ORGANOMETALLICS

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Synthesis and Characterization of Bidentate Rare-Earth Iminophosphorane *o*-Aryl Complexes and Their Behavior As Catalysts for the Polymerization of 1,3-Butadiene

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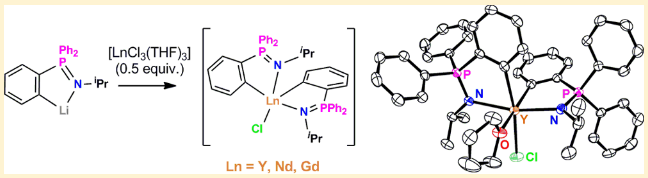
Supporting Information

ABSTRACT: *O*-Aryllithium complexes are easily prepared from stable aminophosphonium salts, and their coordination to rare-earth metals was studied. The ligand to metal ratio in the formed complexes was shown to depend exclusively on the substituent on the nitrogen atom of the ligand. Aryllithium derivatives **3a** and **3b**, exhibiting bulky groups ($SiMe_3$ and ^{t}Bu, respectively), gave monocoordinated yttrium complexes **4a**-Y and **4b**-Y. On the other hand, with aryllithium **3a**, possessing an isopropyl at nitrogen, complexes of Y^{III}, Nd^{III}, and Gd^{III} with a 2:1 ligand to metal ratio could be obtained. Finally with less hindered ligands such as **6c**, featuring an *n*-butyl substituent, triscoordinated Y, Nd, and La complexes were accessible. X-ray crystal structures have been obtained with all three stoichiometries. These complexes were employed as catalyst precursors for 1,3-butadiene polymerization using various activators. Yttrium complexes were found ineffective, but some neodymium complexes achieved highly selective polymerization of 1,3-butadiene, giving up to 95% of 1,4-*cis*-polybutadiene albeit with mild activity.



INTRODUCTION

The search for lanthanide-based catalysts for the *cis*-1,4-selective polymerization of dienes has been a very important research area in the past decades, due to the applications of polydienes with high stereoregularity in the rubber industry. Research on new formulations derived from conventional Ziegler–Natta catalysts, composed of lanthanide carboxylates,[1] phosphates, or alkoxides[2] with alkylaluminum and alkylaluminum chlorides as coactivators, has been a hot topic in both the academic and industrial domains.[3]

In order to improve catalyst activity and solubility for butadiene polymerization, new lanthanide complexes featuring ancillary ligands have been studied. In this area, cyclopentadienyl metal complexes[4] have played a major role. Other ligand systems such as pyridyl-functionalized cyclopentadienyl,[5] bis(phosphinophenyl)amido-ligand,[6] bis(amido)-cyclophosphazane,[7] or imines[8] have also been proposed. Among them, catalysts featuring imine ligands have shown particularly high activity and selectivity. This prompted us to investigate the potential of iminophosphorane ligands (the phosphorus analogue of imines) for such applications. The apparent similarity between the imine and iminophosphorane functional groups stems from the fact that the electronegativities of phosphorus and carbon are roughly the same and thus that the polarization of the C=N and P=N bonds should be similar. However, the P–N bond of an iminophosphorane is by far more polarized than the C–N bond of an imine. In addition, there is no π system in iminophosphoranes, and thus they have no accepting properties; moreover, because of the presence of two lone pairs at the nitrogen atom, they behave as strong donors, and the phosphorus–nitrogen bond is more polarized than in imines. Iminophosphoranes, though less investigated than imines, have shown good potential in coordination chemistry and more recently in catalysis. In particular the Cavell and Stephan groups used such ligands in olefin polymerization.[9] For a few years our group has developed facile and straightforward synthetic methodologies to access different iminophosphorane-based ligand systems,[10] which rely on the Kirsanov reaction[11] involving bromination of a phosphine followed by reaction with a primary amine in the presence of a base. The advantage of such a protocol over the more common Staudinger reaction[12] is that it avoids the handling of azides, which are often hazardous, and allows a greater diversity of substituents on the nitrogen atom. To the best of our knowledge, there is no example of butadiene 1,4-*cis*-polymerization with lanthanide complexes bearing iminophosphorane ligands.

The good results of Cui et al.[8] with tridentate bis(imine) *o*-aryl–rare-earth complexes prompted us to try to synthesize chelating iminophosphorane *o*-aryl–rare-earth complexes. In this paper we present the synthesis and isolation of iminophosphorane *o*-aryllithium complexes, their use as precursors to new iminophosphorane *o*-aryl–rare-earth (Y,

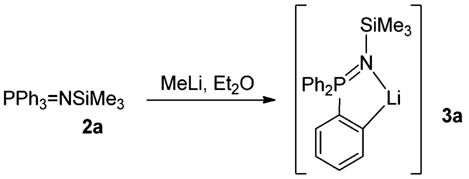
Received: May 9, 2012
Published: June 21, 2012

La, Nd, Gd) complexes, and the use of these complexes in diene polymerization.

■ RESULTS AND DISCUSSION

Ligands Synthesis. Steiner and Stalke have shown that the iminophosphorane $Ph_3P{=}NSiMe_3$ (**2a**) could undergo *o*-lithiation of one phenyl group using an alkyllithium, thus yielding the corresponding lithium salt **3a**, which was structurally characterized as a solvated dimer: $[(o\text{-}C_6H_4\text{-}PPh_2{=}NSiMe_3)Li]_2(Et_2O)$ (**3a**·0.5 $Et_2O)_2$.[13]

Scheme 1. Synthesis of Iminophosphorane Anion 3a



The Kirsanov procedure allows the synthesis of diversely substituted aminophosphonium salts, which can be transformed in situ into the corresponding iminophosphoranes by action of a strong base. Thus, reaction of aminophosphonium salts **1b−d** (respectively bearing ^{t}Bu, ^{i}Pr, and ^{n}Bu groups at nitrogen) with 2 equiv of ^{n}BuLi in toluene/hexane directly generated the iminophosphorane anions as unsolvated lithium salts **3b−d** in a one-pot procedure, without isolation of the intermediate iminophosphoranes (Scheme 2).

Colorless monocrystals of compounds **3b−d** as solvates could be obtained by slow diffusion of pentane in THF or ether after several days at room temperature. The dimeric X-ray solid-state structure of $[(o\text{-}C_6H_4\text{-}PPh_2{=}N^tBu)Li]_2(THF)$, (**3b**·0.5THF)$_2$, is depicted in Figure 1 (there are four independent but similar molecules in the unit cell, and only one is represented), and that of $[(o\text{-}C_6H_4\text{-}PPh_2{=}N^nBu)Li]_2(Et_2O)$, (**3d**·0.5$Et_2O)_2$, is given in the Supporting Information. The crystallographic data of the reported structures are gathered in Table 1. Both structures are similar to that of (**3a**·0.5$Et_2O)_2$,[13] where one lithium atom (Li1) is bonded to the two P=N moieties and the other lithium (Li2) is coordinated to the solvent. For these compounds, Li1 resides in a distorted tetrahedral environment, while Li2 is almost planar trigonal. The Li1−C distances (Li1−C mean = 2.35(4)Å for (**3b**·0.5THF)$_2$, 2.39(3) Å for (**3d**·0.5$Et_2O)_2$) are on average 0.2 Å longer than the Li2−C distances (Li2−C2 mean = 2.13(4) Å for (**3b**·0.5THF)$_2$, 2.15(1) Å for (**3d**·0.5$Et_2O)_2$). In contrast, $[(o\text{-}C_6H_4\text{-}PPh_2{=}N^tBu)Li]_2(THF)_2$, (**3c**·THF)$_2$, displays an original centrosymmetric dimeric structure, which is depicted in Figure 1. The two P=N functions are bonded to different lithium atoms, which are both coordinated to THF (Figure 1). Here, the two lithium atoms have an identical tetrahedral geometry and show different Li−C distances for each lithium atom (Li1−C2 mean = 2.17(1) Å and Li1_1−C2 mean = 2.37(2) Å).

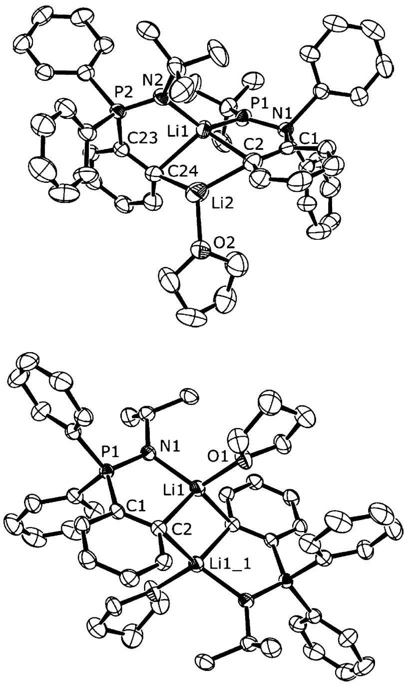


Figure 1. ORTEP plots (50% ellipsoids) of lithium complexes $[(o\text{-}C_6H_4\text{-}PPh_2{=}N^tBu)Li]_2(THF)$, (**3b**·0.5THF)$_2$ (top), and $[(o\text{-}C_6H_4\text{-}PPh_2{=}N^tBu)Li]_2(THF)_2$, (**3c**·THF)$_2$ (bottom). There are four independent but similar molecules of (**3b**·0.5THF)$_2$ and two independent but similar molecules of (**3c**·THF)$_2$ in the unit cells, and only one of each is represented. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for (**3b**·0.5THF)$_2$: C(2)−Li(1) = 2.318(6), C(24)−Li(1) = 2.333(6), N(1)−Li(1) = 2.037(5), N(2)−Li(1) = 2.041(5, C(24)−Li(2) = 2.118(7), C(2)−Li(2) = 2.128(7), O(1)−Li(2) = 1.931(6), N(1)−Li(1)−N(2) = 135.1(3), N(1)−Li(1)−C(2) = 90.3(2), C(2)−Li(1)−C(24) = 107.5(2), N(2)−Li(1)−C(24) = 87.6(2), Li(1)−C(2)−Li(2) = 63.2(2), C(2)−Li(2)−C(24) = 124.1(3), Li(2)−C(24)−Li(1) = 63.1(2), C(24)−Li(1)−C(2) = 107.5(2), O(1)−Li(2)−C(2) = 113.3(3), O(1)−Li(2)−C(24) = 115.5(3); for (**3c**·THF)$_2$: C(2)−Li(1) = 2.199(2), C(2)−Li(1_1) = 2.321(2), N(1)−Li(1) = 2.046(2), O(1)−Li(1) = 1.964(3), Li(1)−C(2)−Li(1_1) = 67.3(1), N(1)−Li(1)−C(2) = 92.2(1), O(1)−Li(1)−C(2_1) = 101.3(1), O(1)−Li(1)−N(1) = 114.8(1), C(2)−Li(1)−C(2_1) = 112.7(1).

Rare-Earth Complexes Synthesis. *Reactions of Aryllithiums 3a−d with $[LnCl_3(THF)_3]$ (Ln = Y, La, Nd, Gd).* Preliminary experiments between aryllithium precursors in varying stoichiometric amounts and $[LnCl_3(THF)_3]$ were performed in NMR tubes and monitored by ^{31}P NMR spectroscopy (except with Ln = Gd, for which complexes are NMR silent because of severe line broadening and isotropic magnetic susceptibility of Gd^{III}). It soon appeared that the ligand:metal ratio in the complexes formed in solution was

Scheme 2. Synthesis of Aminophosphonium Salts 1b−d and Iminophosphorane Anions 3b−d

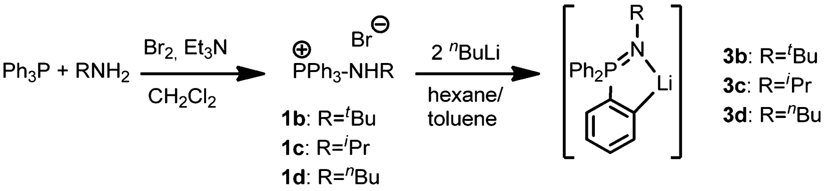
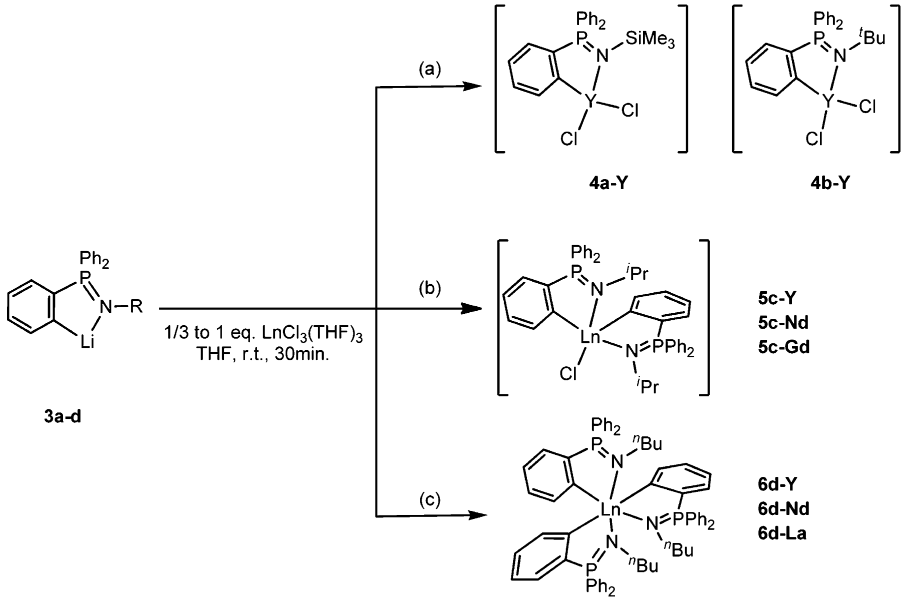


Table 1. Crystal Data and Data Collection Parameters for Compounds (3b·0.5THF)$_2$, (3c·THF)$_2$, (3d·0.5Et$_2$O)$_2$, 4a-Y, 5c-Y·THF, 6d-Nd, and 6d-La

compound	(**3b**·0.5THF)$_2$	(**3c**·THF)$_2$	(**3d**·0.5Et$_2$O)$_2$	**4a**-Y·2LiCl·4THF	**5c**-Y·THF	**6d**-Nd	**6d**-La
molecular formula	$C_{48}H_{54}Li_2N_2O\ P_2$	$C_{50}H_{58}Li_2N_2O_2P_2$	$C_{48}H_{56}Li_2N_2OP_2$	$C_{37}H_{55}Cl_4Li_2NO_4PSiY,1/2(C_4H_8O)$	$C_{46}H_{50}ClN_2OP_2Y,C_4H_8O$	$C_{66}H_{69}N_3NdP_3,C_7H_8$	$C_{66}H_{69}LaN_3P_3,C_4H_8O, C_7H_8$
molecular weight	750.75	794.80	752.77	917.52	905.28	1233.53	1300.30
cryst habit	pale brown block	yellow block	pale yellow block	colorless block	colorless needle	pale yellow block	pale yellow block
cryst dimens (mm)	0.40 × 0.40 × 0.20	0.40 × 0.36 × 0.32	0.18 × 0.16 × 0.12	0.30 × 0.14 × 0.08	0.40 × 0.12 × 0.06	0.30 × 0.30 × 0.30	0.30 × 0.20 × 0.10
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	28.118(1)	10.637(1)	11.164(1)	17.258(1)	19.475(1)	13.147(1)	13.154(1)
b (Å)	33.105(1)	11.054(1)	19.772(1)	11.338(1)	9.673(1)	15.142(1)	15.279(1)
c (Å)	18.385(1)	21.721(1)	19.576(1)	26.404(1)	25.108(1)	18.314(1)	18.133(1)
α (deg)	90.00	80.508(1)	90.00	90.00	90.00	88.807(1)	88.449(1)
β (deg)	90.000(1)	79.326(1)	101.293(1)	115.468(3)	103.016(1)	70.318(1)	69.426(1)
γ (deg)	90.00	62.992(1)	90.00	90.00	90.00	85.995(1)	84.688(1)
V (Å^3)	17113.6(12)	2226.5(3)	4237.4(5)	4664.4(5)	4608.4(6)	3424.4(4)	3397.2(4)
Z	16	2	4	4	4	2	2
d (g cm^{-3})	1.166	1.186	1.180	1.307	1.305	1.196	1.271
F(000)	6400	848	1608	1912	1896	1282	1356
μ (cm^{-1})	0.139	0.138	0.140	1.577	1.433	0.869	0.745
θ_{max}	27.48	30.01	30.01	25.35	27.48	26.02	27.48
reflns measd	76 892	32 520	45 426	25 770	34 490	38 368	49 417
unique data	39 139	12 866	12 333	8440	10 568	13 289	15 476
R_{int}	0.0328	0.0322	0.0288	0.0467	0.0493	0.0320	0.0388
wR2 (all data)	0.1390	0.1410	0.1251	0.1009	0.0989	0.1196	0.1207
R1	0.0574	0.0501	0.0461	0.0498	0.0423	0.0487	0.0474
GoF	0.989	1.084	1.072	1.054	1.013	1.117	1.076

Scheme 3. Reactions of Iminophosphorane Anions 3a−d with $[LnCl_3(THF)_3]$ in Molar Ratios 1:1 (a), 2:1 (b), and 3:1 (c)



much more dependent on the steric properties of the nitrogen substituent of the iminophosphorane than on the size of the rare-earth ion.

For example, it was found that with ligand **3c** the optimum ligand:metal (Y, Gd, or Nd) ratio was 2:1. When $[LnCl_3(THF)_3]$ (Ln = Y or Nd) and **3c** were mixed in proportions 1:1 and slightly above, ^{31}P NMR showed the disappearance of **3c** and the appearance of two new resonances, which were attributed to complexes with 1:1 and 2:1 ligand:metal ratios; when these proportions were raised to 3:1 or above, the reaction did not go to completion since ^{31}P NMR revealed the presence of both 2:1 and 3:1 complexes together with that of starting **3c**. When the **3c**:$LnCl_3$ proportion was exactly 2:1, there was a major peak, and indeed it has been possible to isolate the corresponding 2:1 complex (see below).

Likewise, with ligand **3d**, it has been determined by similar experiments that the optimum ligand:metal ratio was 3:1.

With ligands **3a** and **3b**, the results were only conclusive in the case of yttrium, for which the corresponding 1:1 complexes were isolated. (Scheme 3).

*Monocoordinated Complexes **4a**-Y and **4b**-Y.* Solutions of 1 equiv of compounds **3a** and **3b** in THF were added to a suspension of $[YCl_3(THF)_3]$ (1 equiv) in THF and stirred 30 min. After solubilization of the mixture and appearance of a yellow coloration, the ^{31}P NMR indicated the formation of a new product. Coordination of the ligands to yttrium was evidenced by a downfield shift, from a singlet at 16 ppm (respectively 12 ppm) to a doublet at 28 ppm (respectively 25 ppm), with a J_{PY} coupling constant of 10 Hz (respectively 18 Hz), corresponding to complexes **4a**-Y (respectively **4b**-Y). In the solid state, **4a**-Y is present as an ate-complex, $[o\text{-}C_6H_4\text{-}(Ph_2)P{=}N\text{-}SiMe_3]Y[(\mu\text{-}Cl)_2Li(THF)_2]_2$ (**4a**-Y·2LiCl·4THF), as established by single-crystal X-ray diffraction (Figure 2). Although the conversion appeared complete by NMR, no more than a few crystals of pure compound could be obtained by concentration of the reaction mixture. X-ray analyses showed that complex **4a**-Y·2LiCl·4THF crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The bridging chlorides are bonded with two lithium atoms, which are each solvated by two molecules of THF. The molecule thus adopts a pseudo-octahedral geometry, with the atoms C2, Cl1, Cl2, and Cl4 equatorial and N1 and Cl3 in apical positions.

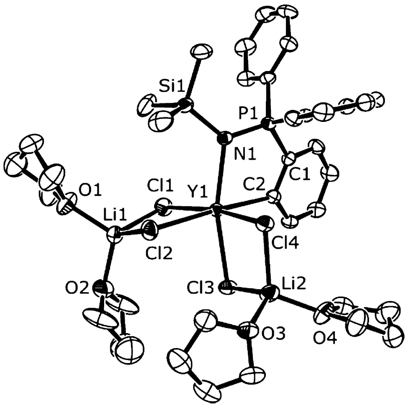
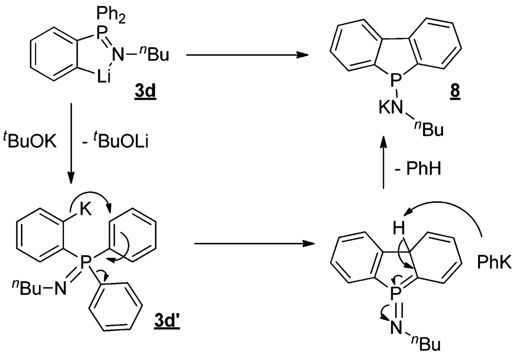


Figure 2. ORTEP plot (50% ellipsoids) of $[o\text{-}C_6H_4\text{-}(Ph_2)P{=}N\text{-}SiMe_3]YCl_4Li_2(THF)_4$ (**4a**-Y·2LiCl·4THF) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bonds lengths [Å] and angles [deg]: Y1−N1 = 2.426(3), Y1−C2 = 2.442(4), Y1−Cl4 = 2.639(1), Y1−Cl1 = 2.657(1), Y1−Cl3 = 2.675(1), Y1−Cl2 = 2.709(1), N1−Y1−C2 = 77.0(1), Cl4−Y1−Cl3 = 83.50(3), Cl1−Y1−Cl2 = 83.75(3), Cl3−Y1−Cl2 = 88.19(3).

4b-Y was characterized only by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. The ^{31}P NMR spectrum confirms that the yttrium is metalated, as the iminophosphorane gives a doublet with a $^{2}J_{PY}$ = 18 Hz, a value that is typical for Y−P coupling. The signal of the proton in *ortho*-position of the metallic center in the ^{1}H NMR is deshielded from 8.31 ppm in **3b** to 8.62 ppm in **4b**-Y.

Formation of rare-earth ate-complexes is less likely to occur when starting from organopotassium precursors because potassium salts are easier to eliminate by precipitation due to their lower solubility. In order to try to synthesize a potassium precursor analogous to **3**, a Li/K exchange was attempted by reacting **3d** with KO^{t}Bu in hexane. However, to our surprise, no potassium analogue **3d′** of **3d** was observed, but a potassium phosphamide **8** was isolated instead; a mechanism for this transformation is proposed in Scheme 4. Presumably, the higher nucleophilicity of the transient potassium anion **3d′** induces a nucleophilic attack on an adjacent phenyl ring. This mechanism is reminiscent of that involved in the formation of dibenzophospholes from the reaction of amides with tetraphenylphosphonium salts.[14]

Scheme 4. Proposed Mechanism for the Formation of Compound 8



Biscoordinated Complexes **5c**-*Ln (Ln = Y, Nd, Gd).* Complexes **5c**-Y and **5c**-Gd have been synthesized with a synthetic protocol similar to **4a**. ^{31}P NMR monitoring confirms the formation of the compounds **5c**-Y and **5c**-Nd, with ^{31}P NMR shifts at 35 and 58 ppm in THF, respectively, and a coupling constant $^{3}J_{Y-P}$ = 17 Hz for the complex **5c**-Y. For small metal centers (Y, Gd) workup by coevaporation of THF with toluene and centrifugation of LiCl salts yielded analytically pure products, while during the workup, **5c-Nd** was always accompanied by an impurity presumably because of ligand redistribution reaction. The NMR data in the Experimental Section thus refer to **5c**-Nd obtained in situ. Monocrystals could be obtained by slow diffusion of pentane in a THF solution of **5c**-Y, which crystallized as a solvate, [*o*-C_6H_4-(Ph_2)P═N-^{i}Pr]$_2$YCl(THF) (**5c**-Y·THF), the solid-state structure of which was established by single-crystal X-ray diffraction (Figure 3). This complex adopts a pseudo-octahedral geometry, with the atoms C2, C23, Cl1, and O in equatorial positions and the nitrogen atom in apical position. The Y–C bonds are nearly equivalent (Y–C = 2.455(2) Å, Y–C = 2.491(3) Å), as are Y–N distances (Y1–N1 2.421(2) Å, Y1–N2 2.386(2) Å). These Y–C and Y–N bond lengths are close to those obtained for the monocoordinated complex **4a**-Y·2LiCl·4THF.

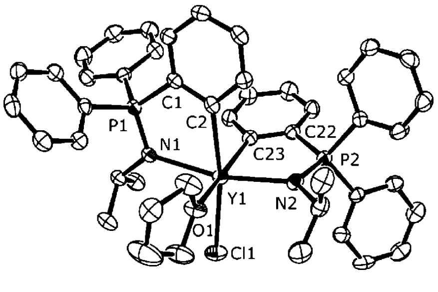


Figure 3. ORTEP plot (50% ellipsoids) of [*o*-C_6H_4-(Ph_2)P═N-^{i}Pr]$_2$YCl(THF) (**5c**-Y·THF) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bonds lengths [Å] and angles [deg]: Y(1)–N(2) 2.386(2), Y(1)–N(1) 2.421(2), Y(1)–C(23) 2.455(2), Y(1)–C(2) 2.491(3), N(2)–Y(1)–N(1) 166.81(7), N(2)–Y(1)–C(23) 76.26(7), N(1)–Y(1)–C(2) 74.98(7), C(23)–Y(1)–C(2) 86.63(8).

Triscoordinated Complexes **6d**-*Ln (Ln = Y, La, Nd).* In the same manner, addition of 3 equiv of the lithiated compound **3d** to 1 equiv of [$LnCl_3(THF)_3$] in THF followed by 30 min of stirring allowed the formation of unsolvated, homoleptic complexes **6d**-Y, **6d**-Nd, and **6d**-La. After evaporation of the solvent, the reaction mixture was extracted with toluene and LiCl separated by centrifugation. Monocrystals of [*o*-C_6H_4-(Ph_2)P═N-^{n}Bu]$_3$Nd (**6d**-Nd) and [*o*-C_6H_4-(Ph_2)P═N-^{n}Bu]$_3$La (**6d**-La) were obtained by a slow diffusion of pentane in THF (5:1) at −30 °C. The solid-state structure of complex **6d**-Nd is presented in Figure 4, and that of complex **6d**-La in the Supporting Information.

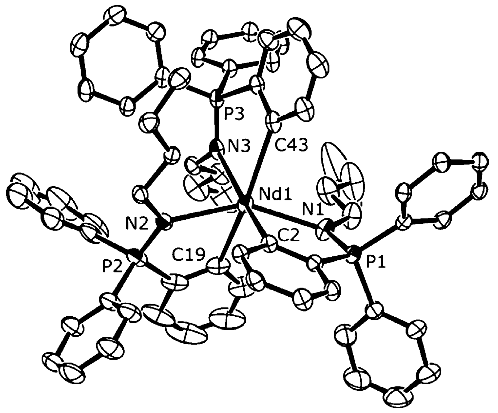


Figure 4. ORTEP plot (30% ellipsoids) of [*o*-C_6H_4-(Ph_2)P═N-^{n}Bu]$_3$Nd (**6d**-Nd) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bonds lengths [Å] and angles [deg]: Nd1–N1 = 2.490(3), Nd1–N2 = 2.500(3), Nd1–N3 = 2.579(3), Nd1–C43 = 2.601(4), Nd1–C19 = 2.611(4), Nd1–C2 = 2.647(3), N3–Nd1–C43 = 68.3(1), N1–Nd1–C2 = 71.2(1), N2–Nd1–C19 = 71.6(1).

Complex **6d**-Nd crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell. The molecule adopts a distorted-octahedral geometry, with the atoms C2, N1, N2, and N3 in equatorial positions and C19 and C43 in apical positions. The steric hindrance around the Nd metal center influences the Nd–N and Nd–C bond lengths. Indeed, one ligand moiety is more distant from Nd with longer Nd–C (2.647(3) Å) and Nd–N (2.579(3) Å) bonds vs 2.606(4) and 2.495(3) Å on average for the two other ligands.

Protonation of **6d**-Y (respectively **6d**-Nd) with stoichiometric $HNEt_3BPh_4$ in THF was monitored by ^{31}P NMR spectroscopy. After 5 min, two new signals, at 40 and 3 ppm (respectively 43 and 3 ppm) in a 2:1 ratio were present in the spectrum; in the yttrium case, a doublet structure with a $^{2}J_{PY}$ = 16.5 Hz was present on the peak at 40 ppm. The peak at 3 ppm corresponds to the chemical shift of free iminophosphorane. These data are consistent with selective protonation of one aryl group by $HNEt_3BPh_4$, thus yielding a neutral iminophosphorane and a biscoordinated cationic lanthanide complex (Scheme 5)

Preliminary Results on Butadiene Polymerization. As noted in the Introduction, *cis*-1,4-selective polymerization of dienes is a very important process in the rubber industry, and among the variety of organometallic complexes used for butadiene polymerization, rare earth metal based ones are efficient and attractive candidates. Among these catalysts, only

Scheme 5. Reaction of 6d-Y and 6d-Nd with a Stoichiometric Amount of $HNEt_3BPh_4$ in THF

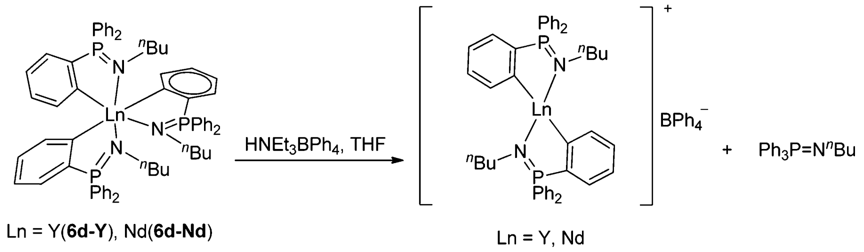
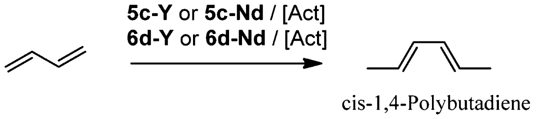


Table 2. Summary of the Butadiene Polymerization Results[a]



entry	complexes ([Ln])	activator ([Act]/[Ln])	conv (%)	1,4-*cis* (%)[b]	1,4-*trans*(%)[b]	1,2 (%)[c]
1	**5c**-Y	HDIBA (10)	2	n.d.	n.d.	n.d.
2	**5c**-Nd	HDIBA (10)	21	95	5	<1
3	**5c**-Nd	$HNMe_2Ph[B(C_6F_5)](1)$/TIBA (10)	40	91	9	<1
4	**5c**-Nd	$HNMe_2Ph[B(C_6F_5)](2)$/TIBA (10)	70	87	8	5
5	**6d**-Y	$HNEt_3BPh_4$/TIBA (10)	3	n.d.	n.d.	n.d.
6	**6d**-Nd	$HNEt_3BPh_4$/TIBA (10)	2	n.d.	n.d.	n.d.

[a] Conditions: 0.1 mmol of [Ln] in 60 mL of methylcyclohexane, Bd/[Ln] = 5000, *T* = 70°C, 2 h. [b] Determined by ^{13}C NMR spectroscopy. [c] Determined by ^1H NMR spectroscopy.

one system involving an amido-iminophosphorane bifunctional ligand had been tested, which has shown medium activity and high *trans*-selectivity.[15] To the best of our knowledge, there are no examples of catalyst systems including iminophosphorane-based complexes yielding *cis*-polybutadiene. The catalytic performance of yttrium and neodymium complexes **5c**-Y, **5c**-Nd, **6d**-Y, and **6d**-Nd for the polymerization of butadiene (Bd) has thus been investigated, in the presence of activators: di(isobutyl)aluminum (HDIBA), tris(isobutyl)aluminum (TIBA), and a proton source, $(HNMe_2Ph)[B(C_6F_5)_4]$. The polymerization data are summarized in Table 2.

These results show that the polymerization activity was drastically affected by the nature of the metal center, since none of the yttrium complexes were found to be active. Although the complexes alone do not induce the polymerization of butadiene, addition of HDIBA (HDIBA/Nd = 10) to complex **5c**-Nd can initiate polymerization, giving high selectivity with 95% 1,4-*cis*-polybutadiene but low activity with only 20% yield of polymer after 2 h. The activity could be increased to 40% after addition of 1 equiv of the proton source $(HNMe_2Ph)[B(C_6F_5)_4]$ and TIBA, with a slight decrease of the selectivity. If another equivalent of proton source is added, activity is again increased, together with a larger decrease in selectivity. No activity was obtained by protonation of complexes **6d**-Y and **6d**-Nd, which may be due to an interaction of the vacant site either with the counterion or with the liberated free iminophosphorane acting as a Lewis base.

CONCLUSION

We have found a simple and efficient method for the synthesis of iminophosphorane *o*-aryllithium complexes directly from stable aminophosphonium salts, without the need to isolate the intermediate iminophosphoranes. These aryllithium salts have been successively used as precursors to the respective rare-earth iminophosphorane *o*-aryl complexes. The optimum ligand:metal ratio in the isolated complexes can be 1:1, 2:1, or 3:1 depending on the nitrogen substituent of the iminophosphorane. X-ray crystal structures have been obtained with all three stoichiometries. Preliminary attempts at the polymerization of 1,3-butadiene with the title complexes were achieved. We report the first example of highly selective (up to 95%) 1,4-*cis*-polybutadiene synthesized with some of these complexes as catalysts, with medium activity, however. Using the complexes in the present study as starting materials, we plan to develop new complexes, such as bis-alkyl *o*-aryl iminophosphorane rare-earth compounds, that may have higher activity in the 1,3-butadiene polymerization reaction.[15]

EXPERIMENTAL SECTION

General Procedures. All reactions involving air-sensitive compounds were performed under a protective atmosphere of dry nitrogen or argon with oxygen-free solvents. Triethylamine was dried on KOH before use, and all other commercially available reagents were obtained from the suppliers and used without further purification. Lithium salt **3a** was prepared from iminophosphorane **2a** as described in the literature.[12] NMR spectra of all synthesized compounds were measured at ambient temperature (20 °C) with a Bruker Avance 300 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane. The microstructure of polymers was determined by NMR using a Bruker DRX 400 spectrometer. Microanalytical data were obtained through the London Metropolitan University Science Centre.

Synthesis of Ph_3P^+-NH-R·Br^-, 1b–d (R = ^{t}Bu, ^{i}Pr, ^{n}Bu). Bromine (38.1 mmol) was slowly added to a solution of triphenylphosphine (38.1 mmol) in dichloromethane (200 mL) cooled to −78 °C. After 30 min, $R\text{-}NH_2$ (38.1 mmol) and triethylamine (38.1 mmol) were added to the cloudy solution of the bromophosphonium salt. The clear solution obtained after cold bath removal was washed twice with water and extracted with dichloromethane (2 × 100 mL). The organic layer was dried over $MgSO_4$ and concentrated to 50 mL under vacuum. Et_2O (150 mL) were then added, whereupon a precipitate appeared. After filtration, this precipitate was washed with Et$_2$O (50 mL) and dried, and compounds **1b−d** were obtained as white solids.

1b (R = ^{t}Bu): yield 80%. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 30.8 (s, P). ^{1}H NMR (CDCl$_3$): δ 7.96 (m, 6H, H$_{\mathrm{Ar}}$), 7.74 (m, 3H, H$_{\mathrm{Ar}}$), 7.62 (m, 6H, H$_{\mathrm{Ar}}$), 7.43 (s, 1H, NH), 1.34 (s, 9H, ^{t}Bu).

1c (R = ^{i}Pr): yield 84%. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 37.9 (s, P). ^{1}H NMR (CDCl$_3$): δ 7.98 (m, 7H, NH and H$_{\mathrm{Ar}}$), 7.71 (m, 3H, H$_{\mathrm{Ar}}$), 7.62 (m, 6H, H$_{\mathrm{Ar}}$), 3.21 (m, 1H, ^{i}Pr), 1.42 (d, 6H, ^{i}Pr).

1d (R = ^{n}Bu): yield 85%. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 36.0 (s, P). ^{1}H NMR (CDCl$_3$): δ 7.99 (m, 1H, NH), 7.84 (m, 9H, H$_{\mathrm{Ar}}$), 7.63 (m, 6H, H$_{\mathrm{Ar}}$), 3.02 (m, 2H,NCH$_2$), 2.62 (m, 2H,NCH$_2\underline{\mathrm{CH}_2}$), 1.18 (m, 2H,$\underline{\mathrm{CH}_2}CH_3$), 0.71 (d, 3H, CH$_3$).

Synthesis of [*o*-C$_6$H$_4$-Ph$_2$P═N-R]Li, 3b−d (R = ^{t}Bu, ^{i}Pr, ^{n}Bu). *n*-Butyllithium (3.75 mL, 1.6 M in hexane, 6 mmol) was added dropwise to a suspension of aminophosphonium salts **1b−d** (6 mmol) in toluene (30 mL) cooled to −78 °C. After cold bath removal, the reaction was stirred for 30 min. Salts were centrifuged, and compounds **3b−d** were obtained as yellow to orange solids after evaporation to dryness, washing of the residue with 20 mL of pentane, and drying under vacuum. The crude, unsolvated **3b−d** were of sufficient purity to be used as starting materials for the synthesis of compounds **4**, **5**, and **6**, as shown by NMR, while analytically pure products were obtained as solvates by slow diffusion of pentane into THF or diethyl ether solutions of the compounds at 25 °C.

3b (R = ^{t}Bu): yield 61%. ^{31}P{^{1}H} NMR (toluene-d_8): δ 12.8 (s, P). ^{1}H (C$_6$D$_6$): δ 8.31 (m, 1H, H$_{\mathrm{Ar}}$), 7.94 (m, 4H, H$_{\mathrm{Ar}}$), 7.28 (m, 2H, H$_{\mathrm{Ar}}$), 7.03 (m, 7H, H$_{\mathrm{Ar}}$), 1.13 (s, 9H, H$^{\mathrm{t}}{}_{\mathrm{Bu}}$). ^{13}C{^{1}H} NMR (C$_6D_6$): δ 35.69 (s, CH$_3$), 52.8 (s, C$_{\mathrm{quat}}$), 125.1 (d, $^2J_{\mathrm{CP}}$ = 16 Hz, *o*-CH (Ph$_{\mathrm{Li}}$P)), 127.8 (s, *p*-CH (Ph$_{\mathrm{Li}}$P)), 128.5 (d, *m*-CH (Ph$_2$P)), 130.5 (d, $^3J_{\mathrm{CP}}$ = 27 Hz, *m*-CH (Ph$_{\mathrm{Li}}$P)), 130.8 (s, *p*-CH (Ph$_2$P)), 134.2 (d, $^2J_{\mathrm{CP}}$ = 9 Hz, *o*-CH (Ph$_2$P)), 136.8 (d, $^1J_{\mathrm{CP}}$ = 73 Hz, C$_{\mathrm{quat}}$-(Ph$_2$P)), 139.8 (d, $^3J_{\mathrm{CP}}$ = 27 Hz, *m*-CH (Ph$_{\mathrm{Li}}$P)), 146.6 (d, $^1J_{\mathrm{CP}}$ = 143 Hz, C$_{\mathrm{quat}}$-(Ph$_{\mathrm{Li}}$P)), 189.6 (d, $^2J_{\mathrm{CP}}$ = 47 Hz, CLi (Ph$_{\mathrm{Li}}$P)). Anal. Calcd for **3b**·Et$_2$O, C$_{26}$H$_{33}$LiNPO (406.52): C, 75.53; H, 8.04; N, 3.39. Found: C, 75.41; H, 7.82; N, 3.28.

3c (R = ^{i}Pr): yield 64%. ^{31}P{^{1}H} NMR (toluene-d_8): δ 22.6 (s, P). ^{1}H NMR (C$_6$D$_6$): δ 8.19 (m, 1H, H$_{\mathrm{Ar}}$), 7.71 (m, 4H, H$_{\mathrm{Ar}}$), 7.28 (m, 2H, H$_{\mathrm{Ar}}$), 7.13 (m, 7H, H$_{\mathrm{Ar}}$), 3.28 (m, 1H, H$_{\mathrm{CH}}$), 0.98 (d, 6H, H$^{\mathrm{i}}{}_{\mathrm{Pr}}$). ^{13}C{^{1}H} NMR (C$_6D_6$) δ 28.9 (d, $^3J_{\mathrm{CP}}$ = 16 Hz, Me), 46.3 (d, $^2J_{\mathrm{CP}}$ = 11 Hz, CH), 124.9 (d, $^2J_{\mathrm{CP}}$ = 15 Hz, *o*-CH (Ph$_{\mathrm{Li}}$P)), 128.7 (s, *p*-CH (Ph$_{\mathrm{Li}}$P)), 129.6 (s, *p*-CH (Ph$_2$P)), 131.1 (d, $^3J_{\mathrm{CP}}$ = 15 Hz, *m*-CH (Ph$_2$P)), 131.3 (d, $^3J_{\mathrm{CP}}$ = 15 Hz, *m*-CH (Ph$_{\mathrm{Li}}$P)), 133.8 (d, $^2J_{\mathrm{CP}}$ = 9 Hz, *o*-CH (Ph$_2$P)), 135.1 (d, $^1J_{\mathrm{CP}}$ = 75 Hz, C$_{\mathrm{quat}}$-(Ph$_2$P)), 140.8 (d, $^3J_{\mathrm{CP}}$ = 26 Hz, *m*-CH (Ph$_{\mathrm{Li}}$P)), 142.5 (d, $^1J_{\mathrm{CP}}$ = 136 Hz, C$_{\mathrm{quat}}$-(Ph$_{\mathrm{Li}}$P)), 190.8 (d, $^2J_{\mathrm{CP}}$ = 47 Hz, CLi (Ph$_{\mathrm{Li}}$P)). Anal. Calcd for **3c**·Et$_2$O, C$_{25}$H$_{31}$LiNPO (399.43): C, 75.17; H 7.82; N, 3.51. Found: C 74.89, H, 7.69; N, 3.68.

3d (R = ^{n}Bu): yield 60%. ^{31}P{^{1}H} NMR (toluene-d_8): δ 25.1 (s, P). ^{1}H NMR (THF-d_8): δ 8.08 (d, 1H, H$_{\mathrm{Ar}}$), 7.65 (m, 4H, H$_{\mathrm{Ar}}$), 7.38(m, 6H, H$_{\mathrm{Ar}}$), 7.01 (m, 1H, H$_{\mathrm{Ar}}$), 6.83 (m, 1H, H$_{\mathrm{Ar}}$), 6.64 (m, 1H, H$_{\mathrm{Ar}}$), 2.93 (m, 2H, H$_{\mathrm{Bu}}$), 1.56 (m, 2H, H$_{\mathrm{Bu}}$), 1.33 (m, 2H, H$_{\mathrm{Bu}}$),0.88 (d, 3H, H$_{\mathrm{Bu}}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 14.4 (s, CH$_3$), 21.2 (s, CH$_2$), 37.8 (d, $^3J_{\mathrm{CP}}$ = 17 Hz, CH$_2$), 45.9 (d, $^2J_{\mathrm{CP}}$ = 6 Hz, CH$_2$), 124.5 (d, $^2J_{\mathrm{CP}}$ = 15 Hz, *o*-CH (Ph$_{\mathrm{Li}}$P)), 130.9 (s, *m*-CH (Ph$_{\mathrm{Li}}$P)), 131.1 (s, *m*-CH (Ph$_2$P)), 133.8 (d, $^2J_{\mathrm{CP}}$ = 8 Hz, *o*-CH (Ph$_2$P)), 133.9. Anal. Calcd for **3d**·THF, C$_{26}$H$_{31}$LiNPO (411.45): C, 75.90; H, 7.59; N, 3.40. Found: C, 75.73; H, 7.92; N, 3.48.

Synthesis of [*o*-C$_6$H$_4$-(Ph$_2$)P═N-SiMe$_3$]YCl$_2$, 4a-Y. To a suspension of [YCl$_3$(THF)$_{3.5}$] (0.2 mmol) in THF was added a solution of **3a** (0.2 mmol) in THF (5 mL) at room temperature. The solution was stirred for 30 min and concentrated to 1 mL under vacuum. Few crystals of [*o*-C$_6$H$_4$-(Ph$_2$)P═N-SiMe$_3$]Y[(μ-Cl)$_2$Li-(THF)$_2$]$_2$ (**4a**-Y·2LiCl·4THF) were obtained at −30 °C. Because of this, the NMR data refer to **4a**-Y obtained in situ.

4a-Y: yield 5%. ^{31}P{^{1}H} NMR (THF-d_8): δ 28.9 (s, $^2J_{\mathrm{YP}}$ = 10.8 Hz). ^{1}H{^{31}P} NMR (THF-d_8): 0.04 (s, 9H, CH$_3$), 6.82 (m, 2H, *p*-CH (Ph$_{\mathrm{Y}}$), 6.96 (m, 1H, *m*-CH (Ph$_{\mathrm{Y}}$)), 7.43 (m, 6H, *p*-H (Ph$_2$P), *m*-H (Ph$_2$P)), 7.7 (dd, 4H, $^2J_{\mathrm{HH}}$ = 1.6 Hz, $^1J_{\mathrm{HH}}$, 8.2 Hz, *o*-H (Ph$_2$P)), 8.05 (d, 1H, J = 7.2 Hz, *o*-CH (Ph$_{\mathrm{Y}}$)). ^{13}C{^{1}H} NMR (THF-d_8): δ 4.7 (d, $^3J_{\mathrm{CP}}$ = 3.7 Hz, CH$_3$), 128.4 (d, $^3J_{\mathrm{CP}}$ = 3.5 Hz, *p*-CH (Ph$_{\mathrm{Y}}$P)), 128.9 (d, $^3J_{\mathrm{CP}}$ = 11.3 Hz, *m*-CH (Ph$_2$P)), 131.5 (d, $^3J_{\mathrm{CP}}$ = 2.7 Hz, *m*-CH (Ph$_{\mathrm{Y}}$P)), 132.1 (d, $^4J_{\mathrm{CP}}$ = 2.2 Hz, *p*-CH (Ph$_2$P)), 132.7 (d, $^2J_{\mathrm{CP}}$ = 10 Hz, *m*-CH (Ph$_{\mathrm{Y}}$P)), 134.0 (d, $^2J_{\mathrm{CP}}$ = 9.8 Hz, *o*-CH (Ph$_2$P)), 134.9 (d, $^1J_{\mathrm{CP}}$ = 85.5 Hz, C$_{\mathrm{quat}}$ (Ph$_2$P)), 140.4 (d, $^1J_{\mathrm{CP}}$ = 26.3 Hz, *o*-CH (Ph$_{\mathrm{Y}}$P)), 143.3 (d, $^1J_{\mathrm{CP}}$ = 124.7 Hz, *o*-CH (Ph$_{\mathrm{Y}}$P)), 195.4 (d, $^1J_{\mathrm{CP}}$ = 45.5 Hz, C$_{\mathrm{quat}}$ (Ph$_{\mathrm{Y}}$P)).

Synthesis of [*o*-C$_6$H$_4$-(Ph$_2$)P═N-^{t}Bu]YCl$_2$, 4b-Y. To a suspension of YCl$_3$(THF)$_{3.5}$] (0.19 mmol) in THF was added a solution of **3b** (0.19 mmol) in THF (5 mL) at room temperature. The solution was stirred for 30 min and evaporated under vacuum. LiCl salts were precipitated with toluene and removed by centrifugation. After evaporation to dryness under vacuum, a yellow powder was obtained.

4b-Y: yield 60%. ^{31}P{^{1}H} NMR (THF-d_8): δ 25.3 (d, 1P, $J_{\mathrm{P-Y}}$ = 18 Hz). ^{1}H NMR (THF-d_8): δ 1.27 (s, 9H, H$_{^t\mathrm{Bu}}$), 6.74 (m, 1H, *o*-Ph$_{\mathrm{Y}}$), 6.90 (m, 2H, *o*-Ph$_{\mathrm{Y}}$, m-Ph$_{\mathrm{Y}}$), 7.43 (m, 6H, *o*-(Ph$_2$P), *p*-(Ph$_2$P)), 7.86 (d, $^3J_{\mathrm{HY}}$ = 6 Hz, 1H, *o*-Ph$_{\mathrm{Y}}$), 8.09 (m, 4H, *o*-Ph$_2$P). ^{13}C{^{1}H} NMR (THF-d_8): δ 26.1 (s, THF$_{\mathrm{solv}}$), 33.3 (d, $^3J_{\mathrm{CP}}$ = 8.4 Hz, CH$_3$), 55.5 (d, $^2J_{\mathrm{CP}}$ = 5.7 Hz, C$_{^t\mathrm{Bu}}$), 68.01 (s, THF$_{\mathrm{solv}}$), 124.8 (d, $^2J_{\mathrm{CP}}$ = 15.5 Hz, *o*-CH (Ph$_{\mathrm{Y}}$)), 127.7 (s, *p*-CH (Ph$_{\mathrm{Y}}$)), 128.6 (d, $^3J_{\mathrm{CP}}$ = 11 Hz, *m*-CH (Ph$_2$P)), 129.1 (s, *m*-CH (Ph$_{\mathrm{Y}}$)), 131.6 (s, *p*-CH (Ph$_2$P)), 133.1 (d, $^3J_{\mathrm{CP}}$ = 9.5 Hz, *o*-CH (Ph$_{\mathrm{Y}}$)), 134.5 (d, $^1J_{\mathrm{CP}}$ = 77.4 Hz, C$_{\mathrm{quat}}$-(Ph$_2$P)), 134.6 (d, $^2J_{\mathrm{CP}}$ = 9.5 Hz, *o*-CH (Ph$_2$P)), 141.5 (d, $^1J_{\mathrm{CP}}$ = 133.3 Hz, *o*-C$_{\mathrm{quat}}$ (Ph$_{\mathrm{Y}}$)), 184.4 (d, $^2J_{\mathrm{CP}}$ = 39 Hz, *i*-C$_{\mathrm{quat}}$ (Ph$_{\mathrm{Y}}$)). No meaningful analysis could be obtained.

Synthesis of [*o*-C$_6$H$_4$-(Ph$_2$)P═N-^{i}Pr]$_2$LnCl, 5c-Ln (Ln = Y, Nd, Gd). Compounds **5c**-Ln were prepared following the same experimental procedure as that described for **4b**-Y, in which [LnCl$_3$(THF)$_3$] (Ln = Y, Nd, Gd) (1 mmol) was reacted with **3c** (2 mmol) in THF (20 mL).

5c-Y: yield 72%. ^{31}P{^{1}H} NMR (THF-d_8): δ 35.7 (d, 1P, $J_{\mathrm{P-Y}}$ = 17 Hz). ^{1}H (THF-d_8): δ 7.87 (m, 8H, H$_{\mathrm{Ar}}$), 7.78 (m, 2H, H$_{\mathrm{Ar}}$), 7.49 (m, 12H, H$_{\mathrm{Ar}}$), 7.09 (m, 2H, H$_{\mathrm{Ar}}$), 6.99 (m, 2H, H$_{\mathrm{Ar}}$), 6.88 (m, 2H, H$_{\mathrm{Ar}}$), 3.65 (2H, CH$_{\mathrm{i\text{-}Pr}}$), 1.23 (d, 12H, H$_{\mathrm{Me}}$). ^{13}C{^{1}H} NMR (THF-d_8): δ 24.9 (d, $^3J_{\mathrm{CP}}$ = 8 Hz, CH$_3$), 46.2 (d, $^2J_{\mathrm{CP}}$ = 5 Hz, CH), 122.1 (d, $^2J_{\mathrm{CP}}$ = 15 Hz, *o*-CH (Ph$_{\mathrm{Y}}$P)), 125.9 (s, *p*-CH (Ph$_y$P)), 126.4 (d, $^3J_{\mathrm{CP}}$ = 11 Hz, *m*-CH (Ph$_2$P)), 127.4 (d, $^3J_{\mathrm{CP}}$ = 28 Hz, *m*-CH (Ph$_{\mathrm{Y}}$P)), 129.5 (s, *p*-CH (Ph$_2$P)), 131.3 (d, $^1J_{\mathrm{CP}}$ = 61 Hz, C$_{\mathrm{quat}}$-(Ph$_2$P)), 131.9 (d, $^2J_{\mathrm{CP}}$ = 9 Hz, *o*-CH (Ph$_2$P)), 135.9 (d, $^1J_{\mathrm{CP}}$ = 128 Hz, C$_{\mathrm{quat}}$-(Ph$_{\mathrm{Y}}$P)), 137.9 (d, $^3J_{\mathrm{CP}}$ = 28 Hz, *m*-CH (Ph$_{\mathrm{Y}}$P)), 195.9 (d, $^2J_{\mathrm{CP}}$ = 42 Hz, CY (Ph$_{\mathrm{Y}}$P)). Anal. Calcd for **5c**-Y, C$_{42}$H$_{42}$ClN$_2$P$_2$Y (761.10): C, 66.28; H, 5.56; N, 3.68. Found: C, 66.12; H, 5.42; N 3.63.

5c-Nd: ^{31}P{^{1}H} NMR (THF-d_8): δ 58 (s, P). ^{1}H NMR (THF-d_8): δ −17.7 (bs, 12H, Me), 7.48 (m, 14H, m-H (Ph$_{\mathrm{Nd}}$), m-H (Ph$_2$P), p-H (Ph$_2$P)), 10.5 (bs, 8H, *o*-H (Ph$_2$P)), 17.52 (bs, 2H), 19.11 (bs, 2H), 25.29 (bs, 2H). No signal for CH-^{i}Pr could be found, presumably because of the paramagnetism of Nd$^{\mathrm{III}}$. ^{13}C{^{1}H} NMR (THF-d_8): δ 28.6 (d, $^3J_{\mathrm{CP}}$ = 13.6 Hz, Me), 127.9 (d, $^2J_{\mathrm{CP}}$ = 11.4 Hz, *m*-CH (Ph$_{\mathrm{Nd}}$)), 128.97 (s, *m*-CH (Ph$_2$P)), 130.48 (s, *p*-CH (Ph$_{\mathrm{Nd}}$)), 131.45 (s, *p*-CH (Ph$_2$P)), 132.3 (d, $^3J_{\mathrm{CP}}$ = 8.8 Hz, *m*-CH (Ph$_{\mathrm{Nd}}$)), 134.1 (d, $^1J_{\mathrm{CP}}$ = 95.4 Hz, C$_{\mathrm{quat}}$ (Ph$_2$P)), 135.6 (bs, *o*-CH (Ph$_{\mathrm{Nd}}$)), 136.8 (s, *o*-CH (Ph$_2$P)), 147.1 (d, $^1J_{\mathrm{CP}}$ = 76.6 Hz, *o*-C$_{\mathrm{quat}}$ (Ph$_{\mathrm{Nd}}$)), 184.4 (bs, *i*-C$_{\mathrm{quat}}$ (Ph$_{\mathrm{Nd}}$)). No meaningful analysis could be obtained.

5c-Gd: yield 64%. Anal. Calcd for **5c**-Gd, C$_{42}$H$_{42}$ClGdN$_2$P$_2$ (829.45): C, 60.82; H, 5.10; N, 3.38. Found: C, 60.90; H, 5.18; N 3.25.

Synthesis of [*o*-C$_6$H$_4$-(Ph$_2$)P═N-^{n}Bu]$_3$Ln, 6d-Ln (Ln = Y, Nd, La). Compounds **6d**-Ln were prepared following the same experimental procedure as that described for **4b**-Y, in which [LnCl$_3$(THF)$_3$] (Ln = Y, Nd, La) (1.2 mmol) was reacted with **3d** (3.6 mmol) in THF (20 mL).

6d-Y: yield 70%. ^{31}P{^{1}H} NMR (THF-d_8): δ 36.4 (d, 1P, $J_{\mathrm{P-Y}}$ = 15 Hz). ^{1}H NMR (THF-d_8): δ 7.95 (m, 3H, H$_{\mathrm{Ar}}$), 7.77 (m, 12H, H$_{\mathrm{Ar}}$), 7.45 (m, 18H, H$_{\mathrm{Ar}}$), 7.13 (m, 3H, H$_{\mathrm{Ar}}$), 6.94 (m, 3H, H$_{\mathrm{Ar}}$), 6.85 (m, 3H, H$_{\mathrm{Ar}}$), 3.19 (m, 6H, H$_{\mathrm{Bu}}$), 1.26 (m, 6H, H$_{\mathrm{Bu}}$), 0.68 (m, 6H, H$_{\mathrm{Bu}}$), 0.37 (t, 9H, H$_{\mathrm{Bu}}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 14.3 (s, CH$_3$), 21.4 (s, CH$_2$), 37.2 (s, CH$_2$), 47.3 (d, $^2J_{\mathrm{CP}}$ = 6 Hz, CH$_2$), 123.5 (d, $^2J_{\mathrm{CP}}$ = 14 Hz, *o*-CH (Ph$_y$P)), 128.7 (s, *m*-CH (Ph$_2$P)), 129.3 (s, *p*-CH (Ph$_{\mathrm{Y}}$P)), 129.6 (s, $^3J_{\mathrm{CP}}$ = 26 Hz, *m*-CH (Ph$_{\mathrm{Y}}$P)), 130.3 (s, *p*-CH (Ph$_2$P)), 132.8 (d, $^1J_{\mathrm{CP}}$ = 76 Hz, C$_{\mathrm{quat}}$-(Ph$_{\mathrm{Y}}$P)), 134.6 (d, $^2J_{\mathrm{CP}}$ = 9 Hz, *o*-CH (Ph$_2$P)), 139.1 (d, $^1J_{CP}$ = 134 Hz, C_{quat}-(Ph_2P)), 141.0 (d, $^3J_{CP}$ = 27 Hz, *m*-CH (Ph_YP)), 200.9 (dd, $^1J_{CY}$ = 37 Hz, $^1J_{CP}$ = 45 Hz, CY (Ph_YP)).

6d-Nd: yield 85%. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 43.9 (s, P). ^1H NMR (THF-d_8): δ −19.2 (bs, 6H, $PNCH_2$), −8.51 (bs, 6H, $PNCH_2\underline{CH_2}$), −5.82 (bs, 6H, $\underline{CH_2}CH_3$), −3.5 (bs, 9H, CH_3), 7.75 (m, 6H, *p*-CH (Ph_2P)), 8.00 (m, 12H, *m*-CH (Ph_2P)), 9.7 (bs, 3H, *m*-CH (Ph_{Nd})), 10.4 (m, 12H, *o*-CH (Ph_2P)), 10.6 (bs, 3H, *p*-CH (Ph_{Nd})), 10.9 (bs, 3H, *m*-CH (Ph_{Nd})), 15.5 (bs, 3H, *o*-CH (Ph_{Nd})). $^{13}C\{^1H\}$ NMR (THF-d_8): δ −14.78 (bs, $PNCH_2$), 9.1 (s, $\underline{CH_2}CH_3$), 10.5 (bs, $PNCH_2\underline{CH_2}$), 12.8 (s, CH_3), 123.6 (d, $^2J_{CP}$ = 15.4 Hz, *m*-CH (Ph_{Nd})), 128.7 (d, $^3J_{CP}$ = 11.4 Hz, *p*-CH (Ph_{Nd})), 129.6 (d, $^3J_{CP}$ = 9.1 Hz, *m*-CH (Ph_2P)), 132.04 (s, P-CH (Ph_2P)), 133.96 (d, $^1J_{CP}$ = 93.8 Hz, C_{quat} (Ph_2P)), 135.4 (d, $^2J_{CP}$ = 7.3 Hz, *o*-CH (Ph_2P)), 144.07 (d, $^1J_{CP}$ = 75.6 Hz, *o*-C_{quat} (Ph_{Nd})), 169.03 (s, *m*-CH (Ph_{Nd})), 176.7 (d, $^3J_{CP}$ = 25.7 Hz, *o*-CH (Ph_{Nd})).

6d-La: yield 79%. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 36.7 ppm. ^1H NMR (THF-d_8): δ 0.36 (t, $^3J_{HH}$ = 7.3 Hz, 9H, H_{Bu}), 0.75 (m, 6H, H_{Bu}), 1.05 (m, 6H, H_{Bu}), 3.15 (m, 6H, H_{Bu}), 6.78 (m, 3H, H_{Ar}), 6.92 (m, 3H, H_{Ar}), 7.11 (m, 3H, H_{Ar}),7.2 (m, 12H, H_{Ar}), 7.34 (m, 6H, H_{Ar}), 7.65 (m, 12H, H_{Ar}), 8.11 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H_{Ar}). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 14.2 (s, CH_3), 21.3 (s, CH_2), 36.4 (s, CH_2), 46.3 (d, $^2J_{CP}$ = 6 Hz, CH_2), 123.85 (d, $^2J_{CP}$ = 14 Hz, *m*-CH (PhLa)), 127.6 (d, $^4J_{CP}$ = 3.9 Hz, *m*-CH (PhLa)), 128.7 (d, $^3J_{CP}$ = 10.8 Hz, *m*-CH (Ph_2P)), 129.51 (d, $^3J_{CP}$ = 28.2 Hz, *p*-CH (PhLa)), 131.5 (s, *p*-CH (Ph_2P)), 133.8 (d, $^1J_{CP}$ = 74.1 Hz, *i*-C_{quat} (Ph_2P)), 133.9 (d, $^2J_{CP}$ = 8.5 Hz, *o*-CH (Ph_2P)), 139.7 (d, $^1J_{CP}$ = 136.8 Hz, *o*-CH (PhLa)), 139.8 (d, $^2J_{CP}$ = 27.7 Hz, *o*-C_{quat}(PhLa)), 214.7 (d, $^2J_{CP}$ =47.6 Hz, *i*-CH (PhLa)).

Synthesis of $C_{12}H_8P$-N(K)-^{n}Bu, 8. To a solution of **3d** (250 mg) in a mixture of diethyl ether (3 mL) and petroleum ether (5 mL) was added ^{t}BuOK in small portions. After 5 min of stirring, the mixture was evaporated to dryness and **8** was obtained as a solid, which was washed with 5 mL of pentane and dried under vacuum.

8: yield 72%. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 45.5 ppm. ^1H NMR (THF-d_8): δ 7.79 (d, 2H, H_{Ar}, *J* = 7.2 Hz), 7.65 (dd, 2H, *J* = 7.2 Hz, *J* = 2.0 Hz), 7.1 (m, 4H, H_{Ar}), 2.51 (q, 2H, *J* = 7.9 Hz), 1.22 (m, 4H), 0.77 (d, 3H, *J* = 7.1 Hz). Anal. Calcd for $C_{16}H_{17}KNP$ (293.38): C, 65.50; H, 5.84; N, 4.77. Found: C, 65.42; H, 5.77; N, 4.69.

Polymerization Procedure. Polymerizations were performed under nitrogen in a 250 mL glass reactor equipped with a stainless steel blade stirrer. The protonating agent or aluminum cocatalysts and the yttrium or neodymium precursor, prepackaged in ampules, were introduced in a flask closed by Teflon and steel caps. After adding 60 mL of methylcyclohexane and butadiene via syringe, the ampules were broken by stirring. The mixture was then stirred for 2 h at 60 °C. At the end of the polymerization reaction, the mixture was quenched with 1 mL of methanol. The polymer was then precipitated with methanol, washed, and dried under vacuum.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financed by the CNRS, Ecole Polytechnique, and the Manufacture Française des Pneumatiques Michelin.

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