DACH-Bridged (DACH = *trans*-1,2-Diaminocyclohexane) Bis(iminophosphonamide) Derivatives of Groups 3 and 13 and Their Use in the Enantiomorphic Polymerization of Methyl Methacrylate

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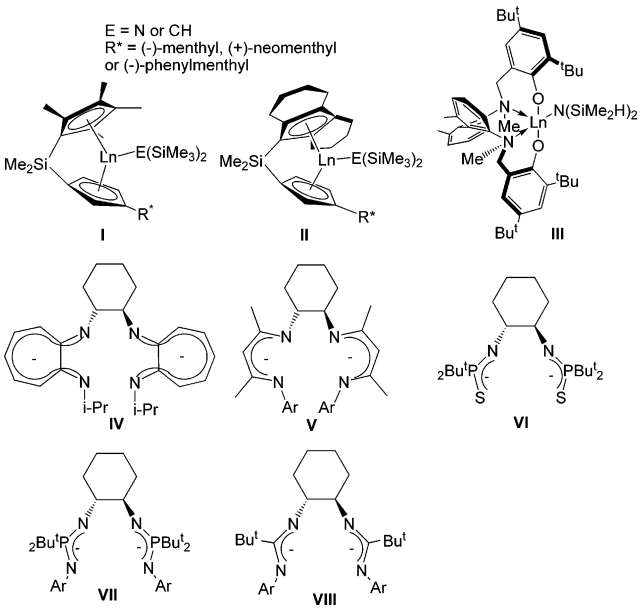
A straightforward and flexible one-pot synthesis of a series of racemic *trans*-1,2-diaminocyclohexyl (DACH)-linked N-aryl bis(iminophosphonamines) is reported. These compounds were readily metalated with either nBuLi or Et_3Al. The five-coordinate asymmetric environments provided by the ligands in the monometallic species were readily apparent from the useful and diagnostic $^{31}P\{^1H\}$ NMR spectra and correlated with the observed solid-state configurations. Similar reactions with the sterically encumbered yttrium amide $[Y\{N(SiMe_3)_2\}_3]$ were only observed to produce the analogous N_5-coordinated amide under forcing conditions, while reactions with the less sterically encumbered $[M\{N(SiHMe_2)_2\}_3(THF)_n]$ (M = Sc (n = 2), Y (n = 3)) gave smooth conversion to the desired monometallic chelate complexes. All of the monometallic and bimetallic group 3 and group 13 compounds were assessed for the stereoselective polymerization of methyl methacrylate. Although the aluminum compounds were inactive as single-component initiators, activation with Gibson's three-component (L_2AlR/MAD/Ni(acac)$_2$) system yielded active catalysts. The isolated polymers revealed a definite syndiotactic (>80%) bias, albeit with broad polydispersity indices (ca. 2) at ambient temperatures. In contrast, the yttrium complexes were found to function as efficient single-component polymerization initiators and yielded PMMA, which was predominantly isotactic (>80%) and, in some cases, close to monodisperse. Comparison to control experiments in which $[Y\{N(SiMe_3)_2\}_3]$ was employed as initiator provided evidence that it was the asymmetric environment of the bis(iminophosphonamide) ligand, which was exerting a pronounced (i.e. enantiomorphic) effect upon polymer propagation.

Introduction

By definition, enantioselective catalysts are chiral and nonracemic and must reproducibly produce a given enantiomer of a product from achiral starting materials.[1] The imposition of a stable chiral environment about a catalytic metal center, a prerequisite if acceptable enantioselectivities are to be achieved, is especially problematic for labile (i.e., largely uninfluenced by ligand field effects) and/or large metal cations. Stereodifferentiation by a trivalent 4f-block or group 13 element, for example, may be achieved by a combination of thermodynamic (chelate) and kinetic (the use of sterically demanding substituents) effects, however, as exemplified by complexes **I**−**III** (Chart 1).[2−4] Suitable non-cyclopentadienyl ligands require hard donors capable of bonding to the metal center by Coulombic interactions, while the ligand must be capable of enforcing its own structure around the ion if it is to exert any influence during the course of a catalytic reaction.

Chart 1



Prompted by our interests in organometallic catalysis and, specifically, alkene hydroamination,[5] we have recently sought to extend this suite of chiral dianions for stereoselective catalysis

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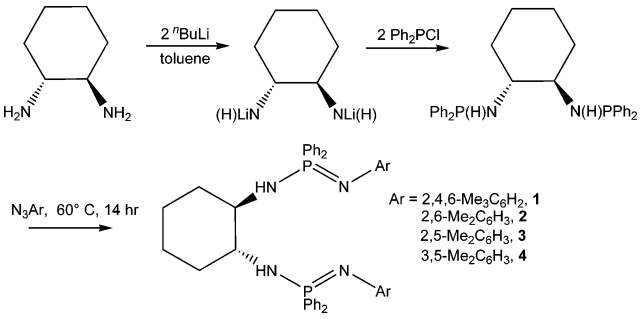
by 4f metal centers to *trans*-1,2-diaminocyclohexane (DACH)-linked bis(amidinates).[6] DACH is one of the most widely used chiral ligand components, and examples of ligands already in use for catalysts in asymmetric synthesis include Jacobsen's salen ligands for epoxidation reactions[7] and the Trost family of ligands used in allylic alkylation reactions.[8] A variety of dianions for use in group 3 and lanthanide-centered catalysis have emerged, including the bis(aminotropiniminates) **IV**,[9] the bis-(β-diketiminates) **V**,[10] and the bis(thiophosphinic)amidates **VI**[11] (Chart 1). Our previously reported ligand scaffold, **VIII**, although readily formed in the form of its dilithium salt, proved to be unsuitable for the formation of monometallic chelate structures as a result of the extreme steric crowding of the bulky proximal amidinates.[6] Simple, bidentate, and uninegative iminophosphonamides have previously been shown to display coordination behavior comparable to that of their amidinato analogues, and a variety of main-group and transition-metal derivatives have been reported.[12] We reasoned, therefore, that the chiral bis(iminophosphonamides) **VII** would offer attractive features similar to those of the bis(amidines) in chiral catalysis, while the longer N−P bond lengths (ca. 1.7 Å compared with 1.34 Å C−N bonds seen in amidinates) and more flexible bonding angles provided by the phosphorus atoms could also allow for more facile complexation. The N substituents may be tuned to impose variable kinetic control of the complex, while the introduction of two $I = {}^1/_2$ and 100% abundant ^{31}P atoms promises to provide convenient solution-state data about ligand coordination behavior.

Although the ligands embodied by the general structure **VII** are unprecedented, Livinghouse has recently reported the use of the closely related bis(thiophosphinic)amidates **VI**[11] and their in situ application in the formation of stereoselective yttrium intramolecular hydroamination catalysts. In this submission we provide a full account of our synthetic routes to a variety of ligand precursors, our initial studies of their coordination behavior toward trivalent aluminum and group 3 centers, and the use of these complexes as catalysts for stereoselective methyl methacrylate (MMA) polymerization at ambient temperatures.

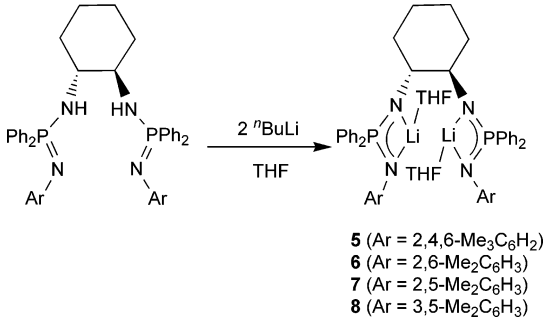
Results and Discussion

Synthesis of Bis(iminophosphonamines) 1−4. The bis-(iminophosphonamines) **1**−**4** were synthesized in high yield, as shown in Scheme 1. Lithiation of *trans*-1,2-diaminocyclohexane in toluene, followed by the addition of 2 equiv of chlorodiphenylphosphine, produced an exothermic reaction and a precipitate of LiCl. The appropriate aryl azide was then added with vigorous evolution of nitrogen. Heating at 60 °C overnight, extraction into toluene, filtration, and crystallization afforded orange or yellow crystals of **1**−**4**. Although the commercially available chlorodiphenylphosphine was employed in all cases, this synthetic route should be amenable to the synthesis of a whole variety of P-alkyl and P-aryl derivatives, providing even

Scheme 1



Scheme 2



greater flexibility for the precise electronic and kinetic tuning of the ligand environment.

Lithiation of **1**−**4** was readily achieved by addition of 2 equiv of ^{n}BuLi in hexanes (Scheme 2) to THF solutions of the appropriate ligand precursor. The isolated yields of pure crystalline samples of **6**−**8** were generally lower than that of the *N*-mesityl derivative **5**, which crystallized readily at lower temperatures. The ligand precursors **1**−**4** and their corresponding lithium derivatives **5**−**8** have been fully characterized by microanalysis, mass spectrometry, and infrared and multinuclear NMR spectroscopy. The X-ray diffraction analyses of compounds **1** and **2** and the dilithiated derivative **5** were also carried out.

The ^{1}H NMR spectra of **1**−**4** displayed the N−H and DACH resonances at frequencies lower than those for the previously reported bis(amidine) derivatives.[6] The ^{1}H spectrum of **1** displayed one peak for the *o*-methyl groups, indicating that the mesityl groups experience free rotation around the N−mesityl bond. This is in contrast with the behavior of the previously reported and apparently more sterically crowded bis(amidine) **VIII** (Ar = mesityl).[6] For the lithiated compounds **5**−**8**, the ^{1}H NMR spectra, although similar in appearance to those of the precursors, displayed additional resonances due to the coordinated THF and evidenced the loss of the N−H protons. The ^{31}P{^{1}H} NMR spectra of **1**−**4** displayed a single environment for the phosphorus atoms, which exhibited downfield shifts of ca. 15 ppm upon lithiation.

The solid-state structures of **1** and **2** were confirmed by X-ray diffraction analyses. The molecular structure of **1** is illustrated in Figure 1; details of the crystallographic analyses for both compounds are provided in Table 1, and selected bond lengths and angles are given in Table 2. Both structures are reminiscent of the previously reported DACH-bridged bis(amidines) and feature the cyclohexyl backbone in its more stabilized chair form, with the iminophosphonamine residues in equatorial positions.[6] Both structures crystallize as the E_{syn}:Z_{syn} isomers with one P═N functionality containing the Ph_2P fragment and the N-aryl groups on the same side of the phosphinimine double bond. Given the simplicity of the NMR spectra at ambient

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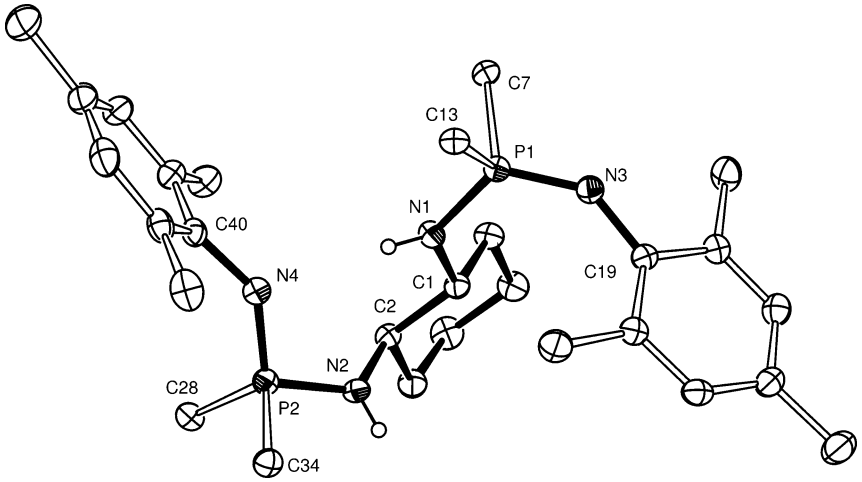


Figure 1. Thermal ellipsoid diagram (25% probability) of compound **1**. C atoms of P−Ph rings (except C ipso carbons) and H atoms (except N−H) are omitted for clarity.

Table 1. Selected Crystallographic and Data Collection Parameters for Compounds 1, 2, and 5

	1	**2**	**5**
chem formula	$C_{48}H_{54}N_4P_2$	$C_{46}H_{50}N_4P_2$	$C_{56}H_{68}Li_2N_4O_2P_2$
formula wt	748.89	720.84	904.96
T (K)	173(2)	173(2)	173(2)
cryst size (mm^3)	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.15
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a (Å)	12.5485(3)	11.7450(3)	21.2255(8)
b (Å)	25.4035(4)	19.6556(6)	11.0889(3)
c (Å)	13.0279(3)	17.8171(6)	22.1562(9)
α (deg)	90	90	90
β (deg)	92.071(1)	106.376(2)	94.607(2)
γ (deg)	90	90	90
Z	4	4	4
V ($Å^3$)	4150.27(15)	3946.3(2)	5198.0(3)
d_c (Mg m^{-3})	1.20	1.21	1.16
μ (mm^{-1})	0.14	0.15	0.13
θ range (deg)	3.74−25.06	3.52−26.03	3.40−26.03
R1, wR2 ($I > 2\sigma(I)$)	0.051, 0.121	0.053, 0.099	0.060, 0.137
R1, wR2 (all data)	0.067, 0.129	0.100, 0.116	0.106, 0.161
no. of measd/indep rflns (R(int))	28 136/7234 (0.056)	32 094/7753 (0.078)	17 922/5085 (0.059)
no. of rflns with $I > 2\sigma(I)$	5918	5079	3282

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 2, and 5

	1	**2**	**5**[c]
P(1)−N(1)	1.646(2)	1.643(2)	1.589(2)
P(1)−N(3)	1.538(2)	1.548(2)	1.601(2)[d]
P(2)−N(2)	1.643(2)	1.639(2)	
P(2)−N(4)	1.542(2)	1.561(2)	
N(3)−P(1)−N(1)	118.69(11)	121.30(10)	112.75(11)[e]
N(4)−P(2)−N(2)	107.20(11)	106.89(10)	
C(1)−N(1)−P(1)	120.79(16)	124.05(16)	118.83(16)
C(2)−N(2)−P(2)	124.71(18)	125.36(17)	
C(19)−N(3)−P(1)	141.16(17)	139.15(17)[a]	131.43(18)[f]
C(40)−N(4)−P(2)	140.37(17)	129.13(15)[b]	

[a] C(31)−N(3)−P(1). [b] C(39)−N(4)−P(2). [c] Li(1)−N(1) = 1.965(5); Li(1)−N(2)′ = 2.007(5); N(1)−Li(1)−N(2)′ = 126.4(2). Symmetry transformations used to generate equivalent atoms: (′) $-x, y, -z + 1/2$. [d] P(1)−N(2). [e] N(1)−P(1)−N(2). [f] C(16)−N(2)−P(1).

temperatures, we conclude that this kinetically disfavored feature is of little relevance to the reaction chemistry exhibited by these species (vide infra) and is, likely, a result of intramolecular NH···N_{imine} hydrogen-bonding and crystal-packing forces.

The crystal structure of the dilithium bis(iminophosphonamide) derivative **5** is illustrated in Figure 2. Selected bond lengths and angles are given in Table 2. The gross structural features of the molecular unit are again comparable to those of the topologically similar bis(amidines).[6,12] The structure of **5** possesses a crystallographic 2-fold rotational axis. The lithium ions are bound in a monodentate fashion by a single nitrogen of each iminophosphonamide moiety such that the lithium atoms bridge symmetrically between the NPN anion skeletons. A similar binding mode was also observed by Arnold in a lithiated *N*-*p*-tolyl-substituted derivative.[12] The Li−N bond length of **5** (1.97 Å) is, however, slightly shorter than those found in similar lithiated bis(amidines) (2.09 Å).[6,12]

Synthesis of Bis(iminophosphonamido) Aluminum Complexes. The monometallic N_4-chelate compounds **9** and **10** were synthesized by careful addition of 1 equiv of triethylaluminum to the respective ligand precursor **1** or **2**, in a stirred toluene solution (Scheme 3). After evolution of ethane had subsided, the reaction mixtures were heated to 60 °C overnight. Concentration of the resultant yellow solutions afforded colorless crystals of **9** and **10** in high yields of 81% and 76%, respectively. The syntheses of the bimetallic compounds **11**−**14** were achieved straightforwardly by addition of 2 equiv of triethylaluminum to the appropriate ligand precursors **1**−**4** in toluene solution (Scheme 3). Crystallization from the reaction mixtures resulted in analytically pure crystalline samples in high yields. The isolation of the 2,5-dimethylphenyl and 3,5-dimethylphenyl monometallic derivatives of the chelated aluminum ethyls proved difficult and usually resulted in a mixture of the target compound as well as the bimetallic species, as indicated by the

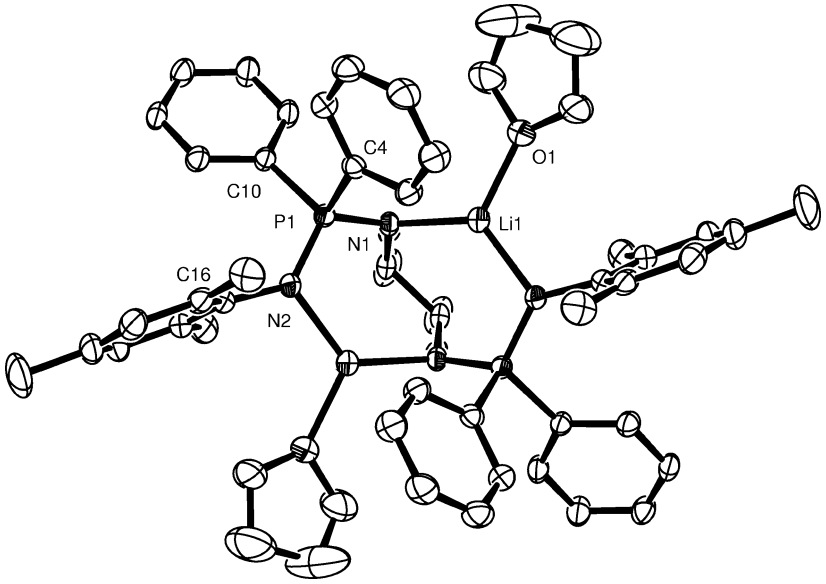
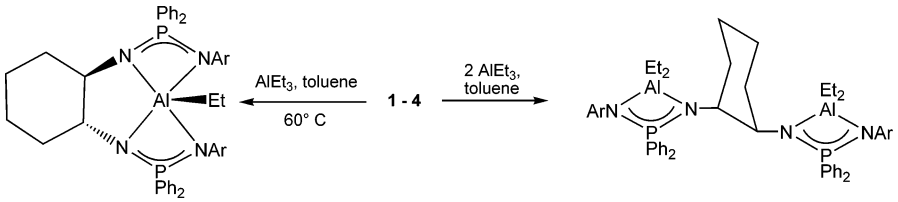


Figure 2. Thermal ellipsoid diagram (25% probability) of compound **5**. H atoms are omitted for clarity.

Scheme 3



9 (Ar = 2,4,6-$Me_3C_6H_2$)
10 (Ar = 2,6-$Me_2C_6H_3$)

11 (Ar = 2,4,6-$Me_3C_6H_2$)
12 (Ar = 2,6-$Me_2C_6H_3$)
13 (Ar = 2,5-$Me_2C_6H_3$)
14 (Ar = 3,5-$Me_2C_6H_3$)

$^{31}P\{^1H\}$ NMR spectra. The compounds **9**−**14** were fully characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectra of all six compounds clearly displayed the ethyl groups, as the expected high-field triplets and quartets. The $^{31}P\{^1H\}$ NMR spectra of the bimetallic compounds **11**−**14** displayed a single environment for the phosphorus atoms and were comparable to those of previously reported dialkylaluminum complexes chelated by a single (phosphinimino)amide ligand.[13,14] The $^{31}P\{^1H\}$ NMR spectra of the chelated aluminum ethyl derivatives **9** and **10** consisted of two single peaks in a 1:1 ratio by integration. Each signal was assigned by its Karplus relationship to the appropriate axial cyclohexane protons. The ^1H NMR data of **9** indicated that there were two axial proton environments assigned to the 1- and 2-positions of the cyclohexyl ring at 2.91 and 3.80 ppm. The $^3J_{PH}$ values were calculated as 30 and 11 Hz, respectively (Figure 3). Selective decoupling at the frequency of each phosphorus resonance indicated that the larger coupling constant corresponded to the signal at 18 ppm and the smaller value to the signal displayed at 30 ppm (Figure 3). The X-ray structure of **9** (vide infra) revealed that the two dihedral angles of H_{ax}−C−N−P were 160.3 and 41.7°. The phosphorus signal seen at 18 ppm was therefore designated as the "down" phosphorus with respect to the C−N bond (in Figure 3, structures shown in color are viewed down the 1,2-C−N bonds to the DACH group; other carbons of the cyclohexyl groups were removed for clarity). The smaller H−C−N−P dihedral angle is associated with the smaller coupling constant and is designated as the "up" phosphorus in Figure 3, which in turn corresponds to the phosphorus signal seen at 30 ppm.

The $^{13}C\{^1H\}$ NMR spectra were similar for all derivatives **9**−**14**, except for the expected differences in the aryl carbon environments. Chemical shifts of the resonances ascribed to the cyclohexane carbons were similar and comparable to those of our previously reported bis(amidinates).[6] Attempts to acquire ^{27}Al NMR data were unsuccessful, presumably due to the breadth of the signals.

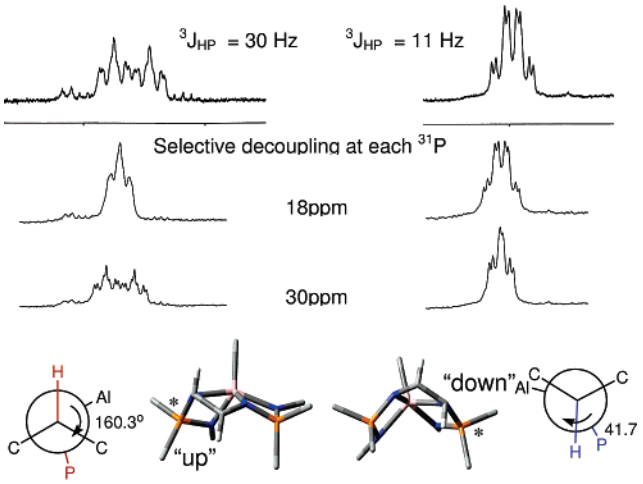


Figure 3. DACH H_{ax}/P correlation and phosphorus assignment within the N_4-chelated structure of compound **9**.

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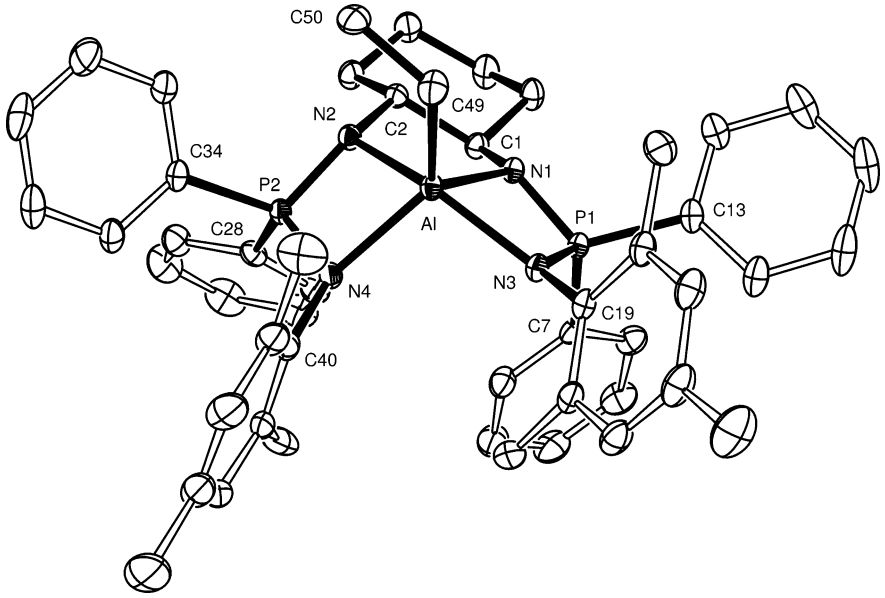

Figure 4. Thermal ellipsoid diagram (25% probability) of compound **9**. H atoms are omitted for clarity.

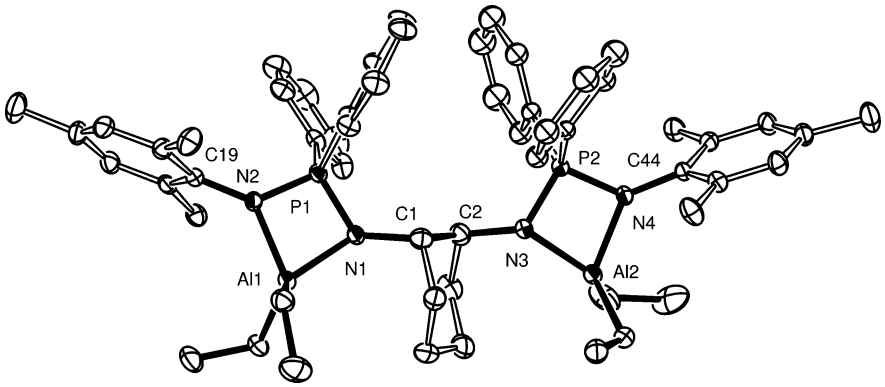

Figure 5. Thermal ellipsoid diagram (25% probability) of compound **11**. H atoms are omitted for clarity.

The $^{31}P\{^{1}H\}$ NMR spectra of compounds **11**−**14** displayed one signal, indicating the equivalence of both phosphorus environments. The protons attached to the 1- and 2-carbons of the cyclohexyl groups were similarly equivalent and appeared as doublets at 3.0 ppm ($^{3}J_{HP} = 17$ Hz) in the ^{1}H NMR spectra. All four compounds also displayed two inequivalent high-field resonances associated with the aluminum ethyl groups.

The relative disposition of the inequivalent ethyl groups was confirmed by a series of decoupling experiments. Selective decoupling of the ^{1}H NMR resonance at 1.23 ppm indicated that it was associated with the 2H multiplet at 0.22 ppm. Irradiation of the resonance at 1.40 ppm caused a similar simplification of the signal at 0.55 ppm. NOE experiments provided confirmation of these assignments and provided evidence for a closer approach of the higher field ethyl group to the equatorial 1- and 2-hydrogens of the cyclohexyl ring.

The solid-state structures of **9**−**12** were confirmed by X-ray diffraction analyses, and representative molecular structures of **9** and **11** are illustrated in Figures 4 and 5. Details of the crystallographic analyses for all four compounds are provided in Table 3, and selected bond lengths and angles are given in Table 4. The crystal structures of both **9** and **10** revealed these compounds to be monomeric, and the ligands behave as N_4-tetradentate chelates. The aluminum ethyl center is, therefore, in a five-coordinate environment that may be described as intermediate between idealized square-pyramidal and trigonal-bipyramidal geometries. The geometric parameter $\tau = (\beta - \alpha)/60°$ is applicable to five-coordinate structures as an index of the degree of trigonality,[15] between trigonal bipyramidal and rectangular pyramidal. The calculated τ values for compounds **9** and **10** (0.43 and 0.31, respectively) indicate that compound **9** may be considered as midway between tetragonal and trigonal bipyramidal with N(1) at the apex, while **10** adopts a geometry that is closer to rectangular pyramidal around the aluminum center with N(1), N(2), N(3), and N(4) forming the base and C(49) at the apex. Given the similarities in the two ligand structures, this finding is most probably due to a crystal-packing effect rather than any factor intrinsic to the slight variation in ligand structure.

The bond lengths within the ligands of the two derivatives **9** and **10** are very similar and effectively identical within the limits of experimental error and indicate complete delocalization about the N−P−N chelates. The bond lengths around the aluminum centers are also similar. The Al−N bonds of ca. 2.0 Å are similar to those previously reported aluminum complexes containing containing a similar NPN functionality.[13,14] The N−Al−N bond angles of **9** (73.95(6), 73.90(6)°) and **10** (73.93(13), 73.99(13)°) are also larger than in the previously reported five-coordinate amidinate $[\{MeC(N^{i}Pr)_2\}_2AlCl]$[16] (67.18(8), 67(18)(8)°) and confirm the greater bite of the NPN chelate ligands.

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Table 3. Selected Crystallographic and Data Collection Parameters for Compounds 9−12

	9	10	11	12
chem formula	$C_{50}H_{57}AlN_4P_2$	$C_{48}H_{53}AlN_4P_2$	$C_{56}H_{72}Al_2N_4P_2$	$C_{54}H_{68}Al_2N_4P_2{\cdot}C_7H_8$
formula wt	802.92	774.86	917.08	981.16
T (K)	173(2)	173(2)	173(2)	173(2)
cryst size (mm^3)	0.40 × 0.30 × 0.15	0.20 × 0.20 × 0.15	0.25 × 0.25 × 0.20	0.40 × 0.40 × 0.35
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	Cc (No. 9)	$P2_1/c$ (No. 14)	$C2/c$
a (Å)	16.9962(3)	11.1385(6)	10.7589(3)	19.9804(6)
b (Å)	15.3015(3)	22.2343(11)	20.0262(5)	17.5058(6)
c (Å)	17.2349(3)	17.2163(8)	24.1643(6)	17.2688(4)
α (deg)	90	90	90	90
β (deg)	94.439(1)	93.876(3)	91.247(1)	109.735(2)
γ (deg)	90	90	90	90
Z	4	4	4	4
V ($Å^3$)	4468.79(14)	4254.0(4)	5205.2(3)	5685.4(3)
d_c ($Mg\ m^{-3}$)	1.19	1.21	1.17	1.15
μ (mm^{-1})	0.16	0.16	0.16	0.15
θ range (deg)	3.71−25.03	3.47−26.01	3.49−26.03	3.42−26.03
R1, wR2 ($I > 2\sigma(I)$)	0.040, 0.100	0.056, 0.104	0.070, 0.155	0.085, 0.238
R1, wR2 (all data)	0.050, 0.107	0.089, 0.118	0.123, 0.180	0.115, 0.264
no. of measd/indep rflns (R(int))	55 066/7858 (0.061)	13 263/7351 (0.054)	31 892/10199 (0.080)	23 763/5584 (0.046)
no. of rflns with $I > 2\sigma(I)$	6709	5523	6397	4073

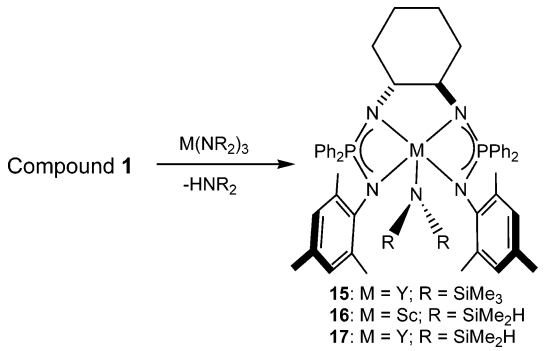
Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 9−12

	9	10	11	12
P(1)−N(1)	1.5990(14)	1.569(3)	1.622(3)	1.610(3)[x]
P(1)−N(3)	1.6149(15)	1.641(3)	1.625(3)[f]	
P(2)−N(2)	1.5824(14)	1.590(3)	1.617(3)[g]	1.623(3)[y]
P(2)−N(4)	1.6391(14)	1.621(3)	1.618(3)	
Al−N(1)	1.9564(15)	1.999(3)	1.938(3)[h]	1.935(3)
Al−N(2)	2.0123(15)	1.966(3)	1.936(3)[i]	1.923(3)
Al−N(3)	2.0338(15)	2.018(3)	1.929(3)[j]	
Al−N(4)	2.0439(15)	2.020(3)	1.936(3)[k]	
Al−C(49)	1.989(2)	1.988(4)[a]	*l*	
N(1)−P(1)−N(3)	96.66(7)	97.58(16)	96.08(13)[m]	95.60(16)[z]
N(2)−P(2)−N(4)	98.37(7)	96.68(16)	96.18(14)[n]	
N(1)−Al−C(49)	114.11(8)	100.55(16)[b]		
N(1)−Al−N(2)	81.73(6)	80.92(13)	77.10(11)[o]	76.74(13)
C(49)−Al−N(2)	100.76(7)	114.26(16)[c]		
N(1)−Al−N(3)	73.95(6)	73.92(13)		
C(49)−Al−N(3)	106.80(7)	115.53(16)[d]		
N(2)−Al−N(3)	148.81(6)	127.20(13)		
N(1)−Al−N(4)	120.83(6)	145.96(13)		
C(49)−Al−N(4)	122.89(8)	110.52(16)[e]		
N(2)−Al−N(4)	73.90(6)	73.99(13)		
N(3)−Al−N(4)	102.06(6)	103.51(14)	77.06(11)[p]	
C(1)−N(1)−Al	117.43(10)	113.0(2)	129.6(2)[q]	131.7(3)
P(1)−N(1)−Al	95.83(7)	95.35 (17)	93.34(12)[r]	93.81(14)[aa]
C(2)−N(2)−P(2)	137.21(12)	132.9(3)	125.0(2)[s]	
C(2)−N(2)−Al	111.30(10)	116.7(2)	132.4(2)[t]	
P(2)−N(2)−Al	95.23(7)	96.14(16)	93.48(13)[u]	
P(1)−N(3)−Al	92.40(7)	92.42(16)	93.31(12)[v]	93.84(13)[bb]
P(2)−N(4)−Al	92.31(7)	93.10(16)	93.19(12)[w]	

[a] Al−C(47). [b] N(1)−Al−C(47). [c] N(2)−Al−C(47). [d] N(3)−Al−C(47). [e] N(4)−Al−C(47). [f] P(1)−N(2). [g] P(2)−N(3). [h] Al(1)−N(1). [i] Al(1)−N(2). [j] Al(2)−N(3). [k] Al(2)−N(4). [l] Al(1)−C(28) = 1.974(3); Al(1)−C(30) = 1.983(4); Al(2)−C(55) = 1.965(4); Al(2)−C(53) = 1.972(4). [m] N(1)−P(1)−N(2). [n] N(3)−P(2)−N(4). [o] N(1)−Al(1)−N(2). [p] N(3)−Al(2)−N(4). [q] C(1)−N(1)−Al(1). [r] P(1)−N(1)−Al(1). [s] C(2)−N(3)−P(2). [t] C(2)−N(2)−Al(2). [u] P(2)−N(3)−Al(2). [v] P(1)−N(2)−Al(1). [w] P(2)−N(4)−Al(2). [x] P−N(1). [y] P−N(2). [z] N(1)−P−N(2). [aa] P−N(1)−Al. [bb] P−N(2)−Al.

The crystal structures of compounds **11** and **12** are monoclinic and the ligands behave as N_2-bidentate chelates. The aluminum centers are in four-coordinate environments and adopt distorted-tetrahedral geometries that are largely unremarkable. The X-ray analysis for compound **12** shows that the molecule lies on a 2-fold axis with the cyclohexyl group being disordered. The bond lengths surrounding the aluminum centers of compounds **11** and **12** are identical within experimental error for both compounds. Because of the reduced coordination number of the aluminum atoms, there is a slight decrease in the Al−N bond lengths of **11** and **12** (1.938(3), 1.936(3) Å and 1.935(3), 1.923(3) Å) in comparison to the Al−N bond lengths of the monometallic compounds **9** and **10** (1.956(2), 2.012(2) Å and 1.999(3), 1.966(3) Å). These former values are also comparable to those reported for the only previously reported four-coordinate aluminum iminophosphonamide (1.923(2), 1.930(2) Å), [{$Ph_2P(NSiMe_3)_2$-$AlPh_2$}].[14] The N−C bonds between the DACH component and the donor nitrogen centers within **11** and **12** (1.513(4) and 1.535(6) Å) are significantly longer than those of **9** and **10** (1.465(2) and 1.461(5) Å), presumably due to possible steric effects around the NPN moieties.

Scheme 4



Reactions of 1 with [Y{N(SiMe$_3$)$_2$}$_3$], [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$], and [Sc{(SiHMe$_2$)$_2$}$_3$(THF)$_2$]. A preliminary NMR-scale reaction between [Y{$N(SiMe_3)_2$}$_3$] and compound **1** gave encouraging results (Scheme 4). The ^1H NMR spectrum indicated complete consumption of the N−H functions and the loss of two Y−$N(SiMe_3)_2$ groups. The $^{31}P\{^1H\}$ NMR spectrum also revealed the complete disappearance of **1** and concomitant formation of four sharp peaks (labeled 1−4 in Figure 6) as well as a number of broader peaks. Peaks 1 and 3 exhibited respective $^2J_{PY}$ couplings of 2.6 and 2.8 Hz, while those displayed by peaks 2 and 4 were 4.1 and 4.8 Hz. Similar values for $^2J_{PY}$ couplings have been reported previously and indicate the successful formation of two yttrium complexes in which the ligand adopts a configuration about the metal center similar to that of the aluminum compounds **9** and **10** described above.[17−20]

(17) Wetzel, T. G.; Dehnen, S.; Roesky, P. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 1086.

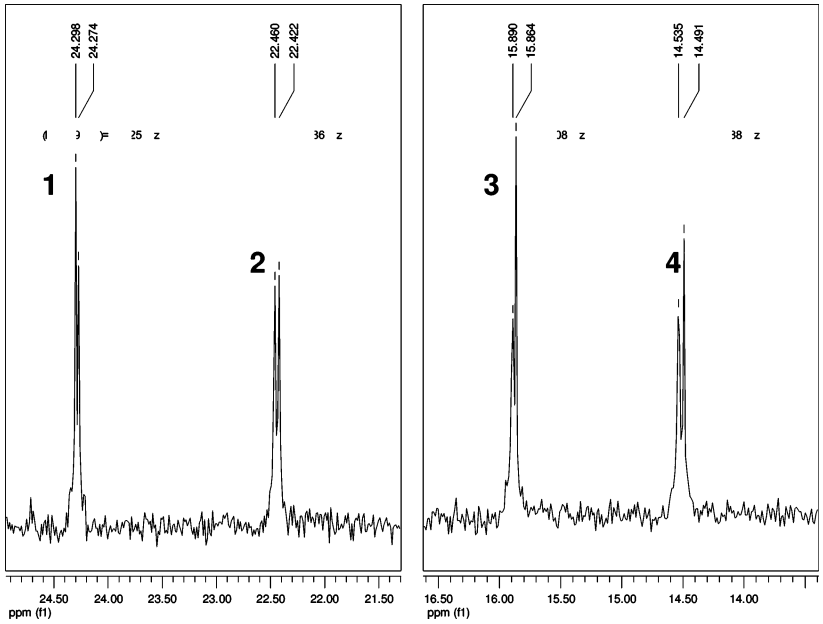


Figure 6. $^{31}P\{^{1}H\}$ NMR resonances attributed to N_4-Y chelation from the NMR-scale reaction of compound **1** and $[Y\{N(SiMe_3)_2\}_3]$ illustrating the $^{2}J_{YP}$ coupling.

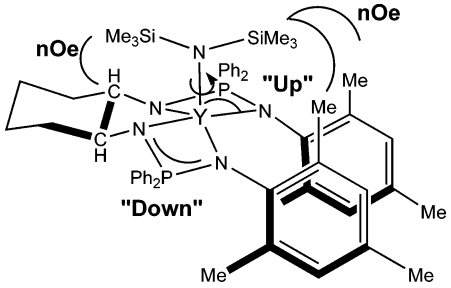


Figure 7. NOE and phosphorus assignments of the sterically congested yttrium environment within compound **15**.

The ^{1}H NMR spectrum displayed two distinct silylamide environments, which were shown to be undergoing slow chemical exchange by spin saturation transfer experiments. NOE experiments performed by double irradiation of these $SiMe_3$ peaks also showed signal enhancement of the mesityl *o*-methyl group protons and of the axial DACH methine protons, respectively (Figure 7). In the ^{29}Si NMR, there was only one signal, however, which showed no coupling to yttrium, most likely due to the relatively long relaxation times of the ^{29}Si nucleus in comparison to the proton. These experiments demonstrate that the desired complex **15**, was made, albeit as part of a mixture of products, and that rotation around the Y−N bond is slow on the ^{1}H NMR time scale but fast on the ^{29}Si time scale.

Upon further heating, this information was lost, along with the ^{1}H and ^{29}Si signals assigned to the N_4-chelated yttrium silylamide, indicating that compound **15** gave rise to the ^{31}P resonances at 22.4 and 14.5 ppm (peaks 2 and 4, respectively). The identity of the compounds giving rise to the further three peaks after continued heating are not yet known.

We then studied the reaction of compound **1** with the less sterically encumbered $[M\{N(SiHMe_2)_2\}_3(THF)_n]$ (M = Sc (*n* = 2), Y (*n* = 3)). Monitoring of the room-temperature reaction of $[Sc\{N(SiHMe_2)_2\}_3(THF)_3]$ with **1** by ^{31}P NMR spectroscopy revealed the formation of a single new species, observed as a resonance at 10.8 ppm in an amount approximately equal to that of the free ligand, **1**, at −5.8 ppm. The ^{1}H NMR spectrum revealed the presence of the $HN(SiHMe_2)$ resonances in approximately a 1:2 ratio with the $Sc-N(SiHMe_2)$ resonances. This initial observation was rationalized as the possible formation of a bimetallic structure, analogous to those of the aluminum compounds **11**−**14**, in which the two phosphorus atoms are in equivalent magnetic environments.

Continued monitoring of this reaction at 70 °C for a total of 72 h led to the development of two peaks at 23.3 and 15.4 ppm in a 1:1 ratio in the $^{31}P\{^{1}H\}$ NMR, as well as concomitant reduction in the free ligand resonance at −5.8 ppm. After 72 h the ^{1}H NMR displayed a $HN(SiHMe_2)$ methyl resonance at 0.11 ppm in an approximate 2:1 ratio with the $ScN(SiHMe_2)$ methyl resonance at 0.36 ppm, consistent with the formation of the intended monometallic scandium complex, **16**.

The NMR-scale reaction of $[Y\{N(SiHMe_2)_2\}_3(THF)_3]$ with **1** proceeded in a similar manner with gradual development of two peaks in the $^{31}P\{^{1}H\}$ NMR at 22.6 and 13.8 ppm as the reaction mixture was heated. After 72 h of heating, the ratio of the free $HN(SiHMe_2)$ to the $Y-N(SiHMe_2)$ resonances was 2:1 and the NH proton environments of **1** were no longer visible in the ^{1}H NMR spectrum. Unlike the reaction with the Sc amide, the NMR of the reaction with the Y amide showed no evidence of formation of the bimetallic species at any stage of the reaction. In comparison to the case for the hexamethyldisilazido derivative **15**, no $^{2}J_{PY}$ coupling constant data were forthcoming from these NMR studies.

Encouraged by these NMR studies, a preparative-scale reaction of an equimolar quantity of $[Y\{N(SiHMe_2)_2\}_3(THF)_2]$ and **1** in toluene for 72 h at 70 °C yielded the yttrium complex **17** as bright yellow crystals from THF. Although this workup procedure produced an analytically pure bulk sample, attempted crystallographic analysis was unsuccessful. The NMR spectroscopic data, however, provided unambiguous confirmation of the identity of compound **17**. The $^{31}P\{^{1}H\}$ NMR indicated the presence of two asymmetric phosphorus environments in a 1:1

(18) Roesky, P. W.; Gamer, M. T.; Pucher, M.; Greiner, A. *Chem. Eur. J.* **2002**, *8*, 5265.
(19) Roesky, P. W.; Gamer, M. T.; Marinos, N. *Chem. Eur. J.* **2004**, *10*, 3537.
(20) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197.

Table 5. Summary of MMA Polymerization Experiments with 9−12

entry	cat.	amt of MMA, equiv	amt of $Ni(acac)_2$, equiv	amt of MAD, equiv	solvent
1	**1**	200	1	3	toluene
2	**1**	200		3	toluene
3	**1**	200	1		toluene

ratio at 22.0 and 14.0 ppm, which were assigned through comparison to the aluminum derivatives **9** and **10** (using the same nomenclature as that employed in Figure 3) as the "up" and the "down" phosphorus environments respectively. The DACH methine protons were also observed as inequivalent multiplets at 3.43 and 3.29 ppm, similar to those observed within the more crowded structure of **15**.

Polymerization of MMA. It was hoped that the easily accessed racemic compounds **9**−**17** would be suitable group 3 and group 13 centered catalysts for enantiomorphic (site-controlled) polymerization of MMA.

Complex **9** was tested for activity as a catalyst for MMA polymerization by heating a solution of the aluminum complex in 200 equiv of MMA to 60 °C for 24 h. Although quenching of the samples with methanol resulted in the production of a gelatinous residue, ^{1}H NMR analysis indicated that the majority of the sample was unreacted MMA, signifying that **9**, in common with previously studied "unactivated" aluminum complexes, was not a good initiator for MMA polymerization.

Complex **9** was then tested on an NMR scale as a potential initiator within Gibson's three-component system for MMA polymerization (L_2AlR, bis(2,6-di-*tert*-butyl-4-methylphenoxide)aluminum methyl (MAD), $Ni(acac)_2$).[21] The conditions employed are displayed in Table 5. The samples were heated to 60 °C, and the ^{1}H NMR spectrum was recorded for each sample after 2 min, 1 h, 5 h, and 24 h. The ^{1}H NMR data of the sample containing all three components (Table 5, entry 1) displayed a gradual increase in the amount of syndiotactic polymer (63% *rr* by 24 h). The sample without $Ni(acac)_2$ (entry 2) displayed no noticeable polymerization activity in the ^{1}H NMR spectra. Similar observations were noted for the sample without the coactivator MAD (entry 3). In common with Gibson's previous observations, neither MAD nor $Ni(acac)_2$ alone was capable of initiating the polymerization of MMA. In order to examine these results further, the experiments were repeated on a preparative scale.

A series of samples were prepared utilizing the three-component system with complex **9** and then repeated using complex **10** within the catalytic system. Both were monitored for PMMA polymerization activity over a 24 h period by removal of aliquots at regular intervals and isolation of the PMMA by methanol quenching. The isolated polymeric materials were analyzed by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC). The ^{1}H NMR analysis of the samples employing complex **9** indicated that predominantly (80% *rr*) syndiotactic polymer was formed at room temperature. Lowering the temperature to 0 °C, while reducing the overall conversion (ca. 40% versus 65%), resulted in no effective change in polymer tacticity (82% *rr*). Similar observations were also produced when using complex **10** as the catalyst (ca. 81% *rr*). The GPC analyses indicated that the molecular weights of each sample were much higher than those predicted (>100 000), most likely due to sluggish initiation and comparatively rapid propagation of the polymerization process. This also resulted in broad molecular weight distributions and high polydispersity indices (2.0).

Table 6. MMA Polymerization Data from Catalysts 15 and 17

initiator	amt of MMA, equiv	amt of isotactic (*mm*),[a] %	M_w[b]	M_w/M_n
15	100	82	1 039 669	1.12
15	200	85	1 238 279	1.05
15	300	88	980 484	1.26
17	100	70	678 116	1.32
17	300	73	885 690	1.24

[a] Determined by ^{1}H NMR. [b] Versus polystyrene standard.

The bimetallic complexes **11** and **12** were also employed as MMA polymerization catalysts within a similar three-component system and monitored over a period of 24 h by taking an aliquot of the solution after 2 min and every 45 min thereafter. The ^{1}H NMR spectra again revealed the formation of polymers with a pronounced syndiotactic bias (84% *rr*) with very high molecular weights (>200 000) and with polydispersity indices >2.1.

For all four aluminum complexes studied, **9**−**12**, there was no clear dependence of polymerization activity on the relative steric bulk around the metal. The results suggest that the sluggish initiation is not controlled solely by the Al−alkyl group but is also a more complex function of both the size of the initiating group and the steric congestion afforded by the 'spectator' bis(iminophosphomamide) ligand.

The ability of the yttrium bis(iminophosphomamide) complexes **15** and **17** to act as single-component initiators for MMA polymerization was also evaluated. One equivalent of each complex was dissolved in toluene, and 100/200/300/400/500 equiv of MMA in toluene were rapidly added to the solution of the initiator. The mixtures were stirred at 25 °C for 2 h before the reactions were quenched with methanol and the polymers dried and analyzed by ^{1}H NMR and GPC. The results are summarized in Table 6.

The ^{1}H NMR data obtained from the polymers clearly showed a strong bias toward the formation of the isotactic polymer by these initiators. The high molecular weights may, again, be attributed to slow initiation by the complexes relative to rapid propagation of the polymerization reaction. The polydispersities of the polymers were, however, close to unity, suggesting that, once activated, the metal centers in these complexes are extremely efficient single-site catalytic systems for MMA polymerization. In an attempt to observe the effect that the bis(iminophosphomamide) ligands have on the environment around the metal center and its subsequent effect on initiation of MMA polymerization, the amide $[Y\{N(SiHMe_2)_2\}_3(THF)_3]$ was tested as an initiator for the polymerization of 300 equiv of MMA. This procedure yielded PMMA that was 70% *syndiotactic*. In contrast, a repeat of this experiment with the addition of 1 equiv of the ligand precursor **1** yielded PMMA that was 63% *isotactic*. From these results it is apparent that the bis(iminophosphanamide) ligands exert a substantial effect on the tacticity of the PMMA produced by initiation from these compounds. Other investigations into lanthanide initiators have found similar results. Visseaux et al. have recently found that bulky samarium complexes showed poor control over chain length, while producing highly stereoregular PMMA.[22] The activities of **15** and **17** are particularly notable, as highly stereoregular polymer was produced at room temperature during relatively short (2 h) reaction times. The only superior system, in terms of stereoregularity, reported to date is Arnold's bis(pyrrolylaldiminato)-

(21) Cameron, P. A.; Gibson, V. C.; Irvine, D. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2141.

(22) Barbier-Baudry, D.; Bouyer, F.; Visseaux, M. *Appl. Organomet. Chem.* **2006**, *20*, 24.

samarium alkyl complex, which gave >90% isotactic PMMA with polydispersities averaging 1.6 at room temperature.[23]

Summary

The activities of the bis(iminophosphonamide) aluminum derivatives **9**−**12** employed in the three-component system for MMA polymerization were somewhat disappointing. Although a clear syndiotactic bias was observed, all four complexes utilized showed little evidence of molecular weight control over the polymerization process. This is most likely due to difficulties in forming the initiating enolate species due to the steric protection afforded to the metal centers by the sterically demanding bis(iminophosphonamide) ligand.

The use of the yttrium complexes **15** and **17** as initiators for MMA polymerization, however, yielded more encouraging results. The formation of highly stereoregular polymer (>80% isotactic) with very low polydispersities (ca. 1.1), particularly in the case of **15**, demonstrated that these complexes are efficient single-site catalytic systems for MMA polymerization. Indeed, there are few other ligand systems that give such low polydispersity with lanthanide centers, indicating that they are systems worthy of further study as initiators for MMA polymerization. We are continuing to study the reactivity of these complexes and of related species.

Experimental Section

General Considerations. Air-sensitive manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and cannula techniques or in a glovebox operating at <5 ppm O_2. Mr. Stephen Boyer at London Metropolitan University performed elemental analyses. NMR spectra were recorded on a JEOL EX270 spectrometer at 270 MHz (^{1}H), 67.9 MHz (^{13}C), and 109.3 MHz (^{31}P), a Bruker AM500 spectrometer at 125.8 MHz (^{13}C) and 202.5 MHz (^{31}P) or a Bruker AV400 spectrometer at 100.6 MHz (^{13}C). DEPT (distortion enhanced by polarization transfer) experiments were performed using standard pulse sequences. ^{1}H and ^{13}C NMR chemical shifts were referenced internally to solvent resonances. Chemical shifts are quoted in δ (ppm), and the data are given as (multiplicity, intensity, assignment, coupling in Hz). Mass spectra were obtained by EI (electron ionization) or FAB (fast atom bombardment) using 3-nitrobenzyl alcohol as the matrix at Imperial College London on a Micromass Platform II instrument. Repeated attempts to accumulate mass spectral data on some compounds were unsuccessful due to their air and moisture sensitivity. A significant number of elemental analyses were not adequate, despite repeated attempts. In all cases, however, other characterizing evidence was unambiguous. Infrared measurements were carried out on a Perkin-Elmer spectrometer with samples pressed into a disk with powdered solid KBr. GPC analyses were carried out by RAPRA Technology, using a Viscotek TDA Model 301 triple array detector, connected to two linear 10 μm columns. The sample solutions were prepared by adding 10 mL of THF to 20 mg of sample and leaving overnight to dissolve. The solutions were thoroughly mixed and filtered through a 0.2 μm polyamide membrane, with glass-fiber prefilter, prior to the chromatography. Diethyl ether, toluene, THF, and dichloromethane were dried and degassed by extended reflux under dinitrogen over appropriate drying agents and stored in ampules fitted with Young taps. The NMR solvents C_6D_6 and d_8-toluene were dried over molten potassium, vacuum-transferred prior to use, and stored in ampules fitted with Young taps. Methyl methacrylate was dried over calcium hydride and vacuum-transferred prior to use. All azides and group 3 amides were synthesized via literature procedures.[24−26] Other chemical reagents were obtained commercially and used as received. In assignments Mes represents 2,4,6-trimethylphenyl and DACH represents *trans*-1,2-diaminocyclohexyl. For the polymerization studies MAD represents bis(2,6-di-*tert*-butyl-4-methylphenoxide)aluminum methyl, which was prepared by literature procedures.[27]

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(H)Ph_2P═N(2,4,6-C_6H_2)}$_2$] (1). To a solution of *trans*-1,2-diaminocyclohexane (1.16 g, 10 mmol) in toluene (50 mL) was added dropwise ^{n}BuLi (8.13 mL, 2.5 M in hexane, 20 mmol), at room temperature with stirring, to form a white precipitate (exothermic). This mixture was stirred for 3 h before the dropwise exothermic addition of Ph_2PCl (4.48 g, 3.65 mL, 20 mmol), to afford a light yellow solution and a colorless precipitate. After the mixture was stirred for a further 2 h, 2,4,6-trimethylphenyl azide (2.99 g, 20 mmol) was added dropwise, resulting in a light brown solution with gas evolution. This solution was heated to 60 °C for 14 h. Removal of the volatile components in vacuo and extraction of the resultant brown solid into toluene (30 mL), followed by filtration, gave a dark red solution. Concentration of this solution afforded pale yellow-orange crystals of **1** (5.65 g, 72%) at room temperature. ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.87 (bm, 4H, 4,5 DACH), 1.21−1.23 (m, 2H, 3,6 ax DACH), 2.03−2.06 (m, 2H, 3,6 eq DACH), 2.30 (s, 6H, *p*-Me), 2.41 (s, 12H, *o*-Me), 3.34−3.43 (m, 2H, 1,2 DACH), 4.57−4.62 (dd, 2H, NH, $^3J_{PH}$ = 13.5 Hz), 6.86 (s, 2H, CH Mes), 6.97−6.99 (m, 20H, Ar H), 7.83−7.92 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 67.9 MHz, 298 K): δ 20.9 (*p*-Me), 22.3 (*o*-Me), 25.3 (4,5 DACH), 35.9 (3,6 DACH), 56.6 (1,2 DACH), 131.4 (d, Ar), 131.7 (d, Ar), 131.8 (d, *i*-PPh), 132.3 (d, *i*-PPh), 145.2 (*i*-NMes). ^{31}P{^{1}H} NMR (C_6D_6, 109.4 MHz, 298 K): δ −5.85. Anal. Calcd for $C_{48}H_{54}N_4P_2$: C, 76.90; H, 7.21; N, 7.48. Found: C, 76.88; H, 7.19; N, 7.52. MS (EI; *m/z*): 748 (5%, M^+), 631 (9%, M^+ − Mes), 538 (50%, M^+ − NMes − Ph), 414 (62%, M^+ − NH_2PPh_2NHMes), 335 (100%, NH_2PPh_2NHMes), 318 (49%, PPh_2NMes), 134 (54%, NMes), 120 (30%, Mes). IR (KBr, ν cm^{-1}): 3375.0 (NH), 3050.1 (CH), 2933.8 (CH), 2850.5 (CH), 1606.0 (NH), 1480.2 (CN), 1435.0 (CH), 1111.9 (P═N), 897.9−694.6 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(H)Ph_2P═N(2,6-$Me_2C_6H_3$)}$_2$] (2). This compound was synthesized by the same general method as that outlined for **1** and isolated as pale orange crystals (7.16 g, 87%) by crystallization from toluene at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 0.80 (bm, 4H, 4,5 DACH), 1.19−1.21 (m, 2H, 3,6 ax DACH), 2.00−2.03 (m, 2H, 3,6 eq DACH), 2.39 (s, 12H, *o*-Me), 3.39−3.40 (m, 2H, 1,2 DACH), 4.54−4.58 (dd, 2H, NH, $^3J_{PH}$ = 20 Hz), 6.94 − 7.03 (m, 20H, Ar H), 7.80−7.87 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 22.4 (*p*-Me), 25.2 (4,5 DACH), 35.9 (3,6 DACH), 56.7 (1,2 DACH), 131.3 (d, Ar), 132.1 (d, Ar), 132.2 (d, *i*-PPh), 147.8 (*i*-NAr). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ −5.74. Anal. Calcd for $C_{46}H_{50}N_4P_2\cdot1.5C_7H_8$: C, 78.92; H, 7.22; N, 6.52. Found: C, 79.19; H, 8.14; N, 7.13. MS (EI; *m/z*): 720 (3%, M^+), 617 (8%, M^+− $(CH_3)_2C_6H_3$), 524 (43%, M^+ − $N(CH_3)_2C_6H_3$ − Ph), 400 (66%, M^+ − $NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (100%, NH_2-$PPh_2NH(CH_3)_2C_6H_3$), 120 (45%, $NH(CH_3)_2C_6H_3$, 91 (100%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 3333.0 (NH), 3055.5 (CH), 2937.2 (CH), 2852.3 (CH), 1589.1 (NH), 1471.9 (CN), 1433.9 (CH), 1116.3 (P═N), 972.6 − 696.4 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(H)Ph_2P═N(2,5-$Me_2C_6H_3$)}$_2$] (3). This compound was synthesized by the same general method as outlined for **1** and isolated as orange crystals (4.65 g, 86%) after

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storage at +5 °C. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 0.71 (bm, 4H, 4,5 DACH), 1.10−1.12 (m, 2H, 3,6 ax DACH), 1.93−1.97 (m, 2H, 3,6 eq DACH), 2.02 (s, 6H, *o*-Me), 2.09 (s, 6H, *m*-Me), 3.34−3.35 (m, 2H, 1,2 DACH), 4.65−4.70 (dd, 2H, NH, $^3J_{PH}$ = 25 Hz), 6.95−7.02 (m, 20H, Ar H), 8.02 − 8.07 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 19.9 (*o*-Me), 21.3 (*m*-Me), 25.0 (4,5 DACH), 36.0 (3,6 DACH), 56.5 (1,2 DACH), 132.1, (d, Ar), 132.2 (d, Ar), 132.7 (d, *i*-PPh), 149.9 (*i*-NAr). ^{31}P-{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 2.96. Anal. Calcd for $C_{46}H_{50}N_4 \cdot 1.5C_7H_8$): C, 78.92; H, 7.22; N, 6.52. Found: C, 78.97; H, 7.03; N, 6.86. MS (EI; *m/z*): 720 (5%, M^+), 617 (4.5%, $M^+ - (CH_3)_2C_6H_3$), 524 (7%, $M^+ - N(CH_3)_2C_6H_3 - Ph$), 400 (100%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (75%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (26%, $NH(CH_3)_2C_6H_3$), 91 (22%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 3360.0 (NH), 3055.5 (CH), 2932.2 (CH), 2855.8 (CH), 1598.3 (NH), 1566.1 (NH), 1496.9 (CN), 1435.9 (CH), 1112.9 (PN), 883.7−695.0 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(H)Ph_2P═N(3,5-C_6H_2)}$_2$] (4). This compound was synthesized by the same general method as outlined for **1** and isolated as orange crystals and an oily residue, which was also identified as **4** by ^{1}H NMR (2.51 g, 51%) by storage of a toluene solution at −30 °C. ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.88 (bm, 4H, 4,5 DACH), 1.36 (m, 2H, 3,6 ax DACH), 1.91 (m, 2H, 3,6 eq DACH), 2.15 (s, 12H, *o*-Me), 3.32 (m, 2H, 1,2 DACH), 5.02−5.05 (dd, 2H, NH, $^3J_{PH}$ = 8.1 Hz), 6.99−7.01 (m, 20H, Ar H), 8.07−8.15 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 21.1 (*m*-Me), 25.3 (4,5 DACH), 36.2 (3,6 DACH), 58.0 (1,2 DACH), 132.5 (d, Ar), 132.6 (d, Ar), 132.8 (d, *i*-PPh), 150.3 (*i*-NAr). ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298 K): δ 7.90. Anal. Calcd for $C_{46}H_{50}N_4P_2$: C, 73.70; H, 6.93; N, 7.77. Found: C, 73.22; H, 5.93; N, 7.03. MS (FAB; *m/z*): 720 (3%, M^+), 624 (14%, M^+ − DACH), 524 (2%, $M^+ - N(CH_3)_2C_6H_3 - Ph$), 400 (100%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (74%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 304 (54%, $PPh_2N(CH_3)_2C_6H_3$), 228 (37%, $PPh_2N(CH_3)_2C_6H_3$), 150 (25%, $PN(CH_3)_2C_6H_3$), 91 (11%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 3355 (NH), 3062.5 (CH), 2933.7 (CH), 2865.0 (CH), 1589.8 (CN), 1436.4 (CH), 1115.2 (P═N), 828.3−693.5 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Li(THF)Ph_2PN(2,4,6-C_6H_2)}$_2$] (5). To a solution of compound **1** (0.70 g, 0.9 mmol) in THF (20 mL) was added ^{n}BuLi (0.75 mL, 2.5 M in hexane, 1.0 mmol), and the pale yellow solution was stirred for 14 h. Removal of the volatile components in vacuo and extraction of the light brown solid into toluene (20 mL) gave a brown solution, concentration of which afforded light brown crystals of **5** (0.69 g, 81%) at room temperature. ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 1.14 (THF), 1.59 (m, 2H, DACH), 1.91 (m, 2H, DACH), 2.15 (m, 2H, DACH), 2.27 (s, 6H, *p*-Me), 2.31 (s, 12H, *o*-Me), 2.75−2.80 (m, 2H, DACH), 3.25 (THF), 4.02 (m, 2H, 1,2 DACH), 6.91 (s, 4H, *m*-Me), 7.03 (m, 2H, Ar H), 7.10 (m, Ar H), 7.68 (m, 2H, Ar H), 8.04 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 21.0 (*p*-Me), 21.5 (*o*-Me), 25.4 (THF), 27.7 (4,5 DACH), 40.8 (3,6 DACH), 61.9 (1,2 DACH), 67.9 (THF), 130.4 (d, Ar H), 131.8 (d, Ar H), 133.1 (d, *i*-PPh),147.8 (*i*-NMes). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 9.60. ^{7}Li{^{1}H} NMR (C_6D_6, 194.4 MHz, 298 K): δ 1.67−3.06 (b). Anal. Calcd for $C_{56}H_{68}N_4P_2Li_2O_2$: C, 74.25; H, 10.17; N, 6.19. Found: C, 74.17; H, 10.05; N, 6.30. MS (FAB; *m/z*): 904 (1%, M^+), 749 (100%, $M^+ - (LiTHF)_2$), 631 (7%, M^+ − Mes), 538 (54%, M^+ − NMes − Ph), 414 (80%, $M^+ - NH_2PPh_2NHMes$), 335 (92%, NH_2PPh_2NHMes), 318 (70%, PPh_2NMes), 134 (30%, NMes), 77 (5%, Ph). IR (KBr, ν cm^{-1}): 3052.7 (CH), 2936.6 (CH), 2854.0 (CH), 1480.6 (CN), 1433.7 (CH), 1112.1 (PN), 897.9−697.9 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Li(THF)Ph_2PN(2,6-C_6H_3)}$_2$] (6). This compound was synthesized by the same general method as outlined for **5** from compound **2** and ^{n}BuLi and isolated as light brown crystals (0.32 g, 52%) by storage of a toluene solution at 5 °C. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 1.17 (THF), 1.31 (m, 2H, DACH), 1.56 (m, 2H, DACH), 1.87 (m, 2H, DACH), 2.29 (s, 12H, *o*-Me), 2.73−2.76 (m, 2H, DACH), 3.30 (THF), 3.95 (m, 2H, 1,2 DACH), 6.85−7.12 (m, Ar H), 7.87−8.01 (m, 8H, Ar H). ^{13}C-{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 21.6 (*p*-Me), 25.4 (THF), 27.6 (4,5 DACH), 40.7 (3,6 DACH), 61.8 (1,2 DACH), 67.8 (THF), 130.4 (d, Ar H), 131.2 (d, Ar H), 132.8 (d, *i*-PPh), 133.0 (d, *i*-PPh), 150.6 (*i*-NMes). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 9.70. Anal. Calcd for $C_{54}H_{64}N_4P_2Li_2O_2$: C, 73.93; H, 7.36; N, 6.39. Found: C, 72.61; H, 6.54; N, 5.72. MS (FAB; *m/z*): 876 (1%, M^+), 721 (100%, $M^+ - (LiTHF)_2$), 617 (6%, $M^+ - (CH_3)_2C_6H_3$), 524 (48%, $M^+ - N(CH_3)_2C_6H_3) - Ph$), 400 (86%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (85%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (40%, $NH(CH_3)_2C_6H_3$, 77 (4%, Ph). IR (KBr, ν cm^{-1}): 3057.8 (CH), 2939.5 (CH), 2855.9 (CH), 1472.4 (CN), 1435.2 (CH), 1116.5 (PN), 895.8−697.9 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Li(THF)Ph_2PN(2,5-$Me_2C_6H_3$)}$_2$] (7). This compound was synthesized by the same general method as outlined for **5** from compound **3** and ^{n}BuLi and isolated as brown crystals (0.14 g, 41%) by storage of a toluene solution at −30 °C. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 1.37 (THF), 1.54 (m, 2H, DACH), 1.69 (m, 2H, DACH), 1.91 (s, 6H, *o*-Me), 2.08 (m, 2H, DACH), 2.12 (s, 6H, *m*-Me), 2.83 (m, 2H, DACH), 3.21 (m, 2H, 1,2 DACH), 3.54 (THF), 6.99−7.14 (m, Ar H), 7.78−8.20 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 19.5 (*o*-Me), 21.4 (*m*-Me), 25.7 (THF), 26.7 (4,5 DACH), 39.4 (3,6 DACH), 62.9 (1,2 DACH), 67.9 (THF), 131.7 (d, Ar), 132.2 (d, Ar), 132.8 (d, *i*-PPh), 133.0 (d, *i*-PPh), 151.8 (*i*-NAr). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 15.81. Anal. Calcd for $C_{54}H_{64}N_4P_2Li_2O_2$: C, 73.93; H, 7.36; N, 6.39. Found: C, 72.45; H, 6.97; N, 6.18. MS (FAB; *m/z*): 876 (1%, M^+), 721 (100%, $M^+ - (LiTHF)_2$), 617 (2%, $M^+ - (CH_3)_2C_6H_3$), 524 (45%, $M^+ - N(CH_3)_2C_6H_3 - Ph$), 400 (80%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (60%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (25%, $NH(CH_3)_2C_6H_3$), 77 (2%, Ph). IR (KBr, ν cm^{-1}): 3052.3 (CH), 2935.5 (CH), 2855.8 (CH), 1480.1 (CN), 1435.8 (CH), 1112.5 (PN), 889.0−696.3 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Li(THF)Ph_2PN(3,5-C_6H_3)}$_2$] (8). This compound was synthesized by the same general method as outlined for **5** from compound **4** and nBuLi and isolated as red-brown crystals (0.45 g, 39%) at −30 °C. ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.88 (m, 2H, DACH), 1.36 (m, 2H, DACH), 2.08 (THF), 2.14 (m, 2H, DACH), 2.21 (s, 12H, *m*-Me), 2.28 (m, 2H, DACH), 3.31 (m, 2H, 1,2 DACH), 3.54 (THF), 7.02−7.09 (m, Ar H), 8.07−8.37 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 21.7 (*m*-Me), 25.7 (THF), 28.2 (4,5 DACH), 39.7 (3,6 DACH), 67.9 (1,2 DACH), 132.0 (d, Ar), 132.4 (d, Ar), 133.7 (d, *i*-PPh), 133.2 (d, *i*-PPh), 150.2 (*i*-NAr). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 27.74. MS (FAB; *m/z*): 721 (54%, $M^+ - (LiTHF)_2$), 524 (4%, $M^+ - N(CH_3)_2C_6H_3 - Ph$), 400 (100%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (44%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (10%, $NH_2(CH_3)_2C_6H_3$), 77 (8%, Ph). IR (KBr, ν cm^{-1}): 3058.8 (CH), 2929.6 (CH), 1589.7 (CN), 1435.9 (CH), 1114.3 (PN), 873.9−695.5 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)Ph_2PN(2,4,6-C_6H_2)}$_2$] (9). To a stirred toluene solution (20 mL) of **1** (1.00 g, 1.34 mmol) was added Et_3Al (0.15 g, 1.34 mmol) dropwise. The mixture was stirred open to the atmosphere of the drybox for approximately 20 min before removal and heating at 60 °C for 16 h. Concentration of the resultant light red solution afforded colorless crystals of **9** (0.87 g, 81%). ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.70 (q, 2H, CH_2CH_3), 1.86 (t, 3H, CH_2CH_3), 2.31 (s, 6H, *p*-Me), 2.42 (s, 12H, *o*-Me), 3.45 (m, 2H, 1,2 DACH), 6.98−7.05 (m, 20H, Ar H), 7.84−7.93 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 20.0 (*p*-Me), 22.3 (*o*-Me), 25.1 (4,5 DACH), 34.7 (3,6 DACH), 56.3 (1,2 DACH), 131.3 (d, Ar), 131.8 (d, Ar), 131.8 (d, *i*-PPh), 145.1 (*i*-NMes). ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298

K): δ 17.97, 29.38. Anal. Calcd for $C_{50}H_{57}N_4P_2Al$: C, 74.72; H, 7.10; N, 6.97. Found: C, 74.52; H, 7.21; N, 6.79. MS (FAB; *m/z*): 774 (58%, $M^+ + C_2H_5$), 748 (100%, M^+), 631 (50%, $M^+ -$ Mes), 414 (65%, $M^+ - NH_2PPh_2NHMes$), 335 (85%, NH_2PPh_2NHMes), 318 (50%, PPh_2NMes), 134 (40%, NMes), 120 (35%, Mes). IR (KBr, ν cm^{-1}): 3119.5 (CH), 2965.2 (CH), 1715.0 (CN), 1454.4 (CN), 1111.5 (PN), 935.0 (CH), 910.2 (CH), 825.0 (CH), 760.5 (CH_2), 695.6 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)$_2$)Ph$_2$PN(2,6-Me$_2$C$_6$H$_3$)}$_2$] (10). This compound was synthesized by the same general method as outlined for **9** from compound **2** and Et_3Al and isolated as colorless crystals (0.69 g, 76%). ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.68 (q, 2H, CH_2CH$_3$), 1.82 (t, 3H, CH$_2$CH_3), 2.10 (s, 12H, *o*-Me), 2.89−2.92 (d, 2H, 1,2 DACH), 7.04 (m, Ar), 7.64 (m, Ph). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz, 298 K): δ 22.2 (*p*-Me), 23.9 (4,5 DACH), 30.6 (3,6 DACH), 67.8 (1,2 DACH), 132.2 (d, Ar), 132.3 (d, Ar), 133.4 (d, *i*-PPh). ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298 K): 18.2, 29.5. Anal. Calcd for $C_{48}H_{53}N_4P_2Al$: C, 74.32; H, 6.84; N, 7.23. Found C, 74.11; H, 6.67; N, 7.18. MS (FAB; *m/z*): 746 (42%, $M^+ + C_2H_5$), 720 (90%, M^+), 617 (47%, $M^+ - (CH_3)_2C_6H_3$), 400 (66%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (80%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (40%, $NH(CH_3)_2C_6H_3$). IR (KBr, ν cm^{-1}): 3060.1 (CH), 2925.0 (CH), 2835.8 (CH), 1465.6 (CN), 1448.1 (CH), 1114.9 (PN), 970.0−695.5 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)$_2$)Ph$_2$PN(2,4,6-C$_6$H$_2$)}$_2$] (11). To a stirred solution of **1** (0.85 g, 1.13 mmol) in toluene (20 mL) was added dropwise Et_3Al (0.26 g, 2.26 mmol). The mixture was stirred open to the atmosphere of the drybox for approximately 10 min (evolution of ethane) before being attached to an external Schlenk line and stirred for a further 14 h. Concentration of the resultant light red solution afforded pale yellow crystals (0.88 g, 83%) at room temperature. ^{1}H NMR (C_6D_6, 270 MHz, 298 K): δ 0.69 (q, 2H, CH_2CH$_3$), 0.86 (bm, 4H, 4,5 DACH), 1.21 (m, 2H, 3,6 ax DACH), 1.32 (t, 3H, CH$_2$CH_3), 1.52 (t, 3H, Et), 2.31 (s, 6H, *p*-Me), 2.41 (s, 12H, *o*-Me), 6.90−6.95 (m, 20H, Ar H), 7.8 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 67.9 MHz, 298 K): δ 20.0 (*p*-Me), 22.3 (*o*-Me), 25.3 (4,5 DACH), 35.9 (3,6 DACH), 56.6 (1,2 DACH), 131.4 (d, Ar), 131.7 (d, Ar), 131.8 (d, *i*-PPh), 132.3 (d, *i*-PPh), 145.2 (*i*-NMes). ^{31}P{^{1}H} NMR (C_6D_6, 109.4 MHz, 298 K): δ 36.6. Anal. Calcd for $C_{56}H_{72}N_4P_2Al_2\cdot C_7H_8$: C, 74.93; H, 7.93; N, 5.55. Found: C, 74.43; H, 8.64; N, 5.60. MS (FAB; *m/z*): 828 (64%, $-4C_2H_5$), 749 (52%, $-2Al(C_2H_5)_2$), 538 (46%, $-2Al(C_2H_5)_2$ − NMes − Ph), 414 (70%, $-2Al(C_2H_5)_2$ − NH_2PPh_2NHMes), 335 (100%, $-2Al(C_2H_5)_2$ − NH_2PPh_2NHMes), 318 (80%, $-2Al(C_2H_5)_2$ − PPh_2NMes), 134 (35%, NMes), 91 (12%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 3100.9 (CH), 2905.1 (CH), 1702.0 (CN), 1478.8 (CN), 1395.7 (CH_3), 1113.9 (PN), 928.0 (CH), 900.2 (CH), 805.0 (CH), 768.2 (CH), 694.0 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)$_2$)Ph$_2$PN(2,6-Me$_2$C$_6$H$_3$)}$_2$] (12). This compound was synthesized by the same general method as outlined for **11** from compound **2** and Et_3Al and isolated as pale yellow crystals (0.27 g, 87%) at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 0.67 (q, 2H, CH_2CH$_3$), 1.27 (t, 3H, CH$_2$CH_3),1.49 (t, 3H, CH$_2$CH_3), 2.10 (s, 12H, *o*-Me), 3.11−3.15 (d, 2H, 1,2 DACH), 6.75−6.80 (m, 2H, Ar H), 6.87−6.93 (m, 20H, Ar H), 7.53−7.54 (m, 8H, Ar H). ^{13}C-{^{1}H} NMR (C_6D_6, 67.9 MHz, 298 K): δ 20.0 (*p*-Me), 21.0 (4,5 DACH), 28.0 (3, 6 DACH), 54.9, (1,2 DACH), 131.9 (d, Ar), 132.6 (d, Ar), 133.2 (d, *i*-PPh). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz, 298 K): δ 37.0. Anal. Calcd for $C_{54}H_{68}N_4P_2Al_2$: C, 72.89; H, 7.65; N, 6.30. Found: C, 71.09; H, 6.78; N, 6.02. MS (FAB; *m/z*): 774 (1%, $4C_2H_5$, 721 (100%, M^+), 618 (3%, $M^+ - (CH_3)_2C_6H_3$), 524 (14%, $M^+ - N(CH_3)_2C_6H_3$) − Ph), 401 (29%, $M^+ - NH_2PPh_2$-$NH(CH_3)_2C_6H_3$), 321 (38%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 120 (19%, $NH(CH_3)_2C_6H_3$, 91 (100%, $CH_3C_6H_4$), 77 (7%, Ph). IR (KBr, ν cm^{-1}): 3050.0 (CH), 2930.1 (CH), 2869.7 (CH), 1482.5 (CN), 1404.1 (CH), 1115.9 (PN), 967.1−695.5 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)$_2$)Ph$_2$PN(2,5-Me$_2$C$_6$H$_3$)}$_2$] (13). This compound was synthesized by the same general method as outlined for **11** from compound **3** and Et_3Al and isolated as pale yellow crystals (0.60 g, 84%) at room temperature. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 0.79 (q, 2H, CH_2CH$_3$), 1.19 (t, 3H, CH$_2$CH_3), 1.22 (t, 3H, CH$_2$CH_3), 1.49 (t, 3H, CH$_2$CH_3), 1.52 (t, 3H, CH$_2$CH_3), 1.87 (s, 6H, *o*-Me), 1.90 (s, 6H, *m*-Me), 3.32 (m, 2H, 1,2 DACH), 6.98−7.07 (m, 20H, Ar H), 7.70−7.74 (m, 8H, Ar H). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 19.5 (*o*-Me), 20.9 (*m*-Me), 25.0 (4,5 DACH), 35.8 (3,6 DACH), 54.1 (1,2 DACH), 132.3 (d, Ar), 132.9 (d, *i*-PPh), 133.1 (d, *i*-PPh). ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298 K): δ 36.9. Anal. Calcd for $C_{54}H_{68}N_4P_2Al_2$: C, 72.89; H, 7.65; N, 6.30. Found: C, 70.94; H, 9.29; N, 6.09. MS (FAB; *m/z*): 774 (1%, $M^+ - 4(C_2H_5)$, 721 (100%, M^+), 524 (4%, $M^+ - N(CH_3)_2C_6H_3) - Ph$), 401 (20%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (28%, NH_2PPh_2NH-$(CH_3)_2C_6H_3$), 120 (6%, $NH(CH_3)_2C_6H_3$, 91 (5%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 2859.6 (CH), 1606.4 (CN), 1505.8 (CN), 1435.1 (CH), 1114.4 (PN), 897.6 (CH), 834.8 (CH), 747.8 (CH), 723.2−693.8 (CH).

Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Al(C_2H_5)$_2$)Ph$_2$PN(3,5-Me$_2$C$_6$H$_3$)}$_2$] (14). This compound was synthesized by the same general method as outlined for **11** from compound **4** and Et_3Al and isolated as pale yellow crystals (0.31 g, 72%) at 5 °C. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 0.74 (q, 2H, CH_2CH$_3$), 0.93 (t, 3H, CH$_2$CH_3), 1.34 (t, 3H, CH$_2$CH_3), 1.57 (t, 3H, CH$_2$CH_3), 1.64 (t, 3H, CH$_2$CH_3), 2.15 (s, 12H, *o*-Me), 3.26 (m, 2H, 1,2 DACH), 6.95−7.02 (m, 20H, Ph), 7.99−8.00 (m, 8H, Ph). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz, 298 K): δ 21.4 (*m*-Me), 24.4 (4,5 DACH), 59.1 (1,2 DACH), 132.4 (d, *ipso*-PPh), 132.8 (d, *ipso*-PPh), 145.2 (*ipso*-NAr). ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298 K): δ 34.0. MS (FAB; *m/z*): 774 (3%, $M^+ - 4(C_2H_5)$, 721 (100%, M^+), 524 (3%, $M^+ - N(CH_3)_2C_6H_3 - Ph$), 401 (35%, $M^+ - NH_2PPh_2NH(CH_3)_2C_6H_3$), 321 (30%, $NH_2PPh_2NH(CH_3)_2C_6H_3$), 91 (10%, $CH_3C_6H_4$). IR (KBr, ν cm^{-1}): 2854.9 (CH), 1593.2 (CN), 1437.0 (CH), 1116.0 (PN), 827.2 (CH), 694.1−512.9 (CH).

NMR-Scale Reaction of 1 with [Y{N(SiMe$_3$)$_2$}$_3$]. Compound **1** (20 mg, 0.026 mmol) and [Y{N(SiMe$_3$)$_2$}$_3$] (15 mg, 0.026 mmol) were dissolved in C_6D_6, and the sample was monitored over 4 days at 60 °C. ^{31}P{^{1}H} NMR (C_6D_6, 109.3 MHz, 298 K): 24 h, δ 24.3 (d, J_{PY} = 4 Hz, 1P), 22.6 (d, J_{PY} = 4 Hz, 0.36P), 15.9 (d, J_{PY} = 4 Hz, 1P), 14.6 (d, J_{PY} = 4 Hz, 0.3P), 10.8 (bm, 6 P), 9.6 (s, 0.57P); 2 days, δ 24.3 (d, J_{PY} = 4 Hz, 1P), 22.6 (d, J_{PY} = 4 Hz, 0.23 P), 15.85 (d, J_{PY} = 4 Hz, 1 P), 14.51 (d, J_{PY} = 4 Hz, 0.31 P), 10.79 (bm, 2 P), 9.61 (s, 1.2 P) (free ligand −5.81).

Preparative-Scale Synthesis of *rac*-[*trans*-1,2-C_6H_{12}{N(Y{N-(SiMe$_3$)$_2$}Ph$_2$PN(2,4,6-C$_6$H$_2$)}$_2$] (15). At −90 °C, a toluene (10 mL) solution of [Y{N(SiMe$_3$)$_2$}$_3$] (0.38 g, 0.67 mmol) was added dropwise to a solution of **1** (0.5 g, 0.67 mmol) in toluene (10 mL) with stirring. The clear yellow solution was warmed to room temperature and was stirred overnight, before removal of volatiles to yield a light yellow powder, which was shown to contain the target complex **15** by NMR spectroscopy. Attempted recrystallization of this product from toluene and/or hexane was unsuccessful. ^{1}H NMR (C_7D_8): δ 8.37 (m), 7.97 (m), 7.68 (m), 7.25−6.97 (m), 6.96 (m), 4.0 (m), 3.75 (m), 3.45 (m), 3.27 (m), 3.18 (m), 2.38 (d), 2.10 (m), 1.88 (m), 1.51 (m), 1.05 (m), 0.65 (m), 0.28 (m). ^{31}P NMR (C_6D_6): 24.30 (d J_{PY} = 2.6 Hz, 1 P), 22.46 (J_{PY} = 4 Hz, 1 P), 15.86 (d, J_{PY} = 2.6 Hz, 1 P), 14.49 (d, J_{PY} = 4 Hz, 1 P), 11.58 (bm, 1.3 P), 10.42−10.09 (bm, 2.6 P).

[*rac*-{*trans*-1,2-C_6H_{10}(N(H)Ph$_2$P=N(2,4,6-C$_6$H$_2$))$_2$}Sc-{N(SiMe$_2$H)$_2$}] (16). This compound was synthesized by a procedure similar to that outlined for **15** from **1** (0.50 g, 0.67 mmol) and [Sc{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.35 g, 1.34 mmol). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.87−6.91 (m, Ar H), 6.64 (s, 2H, CH Mes), 3.60 (broad m, 2H, 1,2 DACH H), 2.37 (s, 12H, Ar *o*Me H), 2.29 (s, 6H, *p*-Ar Me H), 2.15−2.02 (m, 4H, DACH H),

0.90 (m, 2H, DACH H), 0.27 (s, 6H, Si−Me H). ^{31}P NMR (C_6D_6, 400 MHz, 298 K): δ 23.3 (ratio 0.69), 14.4 (ratio, 0.70), 10.8 (ratio 0.38, bimetallic species).

[*rac*-{*trans*-1,2-C_6H_{10}(N(H)Ph_2P=N(2,4,6-C_6H_2))$_2$}Y-{$N(SiMe_2H)_2$}] (17). This compound was synthesized by a procedure similar to that outlined for **15** from **1** (1.00 g, 1.34 mmol) and [Y{$N(SiHMe_2)_2$}$_3$($THF)_3$] (0.85 g, 1.34 mmol) as a golden powder after crystallization from THF (0.61 g, 0.55 mmol, 41%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.85−7.97 (m, 8H, *o*-PAr H), 7.34−6.96 (m, 20H, Ar H), 6.73 (s, 2H, CH Mes), 3.58−3.15 (multiple m, 2H, 1,2 DACH H), 2.41 (s, 12H, *o*-Ar Me H), 2.31(s, 6H, *p*-Ar Me H), 2.23 (s), 2.16−1.97 (m, 2H, 3,6 DACH H eq), 1.39 (m, 2H, 3,6 DACH H ax), 0.87 (m, 4H, 4,5 DACH H), 0.29 (s, Si−CH_3). ^{13}C NMR (C_6D_6, 400 MHz, 298 K): δ 132.45−127.76 (m, Ar) 70.42−63.62 (m, DACH), 56.61 (1,2 DACH uncomplexed ligand), 37.91−35.45 (m, DACH), 25.87−24.14 (m, DACH), 22.37−20.46 (m, Me). ^{31}P NMR (C_6D_6, 400 MHz, 298 K): δ 22.0 (ratio 1), 20.6 (ratio 0.44), 20.1 (ratio 0.66), 14.0 (ratio 0.96), 11.6 (ratio 0.53), 11.3 (ratio 0.45). Anal. Calcd for $C_{52}H_{68}N_5P_2Si_2Y$: C, 64.51; H, 6.87; N, 7.23. Found: C, 64.62; H, 6.80; N, 7.11.

Polymerization of MMA. Typical Procedure. To the appropriate catalyst or catalytic mixture in toluene (2 mL) were added 1, 50, 100, and 200 equiv of MMA. After vigorous stirring the reaction was monitored by ^{1}H NMR spectroscopy after 2 min and then 24 h. The reaction was terminated by exposure to air and the polymer precipitated by quenching in methanol. The polymer was isolated, dried in vacuo, dissolved in $CDCl_3$, and analyzed by ^{1}H NMR spectroscopy and GPC.

Crystal Structure Determinations. Data for **1**, **2**, **5**, and **9**−**11** were collected at 173 K on a Nonius KappaCCD diffractometer; λ(Mo Kα) = 0.710 73 Å. For **1** and **2**, the hydrogens on N(1) and N(2) were refined; other hydrogens were in riding mode. In the structure of **5** the molecule lies on a crystallographic 2-fold rotation axis. In **11**, the two phenyl groups on P(2) were disordered and each component was included as a rigid body with isotropic C atoms. In **12**, the molecule lies on a 2-fold axis. The cyclohexyl group was disordered and included with isotropic C atoms and SADI restraints. C(27) was disordered and refined isotropically. The toluene solvate was disordered about an inversion center and included with isotropic C atoms and H atoms omitted. The structures were solved by direct methods (SHELXS-97)[28] and refined by full matrix least squares (SHELXL-97)[29] with non-H atoms anisotropic and H atoms included in riding mode.

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Supporting Information Available: CIF files giving X-ray crystallographic data and figures giving selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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