeO_2CC_6H_4$	RT	4	97	96
7	*p*-NCC_6H_4	RT	2	69	67
8	2-napthalene	60	20	100	99
9	2-pyridine	60	20	46	40
10	4-pyridine	60	20	61	57

[a] Reaction conditions: Ph_2PH (0.25 mmol), alkene (0.3 mmol), and **1** (0.0125 mmol, 5 mol%) in C_6D_6 (0.4 mL) at the required temperature for the required time. [b] Based on ^1H and ^{31}P NMR spectroscopy. [c] Yield of isolated product.

Table 3. Hydrophosphination of diphenyl alkenes, alkynes, and dienes in C_6D_6.



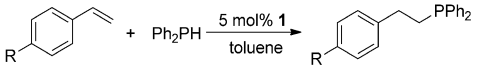
Entry[a]	Substrate	T [°C]	t [h]	Conv. [%][b]	Selectivity[b]
1		RT	4	100 (98[c])	–
2		60	20	25 (22[c])	–
3		60	20	6	–
4		RT	1	100	*Z*/*E* = 85:15
5		RT	2	100	*Z*/*E* = 36:64
6		60	2	94	*Z*/*E* = 39:61
7		60	4	92	*Z*/*E* = 86:14
8		RT	2	100	*Z*/*E* = 90:10
9		RT	5	100	1,4/1,2 = 40:60
10		70	20	25	1,4/1,2 = 70:30

[a] Reaction conditions: $HPPh_2$ (0.3 mmol), alkene or alkyne (0.25 mmol), and **1** (0.0125 mmol, 5 mol%) in C_6D_6 (0.4 mL). [b] On the basis of consumption of the phosphine from integration of the ^1H and ^{31}P NMR spectra. [c] Yield of isolated product.

phenyl alkenes gave only the corresponding products in 6 and 25% yields, respectively (Table 3, entries 2 and 3), which indicated that the reaction is much more efficient for terminal alkenes. The reactions of various terminal alkynes and 1,2-diphenylethyne catalyzed by 5 mol% of complex **1** at room temperature or 60 °C yielded the regioselective products as a mixture of *Z* and *E* isomers (Table 3, entries 4–8),[8j,11] whereas the reaction of isoprene and 2,3-dimethylbuta-1,3-diene yielded mixtures containing the 1,2- and 1,4-addition isomers (Table 3, entries 9 and 10).[8j,11]

It is well known that the main drawback of homogeneous catalysts is the difficulty of their recovery from the reaction medium.[12] This hampers their widespread and practical applications from the viewpoints of catalytic efficiency and cost. Some efforts have been taken to immoblize rare-earth amides for catalytic applications.[13] However, the direct recovery of well-defined rare-earth catalysts has no precedent. Interestingly, catalyst **1** is only sparsely soluble in C_6D_6 and toluene, and it could be recovered from the reaction medium after the catalytic reactions (Table 4). In contrast, $(THF)_2Yb[N(SiMe_3)_2]_2$ is highly soluble in hydrocarbon solvents, which suggests that the electronic factors of the NHCs have pronounced effects on the physical properties of the rare-earth amide. Complex **1** can also be recycled at least four times without loss of activity, as demonstrated in the reaction with styrene (Table 5). The recycling process is simple and straightforward. After one run is complete, complex **1** could be directly collected by filtration and used for the next run without further purification. After recovery and reuse of complex **1** four times, the conversion only slightly decreased as a result of the gradual loss of the precatalyst during the recovery. However, complex **1** might be decom-

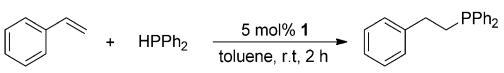
Table 4. Recovery of **1** after the hydrophosphination reaction.



Entry[a]	R	T [°C]	t [min]	Recovery [%][b]
1	H	25	25	50
2	Me	60	60	74
3	F	60	60	57
4	Cl	25	25	56
5	Br	25	25	50

[a] Reaction conditions: Ph_2PH (2.5 mmol), alkene (3.0 mmol), and **1** (0.125 mmol, 5 mol%) in toluene (2 mL) at the required temperature for the required time. [b] Catalyst **1** was recovered by filtration and recrystallization from toluene.

Table 5. Recycling of **1** in the hydrophosphination of styrene.

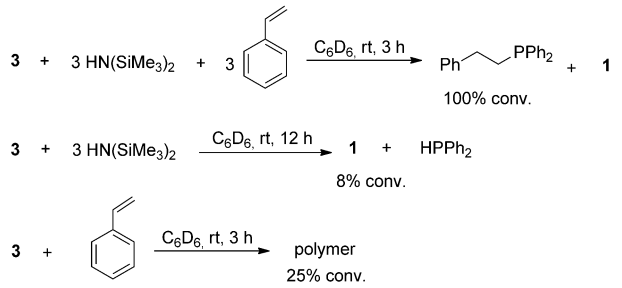


Recycle[a]	1	2	3	4
Conv. [%][b]	98	98	97	95

[a] Reaction conditions: Ph_2PH (2.5 mmol), alkene (3.0 mmol), **1** (0.13 mmol, 5 mol%), and toluene (2 mL) for 2 h at room temperature. [b] Based on ^1H and ^{31}P NMR spectroscopy.

posed with the some functionalized substrates, such as methyl 4-vinylbenzoate, so that recovery is not possible.

In order to probe the mechanism, hydrophosphination of styrene with catalyst **1** (5.0 mg) was monitored by NMR spectroscopy in C_6D_6 at room temperature (Figure S1 in the Supporting Information). It was observed that approximately 18% of the hydrophosphination product was generated, with the formation of a significant amount of $HN(SiMe_3)_2$, in 5 min. The amide catalyst was completely consumed after 5 h, which indicates the very slow protonolysis of the Yb–N bonds with $HPPh_2$. It is noteworthy that the regeneration of complex **1** was observed after Ph_2PH was completely consumed (Figure S1 in the Supporting Information). The reaction of complex **3** with three equivalents of styrene and $HN(SiMe_3)_2$ in C_6D_6 for 3 h led to the clean regeneration of complex **1** with the formation of the hydrophosphination product. However, the reaction of complex **3** with three equivalents of $HN(SiMe_3)_2$ only led to the formation of approximately 8% of complex **1** in 12 h (Scheme 2).

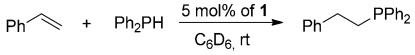


Scheme 2. Reactions of **3** with styrene and $HN(SiMe_3)_2$.

Interestingly, the reaction of **3** with styrene led to the formation of polymer with approximately 25% conversion of styrene in 3 h (Scheme 2 and Table 6).[8c,g] Complex **3** is active for the polymerization of styrenes in toluene to give atactic polymers (Table 6, entries 1–3). In particular, the polymerization of styrene occurred more rapidly with 0.05 mol% of **3** in the absence of solvent (Table 6, entry 1). These results suggested the formation of highly reactive intermediates containing an Yb–C bond by the insertion of styrene into the Yb–P bonds. The polymerization reaction can be extended with 1-chloro-4-vinylbenzene and 1-methoxy-4-vinylbenzene as the monomer, which gave 43 and 22% yields, respectively (Table 6, entries 4 and 6). However, ethene-1,1-diyldibenzene and 1-fluoro-4-vinylbenzene did not polymerize even at 110 °C for 20 h (Table 6, entries 5 and 7).

It was found that an excess of Ph_2PH noticeably suppressed the hydrophosphination reaction, whereas an increase in the amount of styrene accelerated the reaction, probably because of the coordination of the phosphine to the metal. It can be seen from Table 7 that approximately 7% conversion was achieved with two equivalents of Ph_2PH and the reaction was almost completely suppressed with ten equivalents of Ph_2PH (Table 7, entries 1–3). In contrast, approximately 23% conversion was observed with two equivalents of styrene and this was dramatically increased to 63% with ten equivalents of styrene (Table 7, entries 4–6).

Table 7. The effects of concentrations of substrates.

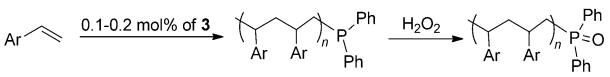


Entry[a]	Styrene [equiv]	Ph_2PH [equiv]	Conv. [%][b]
1	1	2	7
2	1	5	4
3	1	10	1
4	2	1	23
5	5	1	24
6	10	1	63

[a] Reaction conditions: Ph_2PH (0.1–1 mmol, 18.6–186 mg), styrene (0.1–1 mmol, 10.4–104 mg), and catalyst **1** (0.005 mmol, 3.7 mg) in C_6D_6 (1 mL) at room temperature for 1 h. [b] Based on ^1H and ^{31}P NMR spectroscopy.

To obtain mechanistic insights into the reaction, kinetic studies of the hydrophosphination of ethene-1,1-diyldibenzene with Ph_2PH were conducted by monitoring with ^{31}P NMR spectroscopy in C_6D_6 at room temperature with complex **1** as the

Table 6. Polymerization of alkenes with phosphide **3**.



Entry[a]	Ar	Loading [mol%]	Solvent	T [°C]	t [h]	Yield [%][b]	M_n[c]	M_W/M_Z[c]
1	Ph	0.05	neat	RT	0.5	100	37167	2.1
2	Ph	0.1	THF	RT	0.2	100	182049	2.1
3	Ph	0.2	toluene	110	4	32	8546	1.7
4	4-ClC_6H_5	0.2	toluene	110	20	43	49891	3.4
5	4-FC_6H_5	0.2	toluene	110	20	trace	–	–
6	4-$MeOC_6H_5$	0.2	toluene	110	20	22	33073	2.4
7	1,1-diyldibenzene	0.2	toluene	110	20	trace	–	–

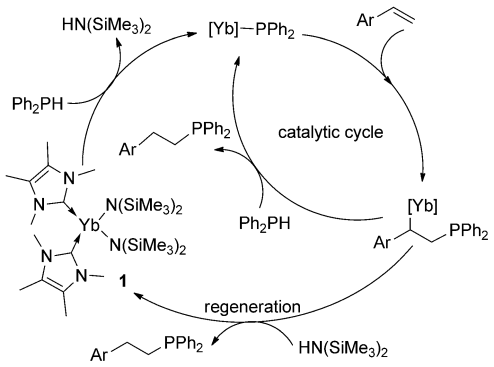
[a] Reaction conditions: alkene (10 mmol) and catalyst **3** (0.005–0.02 mmol) in solvent (1 mL). [b] Yield of isolated product. [c] Determined by gel permeation chromatography in THF at 40 °C against a polystyrene standard. M_n: number average molecular weight; M_W: weight average molecular weight; M_Z: higher average molecular weight.

catalyst. The ethene-1,1-diyldibenzene concentration was maintained in 15-fold excess over the Ph_2PH concentration as the decrease in [Ph_2PH] was monitored. This relationship approaches zero order (Figure S2 in the Supporting Information). Studies were then carried out in which the catalyst concentration was held constant and Ph_2PH concentration was monitored while the ethene-1,1-diyldibenzene concentration was varied from 0.3 to 2.12 M. The linear relationship with a slope of approximately 1.08 ± 0.043 reveals the first order with respect to the alkene (Figure S3 in the Supporting Information). A series of experiments was conducted in which the catalyst concentration was varied from 0.0023 to 0.09 M with [ethene-1,1-diyldibenzene] and [Ph_2PH] in large excess and held constant. From the plot of $-\ln(k_{obs})$ (k_{obs}: observed rate constant) versus $-\ln$([catalyst]), a slope of 1.07 ± 0.049 was obtained (Figure S4 in the Supporting Information). Therefore, complex **1** follows first-order behavior. These results indicated that the reaction of alkenes with the Yb–P bond is the rate-limiting step. The empirically determined rate law is given in Equation (1), in which v is the rate for this equation and k is the rate constant.

$$v = k[\text{catalyst}]^1[\text{alkene}]^1 \quad (1)$$

Based on the Arrhenius equation and k values determined at different temperatures (291–353 K; Figure S5 in the Supporting Information), the activation energy for the hydrosphosphination of styrene with catalyst **1** was estimated to be $E_a = 34.2(1.2)$ kJ mol^{-1}, which indicated a facile hydrophosphination reaction. The activation enthalpy and activation entropy were determined to be $\Delta H^{\neq} = 31.6(1.2)$ kJ mol^{-1} and $\Delta S^{\neq} = -178.9(3.9)$ J mol^{-1} K by the Eyring analysis (Figure S6 in the Supporting Information). These values are substantially lower than those found in the hydrophosphination of styrene with an ytterbium amide supported by a bidentate ligand ($E_a = 60.7(5.4)$ kJ mol^{-1}, $\Delta H^{\neq} = 58.0(5.4)$ kJ mol^{-1}, and $\Delta S \neq = -115.4(22.3)$ J mol^{-1} K).[8k]

Based on the results, a plausible mechanism for the catalytic reaction is shown in Scheme 3. Initially, amide **1** reacted with Ph_2PH to generate the active species with an Yb–P bond and $HN(SiMe_3)_2$. The insertion of styrene into the Yb–P bond yielded an ytterbium alkyl intermediate, which subsequently underwent protonolysis in the presence of Ph_2PH to liberate the product and regenerate the Yb–P bond. After the Ph_2PH was completely consumed, the alkyl intermediate reacted with the $HN(SiMe_3)_2$ formed in the initial step to regenerate catalyst **1**.[14] The formation of polystyrene catalyzed by complex **3** in the absence of $HN(SiMe_3)_2$ strongly supports this mechanism.



Scheme 3. Proposed mechanism for the hydrophosphination and regeneration of the precatalyst **1**.

Conclusion

In summary, we have shown that complexes **1**–**3** are much more efficient precatalysts for the hydrophosphination of alkenes, alkynes, and dienes than the THF-solvated ytterbium(II) amide. Remarkably, complex **1** can be recovered and recycled several times without loss of its activity in some cases. Complex **3** is also active for the polymerization of styrenes and leads to the formation of atactic polystyrenes. The kinetic studies and the reactions of **3** with styrene and $HN(SiMe_3)_2$ provided convincing evidence for the mechanism. The present results demonstrate that NHCs can significantly modulate the reactivity and physical properties of simple rare-earth silylamides, which can lead to high efficiency and recoverable precatalysts. Efforts to discover new features of NHC–lanthanide amides and to expand their catalytic applications are currently in progress.

Experimental Section

General

All manipulations involving air-sensitive materials were carried out under an atmosphere of argon by using modified Schlenk line and glovebox techniques. Alkenes and alkynes were purchased from Alfa-Aesar and J&K Scientific Ltd. All liquid alkenes and alkynes were dried over CaH_2 and freshly distilled. All solvents were distilled from appropriate drying agents. The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data were recorded on Bruker Mercury Plus 400 MHz NMR spectrometers. Chemical shifts (δ) for ^{1}H and ^{13}C spectra are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{31}P spectra are reported relative to an external 85% H_3PO_4 standard. Elemental analysis was carried out on an Elemental Vario EL analyzer. IMe_4,[15] I*i*Pr,[15] $(THF)_2Yb[N(SiMe_3)_2]_2$,[16] $IMesYb[N(SiMe_3)_2]_2$,[2i] and $(THF)_4Yb(PPh_2)_2$[9] were synthesized by following the literature procedures.

Synthesis of $(IMe_4)_2Yb[N(SiMe_3)_2]_2$ (1)

A solution of IMe_4 (0.49 g, 4.0 mmol) in toluene (10 mL) was added to a solution of $(THF)_2Yb[N(SiMe_3)_2]_2$ (1.28 g, 2.0 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 2 h. It was concentrated and stored at $-40\,^{\circ}$C for 12 h to yield black crystals of **1** (1.2 g, 77%). M.p.: 245 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 3.39$ (s, 12H, NCH_3), 1.34 (s, 12H, C*Me*), 0.54 ppm (s, 36H, Si*Me*$_3$); ^{13}C NMR (101 MHz, C_6D_6): $\delta = 201.5$ (s, NCN), 123.8 (s, NC=), 35.1 (s, N*Me*), 8.1 (s, C*Me*), 6.1 ppm (s, Si*Me*$_3$); elemental analysis: calcd for $C_{26}H_{60}YbN_6Si_4$: C 42.08, H 8.15, N 11.32; found: C 42.01, H 8.18, N 11.29.

Synthesis of $(I\mathit{i}Pr)_2Yb[N(SiMe_3)_2]_2$ (2)

A solution of I*i*Pr (0.36 g, 2.0 mmol) in toluene (5 mL) was added to a solution of $(THF)_2Yb[N(SiMe_3)_2]_2$ (0.64 g, 1.0 mmol) in toluene

(5 mL). The mixture was stirred at room temperature for 2 h. It was concentrated and stored at −40 °C for 12 h to yield dark brown crystals of **2** (0.60 g, 70%). M.p.: 111–113 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 4.40 (s, 4H, C*H*Me$_2$), 1.60 (s, 12H, C*Me*), 1.30 (s, 24H, CH*Me*$_2$), 0.48 ppm (s, 36H, Si*Me*$_3$); ^{13}C NMR (101 MHz, [D$_8$]THF): δ = 207.7 (s, NCN), 122.2 (s, NC=), 49.1 (s, N*Me*), 24.8 (s, *C*HMe), 9.2 (s, CH*Me*$_2$), 5.9 ppm (s, Si*Me*$_3$); elemental analysis: calcd for $C_{34}H_{76}YbN_6Si_4$: C 47.80, H 8.97, N 9.84; found: C 47.76, H 8.99, N 9.81.

Synthesis of $(IMe_4)_3Yb(PPh_2)_2$ (3)

Method A: $(IMe_4)_2Yb[N(SiMe_3)_2]_2$ (**1**; 0.37 g, 0.5 mmol) was added to a solution of Ph_2PH (0.19 g, 1.0 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 12 h. It was concentrated and stored at −40 °C for 12 h to yield dark green crystals of **3** (0.19 g, 41%).

Method B: $(THF)_4Yb(PPh_2)_2$ (0.41 g, 0.5 mmol) was added to a solution of IMe_4 (0.19 g, 1.5 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 3 h. It was concentrated and stored at −40 °C for 12 h to yield dark green crystals of **3** (0.29 g, 64%).

M.p.: 170–173 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.60 (s, 8H, Ar), 6.79–6.95 (m, 12H, Ar), 3.43 (s, 18H, NCH_3), 1.41 ppm (s, 18H, CH_3); ^{13}C NMR (101 MHz, C_6D_6): δ = 201.3 (s, NCN), 153.0 (d, J_{C-P} = 39.0 Hz, Ar), 131.4 (d, J_{C-P} = 15.6 Hz, Ar), 127.1 (d, J_{C-P} = 5.4 Hz, Ar), 123.7 (s, Ar), 120.5 (s, NC=), 34.3 (s, N*Me*), 8.2 ppm (s, C*Me*); ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ = 10.7 (br); ^{31}P NMR (162 MHz, [D$_8$]toluene, 80 °C): δ = 12.8 (s); elemental analysis: calcd for $C_{45}H_{56}YbN_6P_2$: C 59.01, H 6.16, N 9.18; found: C 58.92, H 6.18, N 9.21.

NMR-scale catalytic reactions

In a glovebox, $HPPh_2$ (0.25 mmol), C_6D_6 (0.4 mL), and an alkene or alkyne (0.3 mmol) were placed in a Young's tap NMR tube. This was followed by addition of precatalyst **1** (0.0125 mmol, 5 mol%) under the conditions given in Table 2. The conversions of $HPPh_2$ were determined by ^{1}H and ^{31}P NMR spectroscopy.

Polymerization reaction

In a glovebox, alkene (10 mmol), solvent (1 mL), and catalyst **3** (0.005–0.02 mmol) were added into a 10 mL flask. A dark brown mixture was obtained and the polymerization was initiated and carried out for the required temperature and time. The reaction mixture was poured into MeOH (30 mL) to precipitate the polymer product, then 30% H_2O_2 (0.5 mL) was added and the reaction mixture was stirred at room temperature for 1 h. The white polymer product was collected by filtration and dried under vacuum at 60 °C until a constant weight was achieved.

Phosphine-terminated atactic polystyrene: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (br, Ar), 6.65 (br, Ar), 1.92–2.28 (m, PhC*H*), 1.51 ppm (br, CH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.5 ppm (s).

Phosphine-terminated atactic poly(1-chloro-4-vinylbenzene): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05 (br, Ar), 6.40 (br, Ar), 1.81–2.06 (m, PhC*H*), 1.33 ppm (br, CH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.2 ppm (s).

Phosphine-terminated atactic poly(1-methoxy-4-vinylbenzene): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (br, Ar), 6.57 (br, Ar), 3.73 (br, O*Me*), 1.73–2.17 (m, PhC*H*), 1.34 ppm (br, CH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.6 ppm (s).

Typical procedure for the recycling and recovery of precatalyst 1

$HPPh_2$ (2.5 mmol), an alkene (3 mmol), precatalyst **1** (0.125 mmol, 5 mmol%), and toluene (2 mL) were added to a round-bottomed flask. The mixture was stirred under the required conditions. After the catalytic reaction, precatalyst **1** was collected by filtration and directly used for the next run. The recovery could be furnished in 50–74% yields by filtration and recrystallization from toluene.

Preparative-scale catalytic reactions

Diphenylphosphine (1 mmol), an alkene (1.2 mmol), precatalyst **1** (0.05 mmol, 5 mmol%), and toluene (1 mL) were added to a round-bottomed flask. The mixture was stirred. After the reaction was complete, the product was purified by chromatography on silica gel (*n*-hexane/dichloromethane). Alternatively, H_2O_2 (30%, 1 mL) was added to the mixture and it was stirred for 3 h to yield the corresponding oxidation product. The product was extracted with CH_2Cl_2 and dried over $MgSO_4$. After the solvent was removed, the crude product was purified by chromatography on silica gel (*n*-hexane/ethyl acetate).

X-ray crystal structure determination

X-ray data were collected on a Rigaku Saturn CCD diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113 K. The structure was solved by direct methods (SHELXS-97)[17] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with a riding model (SHELXL-97).[18] The crystal data and structure-refinement details are listed in Table S1 in the Supporting Information. CCDC 1406410 (**1**) and 1406411 (**3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Spectroscopic data for the hydrophosphination products

Phenethyldiphenylphosphine:[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.40 (m, 4H, Ar), 7.09–7.29 (m, 11H, Ar), 2.62–2.68 (m, 2H, PhCH_2), 2.27–2.31 ppm (m, 2H, CH_2PPh$_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −15.9 ppm (s).

(4-Methylphenethyl)diphenylphosphine:[8j] ^{1}H NMR (400 MHz, C_6D_6): δ = 6.96–7.41 (m, 14H, Ar), 2.68 (br, 2H, ArCH_2), 2.25 (br, 2H, CH_2PPh$_2$), 2.12 ppm (s, 3H, CH_3); ^{31}P NMR (162 MHz, C_6D_6): δ = −16.2 ppm (s).

(4-Methylphenethyl)diphenylphosphine oxide: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.79 (m, 4H, Ar), 7.48–7.55 (m, 6H, Ar), 7.06 (s, 4H, Ar), 2.86–2.92 (m, 2H, ArCH_2), 2.53–2.60 (m, 2H, CH_2PPh$_2$), 2.30 ppm (s, 3H, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.7 ppm (s).

(4-Methoxyphenethyl)diphenylphosphine:[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.53 (m, 10H, Ar), 7.08 (d, J = 8.3 Hz, 2H, Ar), 6.81 (d, J = 8.4 Hz, 2H, Ar), 3.77 (s, 3H, OCH_3), 2.63–2.69 (m, 2H, ArCH_2), 2.31–2.35 ppm (m, 2H, CH_2PPh$_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.2 ppm (s).

(4-Fluorophenethyl)diphenylphosphine:[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.38 (m, 10H, Ar), 7.02–7.05 (m, 2H, Ar), 6.87 (t, J = 8.4 Hz, 2H, Ar), 2.58–2.65 (m, 2H, ArCH_2), 2.24–2.28 ppm (m, 2H, CH_2PPh$_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.3 ppm (s).

(4-Chlorophenethyl)diphenylphosphine:[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.44 (m, 10H, Ar), 7.14–7.17 (m, 2H, Ar), 7.01 (d, J = 8.4 Hz, 2H, Ar), 2.58–2.64 (m, 2H, ArCH_2), 2.23–2.27 ppm (m, 2H, CH_2PPh$_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.3 ppm (s).

(4-Bromophenethyl)diphenylphosphine:[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.38 (m, 12H, Ar), 6.96 (d, J = 8.2 Hz, 2H, Ar), 2. 65–2.63 (m, 2H, ArCH_2), 2.23–2.27 ppm (m, 2H, CH_2PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.3 ppm (s).

(2,2-Diphenylethyl)diphenylphosphine:[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.33 (m, 4H, Ar), 7.08–7.23 (m, 16H, Ar), 3.83–3.89 (m, 1H, PhC*H*Ph), 2.76 ppm (d, J = 7.9 Hz, 2H, CH_2PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −21.0 ppm (s).

(1,2-Diphenylethyl)diphenylphosphine:[8j] ^{1}H NMR (400 MHz, C_6D_6): δ = 7.00–7.77 (m, 20H, Ar), 3.67–3.72 (m, 1H, PhCH_2), 3.02–3.12 ppm (m, 2H, PhC*H*PPh_2); ^{31}P NMR (162 MHz, C_6D_6): δ = −0.8 ppm (s).

(1,2-Diphenylethyl)diphenylphosphine oxide: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–8.02 (m, 2H, Ar), 7.58 (s, 3H, Ar), 7.41–7.46 (m, 2H, Ar), 7.31 (t, J = 7.3 Hz, 1H, Ar), 7.07–7.23 (m, 10H, Ar), 6.81 (d, J = 6.5 Hz, 2H, Ar), 3.62–3.68 (m, 1H, PhCH_2), 3.24–3.37 ppm (m, 2H, PhC*H*PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 32.8 ppm (s).

2-(2-(Diphenylphosphino)ethyl)pyridine:[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 4.5 Hz, 1H, Ar), 7.55 (t, J = 7.6 Hz, 1H, Ar), 7.44–7.47 (m, 4H, Ar), 7.32 (d, J = 5.5 Hz, 5H, Ar), 7.09 (t, J = 7.5 Hz, 2H, Ar), 2.87–2.93 (m, 2H, PyCH_2), 2.48–2.52 ppm (m, 2H, CH_2PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −15.5 ppm (s).

4-(2-(Diphenylphosphino)ethyl)pyridine:[19] ^{1}H NMR (400 MHz, C_6D_6): δ = 8.49 (br, 2H, Ar), 6.57–7.38 (m, 12H, Ar), 2.39–2.44 (m, 2H, PyCH_2), 2.04–2.08 ppm (m, 2H, CH_2PPh_2); ^{31}P NMR (162 MHz, C_6D_6): δ = −16.2 ppm (s).

Diphenyl(2-(pyridin-4-yl)ethyl)phosphine oxide: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 4.8 Hz, 2H, Ar), 7.67–7.72 (m, 4H, Ar), 7.40–7.50 (m, 6H, Ar), 7.02 (d, J = 5.0 Hz, 2H, Ar), 2.83–2.89 (m, 2H, PyCH_2), 2.47–2.54 ppm (m, 2H, $CH_2P(O)Ph_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.1 ppm (s).

(2-(Naphthalen-2-yl)ethyl)diphenylphosphine:[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.96 (m, 3H, Ar), 7.46–7.77 (m, 14H, Ar), 3.05–3.09 (m, 2H, PhCH_2), 2.62–2.66 ppm (m, 2H, CH_2PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −15.8 ppm (s).

Methyl 4-(2-(diphenylphosphino)ethyl)benzoate: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.2 Hz, 2H, Ar), 7.47–7.51 (m, 4H, Ar), 7.37–7.41 (m, 5H, Ar), 7.26–7.29 (m, 2H, Ar), 3.93 (s, 3H, COO*Me*), 2.77–2.84 (m, 2H, PhCH_2), 2.38–2.43 ppm (m, 2H, CH_2PPh_2); ^{13}C NMR (101 MHz, C_6D_6): δ = 166.6 (s, *C*OOMe), 148.1 (d, J_{C-P} = 13.0 Hz, Ar), 139.1 (d, J_{C-P} = 14.5 Hz, Ar), 133.1 (d, J_{C-P} = 18.7 Hz, Ar), 130.1 (s, Ar), 128.8 (s, Ar), 128.8 (s, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 51.5 (s, COO*Me*), 32.5 (d, J_{C-P} = 18.7 Hz, $PhCH_2$), 30.0 ppm (d, J_{C-P} = 14.3 Hz, CH_2PPh_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.0 ppm (s); elemental analysis: calcd for $C_{17}H_{19}O_2P$: C 71.32, H 6.69; found: C 71.21, H 6.70.

4-(2-(Diphenylphosphino)ethyl)benzonitrile: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.2 Hz, 2H, Ar), 7.46–7.50 (m, 4H, Ar), 7.38–7.40 (m, 6H, Ar), 7.29 (d, J = 8.2 Hz, 2H, Ar), 2.78–2.85 (m, 2H, PhCH_2), 2.37–2.42 ppm (m, 2H, CH_2PPh_2); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.9 (d, J = 12.3 Hz, Ar), 137.8 (d, J = 12.8 Hz, Ar), 132.6 (d, J = 18.7 Hz, Ar), 132.1 (s, Ar), 128.9 (s, Ar), 128.8 (s, Ar), 128.5 (d, J = 6.7 Hz, Ar), 118.9 (s, *C*N), 109.8 (s, Ar), 32.3 (d, J = 18.2 Hz, CH_2PPh_2), 29.5 ppm (d, J = 13.7 Hz, $PhCH_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ = −16.3 ppm (s); elemental analysis: calcd for $C_{21}H_{18}NP$: C 79.98, H 5.75, N 4.44; found: C 79.81, H 5.73, N 4.47.

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Keywords: carbene ligands · homogeneous catalysis · hydrophosphination · nitrogen heterocycles · ytterbium

[1] a) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; b) R. Waterman, *Organometallics* **2013**, *32*, 7249–7263; c) D. Liu, C. Yao, R. Wang, M. Wang, Z. Wang, C. Wu, F. Lin, S. Li, X. Wan, D. Cui, *Angew. Chem. Int. Ed.* **2015**, *54*, 5205–5209; *Angew. Chem.* **2015**, *127*, 5294–5298.

[2] a) S. Y. Seo, T. J. Marks, *Chem. Eur. J.* **2010**, *16*, 5148–5162; b) Q. Li, S. Wang, S. Zhou, G. Yang, X. Zhu, Y. Liu, *J. Org. Chem.* **2007**, *72*, 6763–6767; c) Q. Shen, W. Huang, J. Wang, X. Zhou, *Organometallics* **2008**, *27*, 301–303; d) X. Yu, S. Y. Seo, T. J. Marks, *J. Am. Chem. Soc.* **2007**, *129*, 7244–7245; e) S. Y. Seo, X. Yu, T. J. Marks, *J. Am. Chem. Soc.* **2009**, *131*, 263–276; f) S. Y. Seo, T. J. Marks, *Org. Lett.* **2008**, *10*, 317–319; g) Q. Wu, J. Zhou, Z. Yao, F. Xu, Q. Shen, *J. Org. Chem.* **2010**, *75*, 7498–7501; h) G. Li, M. Lamberti, M. Mazzeo, D. Pappalardo, G. Roviello, C. Pellecchia, *Organometallics* **2012**, *31*, 1180–1188; i) W. Xie, H. Hu, C. Cui, *Angew. Chem. Int. Ed.* **2012**, *51*, 11141–11144; *Angew. Chem.* **2012**, *124*, 11303–11306.

[3] a) P. G. Eller, D. C. Bradley, M. B. Hursthouse, D. W. Meek, *Coord. Chem. Rev.* **1977**, *24*, 1–95; b) R. Anwander, *Top. Curr. Chem.* **1996**, *179*, 33–112; c) H. Nagae, Y. Shibata, H. Tsurugi, K. Mashima, *J. Am. Chem. Soc.* **2015**, *137*, 640–643; d) K. Komeyama, D. Sasayama, T. Kawabata, K. Takehira, K. Takaki, *Chem. Commun.* **2005**, 634–636; e) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* **2001**, *7*, 3078–3085; f) L. Hong, W. Lin, F. Zhang, R. Liu, X. Zhou, *Chem. Commun.* **2013**, *49*, 5589–5591.

[4] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; *Angew. Chem.* **2002**, *114*, 1342–1363; b) S. Díez-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874–883; c) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem.* **2007**, *119*, 3046–3058; *Angew. Chem. Int. Ed.* **2007**, *46*, 2988–3000; d) P. L. Arnold, I. J. Casely, *Chem. Rev.* **2009**, *109*, 3599–3611; e) S. Bellemin-Laponnaz, S. Dagorne, *Chem. Rev.* **2014**, *114*, 8747–8774.

[5] a) Z. R. Turner, R. Bellabarba, R. P. Tooze, P. L. Arnold, *J. Am. Chem. Soc.* **2010**, *132*, 4050–4051; b) P. L. Arnold, Z. R. Turner, R. Bellabarba, R. P. Tooze, *J. Am. Chem. Soc.* **2011**, *133*, 11744–11756; c) P. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, R. Bellabarba, R. P. Tooze, *Dalton Trans.* **2010**, *39*, 6808–6814; d) P. L. Arnold, I. A. Marr, S. Zlatogorsky, R. Bellabarba, R. P. Tooze, *Dalton Trans.* **2014**, *43*, 34–37; e) K. Lv, D. Cui, *Organometallics* **2010**, *29*, 2987–2993; f) B. Wang, D. Wang, D. Cui, W. Gao, T. Tang, X. Chen, X. Jing, *Organometallics* **2007**, *26*, 3167–3172; g) B. Wang, D. Cui, K. Lv, *Macromolecules* **2008**, *41*, 1983–1988; h) K. Lv, D. Cui, *Organometallics* **2008**, *27*, 5438–5440; i) C. Yao, C. Wu, B. Wang, D. Cui, *Organometallics* **2013**, *32*, 2204–2209; j) Z. G. Wang, H. M. Sun, H. S. Yao, Q. Shen, Y. Zhang, *Organometallics* **2006**, *25*, 4436–4438; k) J. Zhang, H. Yao, Y. Zhang, H. Sun, Q. Shen, *Organometallics* **2008**, *27*, 2672–2675; l) H. Yao, Y. Zhang, H. Sun, Q. Shen, *Eur. J. Inorg. Chem.* **2009**, 1920–1925; m) H. Yao, J. Zhang, Y. Zhang, H. Sun, Q. Shen, *Organometallics* **2010**, *29*, 5841–5846.

[6] a) W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte, R. Anwander, *Organometallics* **1997**, *16*, 682–688; b) C. Meermann, G. Gerstberger, M. Spiegler, K. W. Törnroos, R. Anwander, *Eur. J. Inorg. Chem.* **2008**, 2014–2023.

[7] a) O. Delacroix, A. C. Gaumont, *Curr. Org. Chem.* **2005**, *9*, 1851–1882; b) M. Tanaka, *Top. Curr. Chem.* **2004**, *232*, 25–54; c) V. Koshti, S. Gaikwad, S. H. Chikkali, *Coord. Chem. Rev.* **2014**, *265*, 52–73; d) L. Rosenberg, *ACS Catal.* **2013**, *3*, 2845–2855; e) M. Kamitani, M. Itazaki, C. Tamiya, H. Nakazawa, *J. Am. Chem. Soc.* **2012**, *134*, 11932–11935.

[8] a) M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824–1825; b) M. R. Douglass, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2001**, *123*, 10221–10238; c) A. M. Kawaoka, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 6311–6324; d) A. M. Kawaoka, M. R. Douglass, T. J. Marks, *Organometallics* **2003**, *22*, 4630–4632; e) A. Motta, I. L. Fragalà, T. J. Marks, *Or-*

ganometallics **2005**, *24*, 4995 – 5003; f) M. R. Douglass, M. Ogasawara, S. Hong, M. V. Metz, T. J. Marks, *Organometallics* **2002**, *21*, 283 – 292; g) A. M. Kawaoka, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 12764 – 12765; h) I. V. Basalov, S. C. Rosca, D. M. Lyubov, A. N. Selikhov, G. K. Fukin, Y. Sarazin, J. F. Carpentier, A. A. Trifonov, *Inorg. Chem.* **2014**, *53*, 1654 – 1661; i) I. V. Basalov, V. Dorcet, G. K. Fukin, J. F. Carpentier, Y. Sarazin, A. A. Trifonov, *Chem. Eur. J.* **2015**, *21*, 6033 – 6036; j) H. Hu, C. Cui, *Organometallics* **2012**, *31*, 1208 – 1211; k) B. Liu, T. Roisnel, J. F. Carpentier, Y. Sarazin, *Chem. Eur. J.* **2013**, *19*, 13445 – 13462.

[9] a) G. W. Rabe, G. P. A. Yap, A. L. Rheingold, *Inorg. Chem.* **1995**, *34*, 4521 – 4522; b) G. W. Rabe, J. Riede, A. Schier, *Main Group Chem.* **1996**, *1*, 273 – 277.

[10] a) V. H. Schumann, E. Palamidis, G. Schmid, R. Boese, *Angew. Chem.* **1986**, *98*, 726 – 727; b) H. Schumann, E. Palamidis, J. Loebel, *J. Organomet. Chem.* **1990**, *384*, C49 – C52; c) I. V. Basalov, D. M. Lyubov, G. K. Fukin, A. V. Cherkasov, A. A. Trifonov, *Organometallics* **2013**, *32*, 1507 – 1516; d) W. Yi, J. Zhang, L. Hong, Z. Chen, X. Zhou, *Organometallics* **2011**, *30*, 5809 – 5814; e) W. X. Zhang, M. Nishiura, T. Mashiko, Z. Hou, *Chem. Eur. J.* **2008**, *14*, 2167 – 2179.

[11] a) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, *Organometallics* **2007**, *26*, 2953 – 2956; b) B. Liu, T. Roisnel, J. F. Carpentier, Y. Sarazin, *Angew. Chem. Int. Ed.* **2012**, *51*, 4943 – 4946; *Angew. Chem.* **2012**, *124*, 5027 – 5030; c) T. M. A. Al-Shboul, H. Görls, M. Westerhausen, *Inorg. Chem. Commun.* **2008**, *11*, 1419 – 1421; d) K. Takaki, M. Takeda, G. Koshoji, T. Shishido, K. Takehira, *Tetrahedron Lett.* **2001**, *42*, 6357 – 6360; e) K. Takaki, G. Koshoji, K. Komeyama, M. Takeda, T. Shishido, A. Kitani, K. Takehira, *J. Org. Chem.* **2003**, *68*, 6554 – 6565; f) I. V. Basalov, O. S. Yurova, A. V. Cherkasov, G. K. Fukin, A. A. Trifonov, *Inorg. Chem.* **2016**, 55, 1236 – 1244.

[12] D. J. Cole-Hamilton, R. P. Tooze, Catalyst Separation, Recovery and Recycling: Chemistry and Process Design Springer Dordrecht 2006, 1 – 36.

[13] a) J. Zhao, T. J. Marks, *Organometallics* **2006**, *25*, 4763 – 4772; b) E. L. Roux, Y. Liang, M. P. Storz, R. Anwander, *J. Am. Chem. Soc.* **2010**, *132*, 16368 – 16371.

[14] a) A. Motta, G. Lanza, I. L. Fragalà, T. J. Marks, *Organometallics* **2004**, *23*, 4097 – 4104; b) S. Tobisch, *J. Am. Chem. Soc.* **2005**, *127*, 11979 – 11988; c) J. S. Ryu, G. Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 12584 – 12605.

[15] N. Kuhn, T. Kratz, *Synthesis* **1993**, *6*, 561 – 562.

[16] P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, A. V. Protchenko, *J. Organomet. Chem.* **2002**, *647*, 198 – 204.

[17] G. M. Sheldrick, SHELXS-90/96, Program for Structure Solution, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[18] G. M. Sheldrick, SHELXL 97, Program for Crystal structure Refinement, University of Goettingen:Geottingen, Germany, **1997**.

[19] M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, *Org. Lett.* **2002**, *4*, 761 – 763.

[20] A. Leyva-Pérez, J. A. Vidal-Moya, J. R. Cabrero-Antonino, S. S. Al-Deyab, S. I. Al-Resayes, A. Corma, *J. Organomet. Chem.* **2010**, *695*, 362 – 367.

[21] F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Green Chem.* **2012**, *14*, 2699 – 2702.

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