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Synthesis of Acyclic NPNCN Systems and Metalation Reactions with Organolithium, -magnesium, and -aluminum Reagents

Tristram Chivers,* May C. Copsey, Chantall Fedorchuk, Masood Parvez, and Michael Stubbs

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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The preparation of a new family of acyclic DippN(H)P(Ph)NRCR′NR systems (**2a**−**c**) has been achieved by the reaction of the mono(amino)chlorophosphine PhP(Cl)N(H)Dipp (**1**; Dipp = 2,6-(^{i}Pr)$_2$C$_6$H$_3$) with 1 equiv of Li[CR′(NR)$_2$] (**2a**, R = ^{t}Bu, R′ = ^{n}Bu; **2b**, R = Cy, R′ = ^{t}Bu; **2c**, R = Cy, R′ = ^{n}Bu). Metalation reactions of **2a**−**c** using ^{n}BuLi, Me$_3$Al, and Bu$_2$Mg have shown that the NPNCN backbone is susceptible to nucleophilic attack. Reactions of **2a** or **2b** with ^{n}BuLi or Me$_3$Al, respectively, produce the complexes Li[DippNPhP−P(^{n}Bu)PhNDipp]·Et$_2$O (**3**) and Al(Me)$_2$[DippNPhP−P(Me)PhNDipp] (**4**). These complexes involve a new type of N,N′ bidentate ligand with a chiral phosphorus center bearing bulky organic substituents on the nitrogen atoms. Reaction of **2c** with Bu$_2$Mg proceeds in a different manner, producing the amidinate complex Mg[CyNC(^{n}Bu)NCy][DippNP(^{n}Bu)Ph]·Et$_2$O (**5**). A more direct route to **3** and the analogous methyl-substituted complex Li[DippNPhP−P(Me)PhNDipp]·Et$_2$O (**6**), involving the reaction of **1** with the appropriate organolithium reagent in the molar ratio 2:3, has been developed. The oxidation product of **3**, {Li[DippNPhP(O)P(^{n}Bu)PhNDipp]}$_2$ (**7**), has also been synthesized via an alternative route. Complexes **1**, **2a**,**b**, and **5**−**7** were fully characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray crystallography.

Introduction

Interest in the coordination chemistry of β-diketiminato (nacnac) ligands has increased significantly over the past few years.[1,2] These versatile ligands bearing bulky N substituents have been shown to be effective in stabilizing low-coordinate complexes for both main-group[3,4] and transition-metal elements.[5] In the 1990s, it was realized that β-diketiminates could play a useful role as spectator ligands when they were complexed to transition metals. The first such example was the complex [ZrL′Cl$_3$] (L = N(R)C(Ph)C(H)C(^{t}Bu)NR), which was shown to be an effective catalyst (with methylaluminoxane as cocatalyst) for the polymerization of C$_2$H$_4$ and C$_3$H$_6$.[6] Another significant development was the synthesis of the new β-diketimine {N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH$_2$.[7] The ligand L″ [{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH]$^-$, which contains a bulky N-aryl substituent, has been used to stabilize complexes of the type ML″ (M = Al,[3] Ga[4]) with the metal in the rare M(I) oxidation state. Other examples of the applications of this ligand include the use of (a) a combination of [Cr(L″)(Me)(μ-Cl)]$_2$ and AlClEt$_2$ as a catalyst for C$_2$H$_4$ polymerization[8] and (b) the complexes [Zn(L″)O^{i}Pr]$_2$[9] and [Sn(L″)O^{i}Pr][10] as catalysts for the living polymerization of *rac*- and *meso*-lactide, yielding polylactic acid.[9]

One of the reasons for the success of the β-diketiminates **I** (Chart 1) is the relative ease with which the steric demands of the ligand can be tuned by changing the organo substituents on the coordinating nitrogen atoms. In comparison, relatively little work has been reported on varying the elements in the ligand backbone and assessing the electronic influence this may have on the coordinated metal center and any potential catalytic activity. Recent studies from the groups of Stephan and Piers have focused on the inclusion of phosphinimine donors in the ligand backbone **II**.[11] It has been found that the incorporation of the R$_2$PNR′ fragment has allowed the isolation of monometallic aluminum complexes, due to the increased steric bulk and strong donor abilities of the ligand. We have described a high-yielding synthesis of the first hybrid boraamidinate/amidinate (bamam) neutral systems, which can be readily depro-

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* To whom correspondence should be addressed. E-mail: chivers@ucalgary.ca. Tel: (403) 220-5741. Fax: (403) 289-9488.

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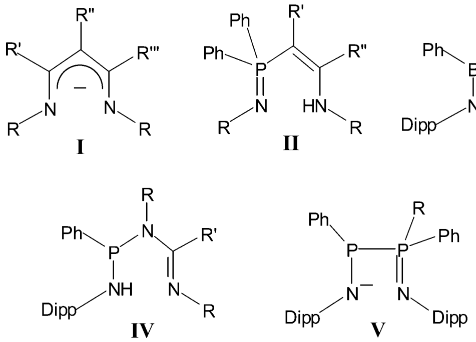
Chart 1



tonated with alkyllithium reagents to give monoanionic ligands of the type **III**, which are formally isoelectronic with β-diketiminate (nacnac) ligands **I**.[12] The bamam ligands have also been shown to form complexes containing low-coordinate magnesium centers, which are active catalysts for the polymerization of *rac*-lactide.[13] To broaden our knowledge of this family of hybrid amidinate ligands, we have developed a synthesis of the related phosphorus-containing neutral system **IV**.

In a preliminary communication we reported that metalation reactions of acyclic NPNCN systems of the type **IV** with ^{n}BuLi or Me_3Al did not proceed to give the expected NPNCN anion, analogous to the boron-containing anion **III**. Instead, these reactions involved P−N bond cleavage and the formation of complexes containing anions of the type **V** with an NPPN backbone and a chiral phosphorus center.[14] The yields of the resulting lithium and aluminum complexes were low, and an alternative, higher yielding route to this novel chelating ligand system is desirable.

In this article we report the details of (a) the synthesis and structural characterization of several examples of the neutral NPNCN systems **IV**, (b) the generation of an amidinate complex from the reaction of **IV** with Bu_2Mg, (c) a more direct route for the synthesis of the chelating anions **V** in good yields, and (d) the formation and structural characterization of an N,O bidentate ligand, which is the oxidized product of **V**.

Results and Discussion

Synthesis and X-ray Structure of PhP(Cl)N(H)Dipp (1). Recently we developed a high-yielding synthesis for the mono(amino)chloroborane PhB(Cl)N(H)Dipp by the reaction of 2 equiv of 2,6-diisopropylaniline ($DippNH_2$) with dichlorophenylborane.[12] The analogous reaction using dichlorophenylphosphine in diethyl ether produces the corresponding phosphine PhP(Cl)N(H)Dipp (**1**) as an analytically pure powder in excellent yield (92%). Characterization was carried out using multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P) and elemental analysis (CHN). The ^{31}P NMR spectrum in C_6D_6 shows a singlet at δ 123.4 ppm. This chemical shift is consistent with those of other reported examples of mono(amino)chlorophosphines (δ 121.1 ppm (in toluene) for PhP(Cl)N(H)^{i}Pr and δ 116.5 ppm for PhP(Cl)N(H)^{t}Bu).[15] The solid-state structure of **1** was determined by X-ray crystallography, as shown in Figure 1, and selected bond lengths and bond angles are shown in the caption.

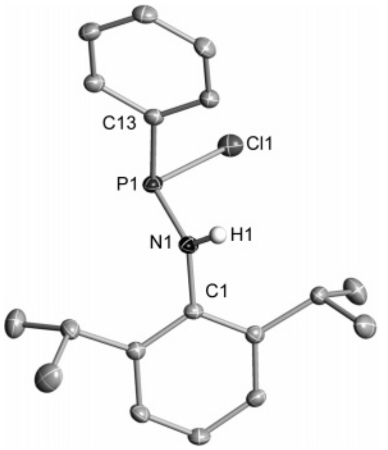


Figure 1. Molecular structure of PhP(Cl)N(H)Dipp (**1**) (30% thermal ellipsoids are shown). Hydrogen atoms, except for H1, have been omitted for clarity. P(1) and Cl(1) have partial occupancy (91%). P(1′) and Cl(1′) (9%) are not shown. Selected bond lengths (Å) and angles (deg): P(1)−N(1) = 1.674(2), P(1)−Cl(1) = 2.142(1), P(1)−C(13) = 1.817(2), N(1)−C(1) = 1.443(2); N(1)−P(1)−Cl(1) = 105.14(7), N(1)−P(1)−C(13) = 100.23(9), C(13)−P(1)−Cl(1) = 96.34(7), C(1)−N(1)−P(1) = 119.98(12).

Aminophosphines of this type have been known for some time;[16] however, compound **1** is the first structurally characterized example of a mono(amino)chloroorganophosphine, RP(Cl)NHR′, a potentially useful synthetic reagent. A phosphine of this type (when R = ^{i}Pr) has also been shown to act as a ligand to a transition metal in the complex $[PhP(Cl)N^iPr(H)]_2Mo(CO)_4$.[15] As expected, the solid-state structure shows **1** has a P−N bond length (1.67 Å) intermediate between those of a related dichloroaminophosphine, $Cl_2PN(H)Dipp$ (P−N bond length 1.64 Å), structurally characterized by Burford and co-workers,[17] and known bis(amino)organophosphines of the type $PhP\{N(H)R\}_2$ (average 1.68 Å, R = ^{i}Pr;[15] average 1.70 Å, R = Ph[18]).

Syntheses and X-ray Structures of DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (2a) and DippN(H)PhPNCyC^{t}BuNCy (2b). The reaction of PhP(Cl)N(H)Dipp (**1**) with Li[C^{n}Bu(N^{t}Bu)$_2$] in *n*-hexane in a 1:1 stoichiometry produced DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (**2a**) in 73% yield. Reaction of **1** with Li[C^{t}Bu(NCy)$_2$] and Li[C^{n}Bu(NCy)$_2$] produced two further derivatives, DippN(H)PhPNCyC^{t}BuNCy (**2b**) and DippN(H)PhPNCyC^{n}BuNCy (**2c**), in 76% and 72% yields, respectively (Scheme 1). Elemental analyses (CHN) and multinuclear NMR spectra (^{1}H, ^{13}C, and ^{31}P) identified these products as neutral aminophosphino(amidinate) species of the type **IV**. Single resonances were observed in the ^{31}P NMR spectra in the 69−74 ppm region, and the ^{1}H NMR

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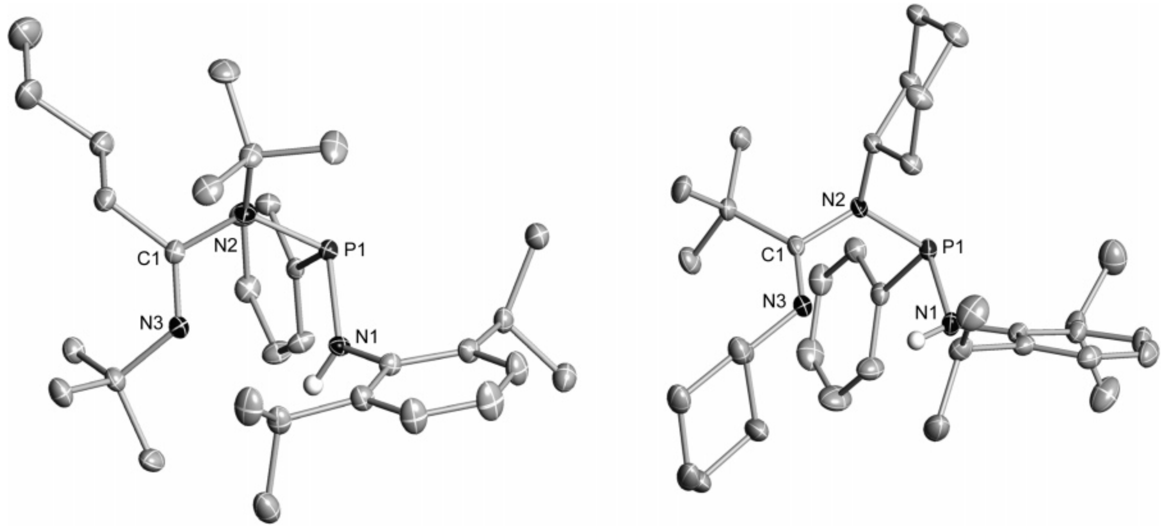
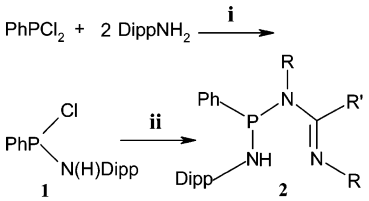


Figure 2. Molecular structures of DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (**2a**) and DippN(H)PhPNCyC^{t}BuNCy (**2b**) (30% thermal ellipsoids are shown). Hydrogen atoms, except for those on nitrogen, have been omitted for clarity.

Scheme 1[a]



[a] Reagents and conditions: (i) Et_2O, −78 °C; (ii) Li[CR′(NR)$_2$] in hexane, −78 °C (**2a**, R = Bu^t, R′ = Bu^n; **2b**, R = Cy, R′ = Bu^t; **2c**, R = Cy, R′ = Bu^n).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 2a and 2b

DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (**2a**)		DippN(H)PhPNCyC^{t}BuNCy (**2b**)[a]	
	Bond Lengths		
P(1)−N(1)	1.711(2)	P(1)−N(1)	1.712(1)
P(1)−N(2)	1.735(2)	P(1)−N(2)	1.710(1)
P(1)−C(14)	1.826(2)	P(1)−C(30)	1.836(2)
N(2)−C(1)	1.430(3)	N(3)−C(1)	1.272(2)
N(3)−C(1)	1.274(2)	N(2)−C(1)	1.441(2)
	Bond Angles		
N(1)−P(1)−N(2)	107.57(8)	N(2)−P(1)−N(1)	108.62(6)
N(1)−P(1)−C(14)	101.11(9)	N(2)−P(1)−C(30)	97.41(6)
N(2)−P(1)−C(14)	99.02(9)	N(1)−P(1)−C(30)	100.56(7)
C(2)−N(1)−P(1)	121.6(1)	C(1)−N(3)−C(6)	124.29(1)
C(1)−N(2)−C(20)	120.2(2)	C(1)−N(2)−C(12)	113.6(1)
C(1)−N(2)−P(1)	119.3(1)	C(1)−N(2)−P(1)	122.4(1)
C(20)−N(2)−P(1)	118.1(1)	C(12)−N(2)−P(1)	118.22(9)
C(1)−N(3)−C(28)	126.0(2)	C(18)−N(1)−P(1)	123.0(1)
N(3)−C(1)−N(2)	115.9(2)	N(3)−C(1)−N(2)	116.5(1)
N(3)−C(1)−C(24)	127.4(2)	N(3)−C(1)−C(2)	127.9(1)
N(2)−C(1)−C(24)	116.6(2)	N(2)−C(1)−C(2)	115.6(1)

[a] Bond lengths and angles for only one of the independent molecules in the unit cell are shown.

spectrum of **2a** indicated the presence of two inequivalent *tert*-butyl groups.

The acyclic structure was confirmed by X-ray structural analyses of **2a**,**b** (Figure 2). Selected bond lengths and bond angles are shown in Table 1.

The terminal and internal C−N distances differ markedly in both cases (N(2)−C(1) = 1.430(3) Å and N(3)−C(1) = 1.274(2) Å for **2a**, N(2)−C(1) = 1.441(2) Å and N(3)−C(1) = 1.272(2) Å for **2b**), indicating the localization of the C−N double bond. The two P−N bonds in both derivatives are similar in length (range 1.735(2)−1.710(1) Å), indicative of single P−N bonds. They are, however, significantly longer than the P−N bond length observed in the precursor **1** (1.674(2) Å). This may be due to a combination of the replacement of the more electronegative chloride substituent by nitrogen and the minimization of steric congestion between the bulky organic substituents. The phosphorus centers have a distorted-pyramidal geometry (bond angles around phosphorus range from 97.41(6) to 109.27(6)°), and the three nitrogen centers have a distorted-trigonal-planar arrangement (bond angles around nitrogen are in the range 113.6(1)−126.0(2)°).

Metalation Reactions of 2a,b using ^{n}BuLi and Me_3Al. In a preliminary communication we reported that the deprotonation reaction of **2a** with 1 equiv of ^{n}BuLi gives rise to the cyclic lithium complex Li[DippNPhP−P(^{n}Bu)PhNDipp]·OEt_2 (**3**) (Figure 3), containing a new type of chelating NPPN ligand with a chiral phosphorus center in the backbone.[14] Following this report an alternative higher yielding synthesis of **3** has been developed, and this is discussed later. A similar aluminum-containing complex, Al(Me)$_2$[DippNPhP−P(Me)PhNDipp] (**4**), was also isolated from the reaction of equimolar amounts of Me_3Al and **2b** (Figure 3).

A previously reported aluminum complex, containing an intramolecular P−P coordination, also has an NPPN backbone.[19] In that case, however, the two phosphorus centers are bridged by an $NSiMe_3$ group to form a three-membered azadiphosphiridene ring.

Synthesis and X-ray Structure of Mg[DippNPPh(^{n}Bu))(NCyC^{n}BuNCy)]·OEt_2 (5). The outcome of the reaction of **2c** with Bu_2Mg is different from that of the reactions of **2a** or **2b** with organolithium reagents or Me_3Al, respectively. Although cleavage of the P−N bond is again observed, the ^{31}P NMR spectrum of the reaction solution showed the formation of a new product with a single resonance at δ 43.0 ppm. A single-crystal X-ray analysis revealed this product to be Mg[DippNPPh(^{n}Bu)(NCyC^{n}BuNCy)]·OEt_2 (**5**) (Figure 4). Selected bond lengths and bond angles are shown in Table 2.

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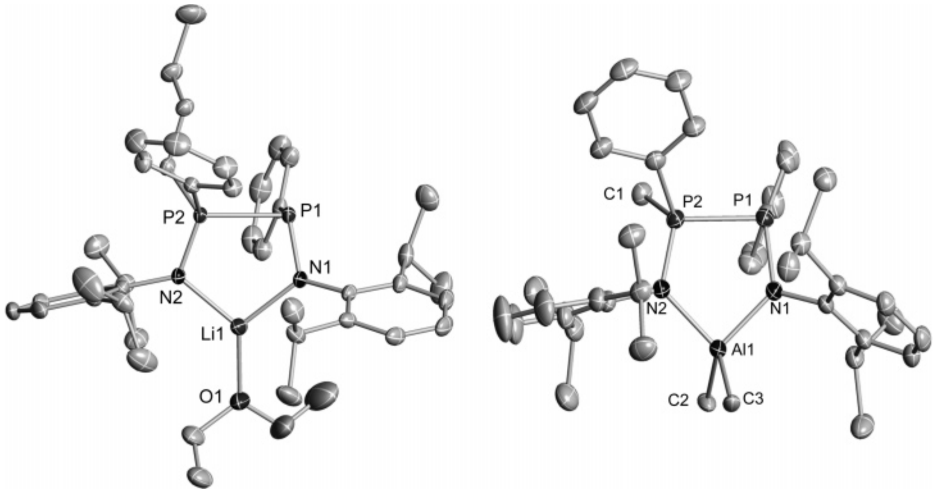


Figure 3. Molecular structures of Li[DippNPhP−P(^{n}Bu)PhNDipp]·OEt$_2$ (**3**) and Al(Me)$_2$[DippNPhP−P(Me)PhNDipp](**4**) (30% thermal ellipsoids are shown). Hydrogen atoms have been omitted for clarity.

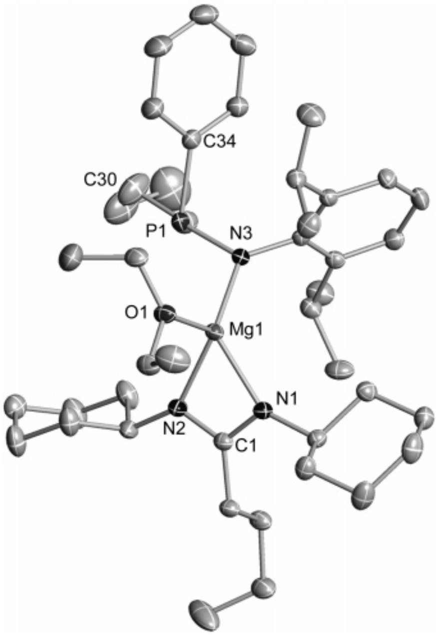


Figure 4. Molecular structure of Mg[DippNPPh(^{n}Bu)-(NCyC^{n}BuNCy)]·OEt$_2$ (**5**) (30% thermal ellipsoids are shown). Hydrogen atoms have been omitted for clarity.

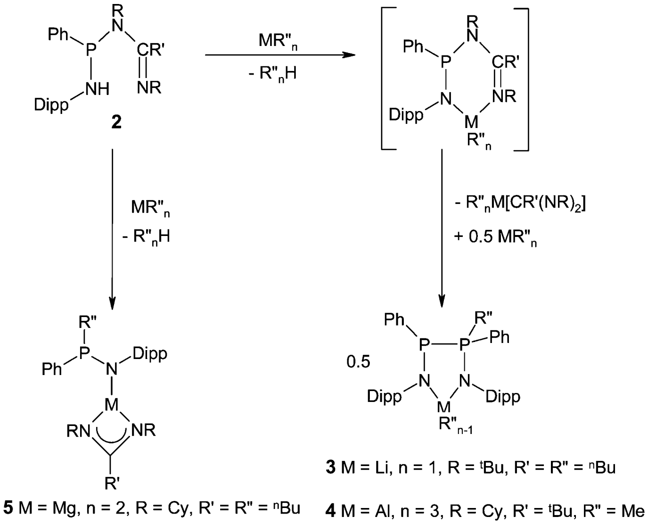
Complex **5** consists of a bidentate amidinate ligand coordinated to a magnesium metal center, which is then further ligated by the monodentate amido anion [NDippP(^{n}Bu)Ph]$^-$ and by one molecule of diethyl ether. The P−N bond length of 1.674(2) Å is longer than those observed in complexes **3** and **4**.[14] The magnesium−nitrogen bond lengths of 2.044(2) and 2.068(2) Å in the four-membered MgN$_2$C ring are similar to those reported for magnesium amidinate complexes,[20] while the exocyclic Mg−N bond distance is slightly shorter at 1.986(2) Å. This difference presumably reflects a stronger electrostatic attraction to the metal center due to the negative charge being located on one nitrogen center, whereas in the amidinate ligand it is delocalized over two sites.

In the preliminary communication it was proposed that the formation of complexes **3** and **4** occurred via the elimination of the corresponding metal amidinate from the initially formed metalation product accompanied by dimerization of the eliminated iminophosphane PhP=NDipp prior to reaction with MeLi or Me$_3$Al present in solution (Scheme 2).[14] The isolation of Me$_2$-Al[NCyC^{t}BuNCy] from the reaction of **2b** with Me$_3$Al provided support for that proposition. By analogy, the

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Mg[DippNPPh(^{n}Bu)(NCyC^{n}BuNCy)]·OEt$_2$ (5)

	Bond Lengths		
P(1)−N(3)	1.674(2)	Mg(1)−O(1)	2.038(1)
P(1)−C(30)	1.863(2)	N(1)−C(1)	1.331(2)
Mg(1)−N(3)	1.986(2)	N(2)−C(1)	1.337(2)
Mg(1)−N(1)	2.044(2)	N(2)−C(12)	1.462(2)
Mg(1)−N(2)	2.068(2)	N(3)−C(18)	1.426(2)
	Bond Angles		
N(3)−P(1)−C(34)	107.35(8)	C(6)−N(1)−Mg(1)	143.6(1)
N(3)−P(1)−C(30)	109.10(9)	C(1)−N(2)−C(12)	122.1(2)
N(3)−Mg(1)−N(1)	127.15(7)	C(12)−N(2)−Mg(1)	147.8(1)
N(3)−Mg(1)−O(1)	112.54(6)	C(18)−N(3)−P(1)	123.6(1)
O(1)−Mg(1)−N(2)	108.06(6)	C(18)−N(3)−Mg(1)	126.9(1)
N(1)−Mg(1)−N(2)	65.68(6)	P(1)−N(3)−Mg(1)	109.27(8)
O(1)−Mg(1)−N(1)	106.42(7)	N(1)−C(1)−N(2)	113.5(2)
N(3)−Mg(1)−N(2)	128.33(7)	N(2)−C(1)−C(2)	123.7(2)
C(1)−N(1)−C(6)	125.3(1)	N(1)−C(1)−C(2)	122.8(2)
C(1)−N(1)−Mg(1)	91.0(1)		

Scheme 2



3 M = Li, n = 1, R = ^{t}Bu, R' = R" = ^{n}Bu

5 M = Mg, n = 2, R = Cy, R' = R" = ^{n}Bu

4 M = Al, n = 3, R = Cy, R' = ^{t}Bu, R" = Me

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reaction of **2c** with Bu_2Mg will produce the complex $^{n}BuMg[NDippPhPNCyC^{t}BuNCy]$, which likely decomposes to give $^{n}BuMg[NCyC^{t}BuNCy]$ and PhP═NDipp. Nucleophilic addition of the alkylmagnesium amidinate to the iminophosphane would then afford the observed complex **5**. The formation of a five-membered cyclic magnesium complex analogous to **3** and **4** would require the presence of Bu_2Mg in solution upon generation of the iminophosphane. It is conceivable that the formation of complex **5**, in preference to the five-membered alternative, is due to the elimination of the alkylmagnesium amidinate occurring much less readily than that of the lithium and aluminum derivatives. We tentatively suggest that the deprotonation of **2c** with Bu_2Mg is complete at low temperature (−78 °C), but the elimination of the alkylmagnesium amidinate does not occur until the reaction has reached a higher temperature. Consequently, in contrast to the formation of **3** and **4,** no Bu_2Mg would remain in solution to react with the iminophosphane dimer. Instead, the eliminated iminophosphane PhP═NDipp is trapped by the alkylmagnesium amidinate to give complex **5**. To support this proposal, the addition of Bu_2Mg to a solution of **2c** in hexane, in the molar ratio 3:2, was carried out at room temperature. The ^{31}P NMR spectrum of the resulting reaction solution showed the presence of two mutually coupled doublets at 41.4 and 32.0 ppm ($^{1}J_{P-P} = 274$ Hz).

Surprisingly few magnesium amidinate complexes have been reported so far,[20,21] although they have a wide range of potential applications, e.g., as sources of magnesium for doping semiconductor films, due to their low molecular weight and all-nitrogen coordination sphere, which minimizes the risk of hydrocarbon contamination.[20] Magnesium nacnac complexes have been shown to adopt π as well as η^2 coordination modes.[22]

Synthesis and X-ray Structure of Li[DippNPhP(Me)PPhNDipp]·Et_2O (6). The yields of **3** and **4** reported in the preliminary communication are low,[14] and an alternative synthesis of this novel ligand system is desirable. The decomposition of N-lithiated aminohalogenophosphanes, where the halogen is chloride, occurs below 20 °C.[23] Consequently, a direct synthesis of the lithiated NPPN complexes was devised in which the aminochlorophosphane PhP(Cl)N(H)Dipp (**1**) is treated with an organolithium reagent in a 2:3 molar ratio. Complex **3** can be synthesized from the reaction of **1** with *n*-butyllithium in the ratio 2:3, as verified by ^{1}H and ^{31}P NMR spectroscopy. The synthesis can also be varied to change the organic group bonded to the four-coordinate phosphorus center and, hence, provides a simple preparation of a ligand with a chiral phosphorus center and easily tunable sterics. This was demonstrated by the isolation and characterization of the methyl-substituted complex Li[DippNPhP(Me)PPhNDipp]·Et_2O (**6**).

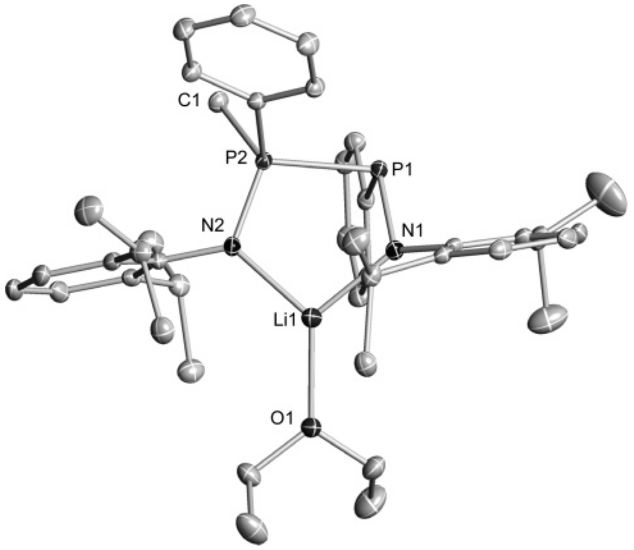

Figure 5. Molecular structure of Li[DippNPPh(Me)PPhNDipp]·OEt_2 (**6**) (30% thermal ellipsoids are shown). Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 3 and 6

Li[DippNPPh(^{n}Bu)PPhNDipp]·OEt_2 (**3**)		Li[DippNPPh(Me)PPhNDipp]·OEt_2 (**6**)	
Bond Lengths			
P(1)−N(1)	1.652(2)	P(1)−N(1)	1.665(2)
P(2)−N(2)	1.607(2)	P(2)−N(2)	1.607(2)
P(1)−P(2)	2.2436(7)	P(1)−P(2)	2.2365(8)
P(1)−C(1)	1.858(2)	P(1)−C(2)	1.849(2)
P(2)−C(7)	1.822(2)	P(2)−C(1)	1.817(2)
P(2)−C(13)	1.823(2)	P(2)−C(8)	1.831(2)
N(1)−Li(1)	1.939(3)	N(1)−Li(1)	1.968(4)
N(2)−Li(1)	1.965(4)	N(2)−Li(1)	1.973(4)
Li(1)−O(1)	1.927(3)	Li(1)−O(1)	1.919(4)
N(1)−C(17)	1.419(2)	N(1)−C(14)	1.419(3)
N(2)−C(29)	1.435(2)	N(2)−C(26)	1.434(3)
Bond Angles			
N(1)−P(1)−C(1)	108.90(8)	N(1)−P(1)−C(2)	106.18(9)
N(1)−P(1)−P(2)	97.83(6)	N(1)−P(1)−P(2)	97.95(6)
C(1)−P(1)−P(2)	93.04(6)	C(2)−P(1)−P(2)	94.21(7)
N(2)−P(2)−C(7)	114.54(8)	N(2)−P(2)−C(1)	113.56(10)
N(2)−P(2)−C(13)	114.06(8)	N(2)−P(2)−C(8)	115.43(9)
C(7)−P(2)−C(13)	103.44(8)	C(1)−P(2)−C(8)	101.60(9)
N(2)−P(2)−P(1)	108.70(6)	N(2)−P(2)−P(1)	108.43(6)
C(7)−P(2)−P(1)	105.96(6)	C(8)−P(2)−P(1)	105.60(7)
C(13)−P(2)−P(1)	109.75(6)	C(1)−P(2)−P(1)	108.43(6)
C(17)−N(1)−P(1)	118.3(1)	C(14)−N(1)−P(1)	114.8(1)
C(17)−N(1)−Li(1)	126.2(2)	C(14)−N(1)−Li(1)	131.6(2)
P(1)−N(1)−Li(1)	114.4(1)	P(1)−N(1)−Li(1)	110.4(1)
C(29)−N(2)−P(2)	121.1(1)	C(26)−N(2)−P(2)	120.9(1)
C(29)−N(2)−Li(1)	129.2(1)	C(26)−N(2)−Li(1)	131.0(2)
P(2)−N(2)−Li(1)	109.71(1)	P(2)−N(2)−Li(1)	107.9(1)
O(1)−Li(1)−N(1)	126.5(2)	O(1)−Li(1)−N(1)	126.7(2)
O(1)−Li(1)−N(2)	129.2(2)	O(1)−Li(1)−N(2)	126.9(2)
N(1)−Li(1)−N(2)	102.8(2)	N(1)−Li(1)−N(2)	104.0(2)

MeLi was added dropwise to a stirred solution of **1** in a 3:2 ratio at −78 °C in *n*-hexane. The ^{31}P NMR spectrum of the reaction solution exhibited two mutually coupled doublets observed at δ 67.3 and 19.0 ppm ($J_{P-P} = 285$ Hz) consistent with the formation of the desired product **6**, which was isolated in 50% crystalline yield. A single-crystal X-ray diffraction experiment confirmed that the product is isostructural with complex **3**, where the substituent on the four-coordinate phosphorus center is a methyl group instead of an *n*-butyl group (Figure 5). Selected bond lengths and bond angles for **3** and **6** are compared in Table 3.

The structural parameters of the two complexes are very similar. The NPPN ligand backbone is asymmetrical, with the four-coordinate phosphorus−nitrogen

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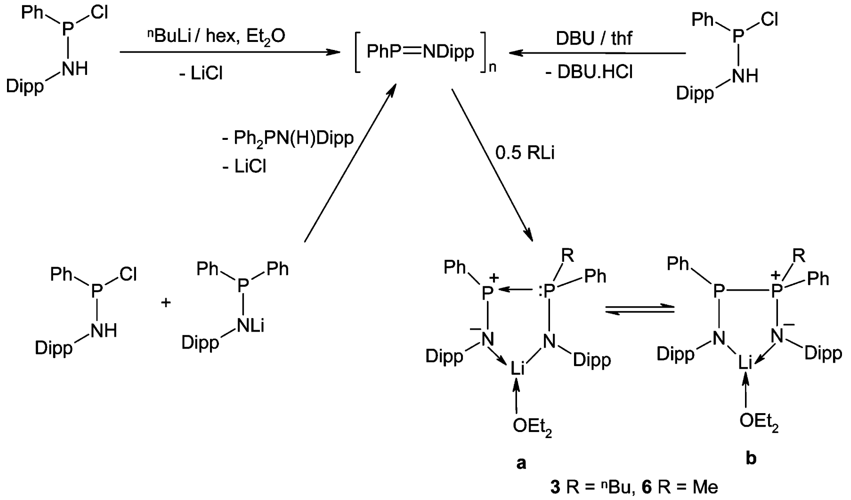
[21] Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2517.

[22] El-Kaderi, H. M.; Xia, A.; Heeg, M. J.; Winter, C. H. *Organometallics* **2004**, *23*, 3488.

[23] Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1034.

Scheme 3



bond P(2)−N(2) = 1.607(2) Å being significantly shorter than P(1)−N(1) = 1.665(2) Å. The shorter bond length would indicate a larger ionic contribution to the bonding on this side of the ligand: hence, a significant contribution of the phosphine−phosphonium resonance form **6b** (Scheme 3). In complex **6** the nitrogen−lithium contacts are indistinguishable within error and suggest the metal is coordinated equally to both nitrogen centers in this case. The four-coordinate phosphorus center P(2) has a distorted-tetrahedral geometry with bond angles in the range 113.56(10)−101.60(9)°, whereas P(1) adopts a pyramidal geometry with bond angles in the range 94.21(7)−106.18(9)°, reflecting the presence of a lone pair.

Since there are two chiral centers in **3** and **6**, there is a possibility of forming diastereomers. Both complexes crystallize in centrosymmetric space groups, and hence, both the *R* and *S* enantiomers of P(2) are observed in the solid state. However, no evidence for diastereomers is observed in the solution NMR spectra of these complexes, suggesting that the reaction leading to these products is diastereospecific. In the case of **4**, this complex crystallizes in the chiral space group $P2_12_12_1$ and is obtained purely as the *R* enantiomer of P(2). Again, no evidence is observed for the presence of diastereomers in the solution NMR spectra.

NMR Studies of the Formation of 3 and 6. In an attempt to provide evidence for the mechanism of formation of the lithium derivatives **3** and **6**, the sequential addition of stoichiometric aliquots of ^{n}BuLi to PhPClN(H)Dipp (**1**) was followed by ^{31}P NMR spectroscopy. Addition of an equimolar amount of ^{n}BuLi to a solution of **1** in hexane and Et$_2$O produces a bright yellow solution and a white precipitate of LiCl. The ^{31}P NMR spectrum of the yellow solution (in C$_6$D$_6$ at 298 K) showed complete reaction of **1** (singlet at 120 ppm) to give two singlets at 210 and 281 ppm in the ratio of ca. 6:1. Addition of a further $^1/_2$ equiv of ^{n}BuLi (**1**:^{n}BuLi = 2:3) resulted in the complete conversion of the resonances at 210 and 281 ppm to two mutually coupled doublets attributable to **3.** The intermediate at 210 ppm was also generated, together with Ph$_2$PN(H)Dipp (δ 42 ppm), from the reaction of Li[NDippPPh$_2$] and PhP(Cl)NHDipp in Et$_2$O (Scheme 3). On the assumption that the complex Li[NDippPPh$_2$] would react in a manner similar to that for the analogous *n*-butyl derivative, the reaction of Li[NDippP(^{n}Bu)Ph] with PhP(Cl)NHDipp does not result in P−P bond formation. The resonance at δ 210 ppm was also produced, together with the resonance at 281 ppm, upon treatment of PhP(Cl)NHDipp with an equimolar of amount of DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) in thf (Scheme 3).

It seems reasonable to suggest that the common intermediate (δ 210 ppm) in the reactions depicted in Scheme 3 is a dimer (or higher oligomer) of the iminophosphane PhP=NDipp. As pointed out in the preliminary communication,[14] P-aryl or P-alkyl iminophosphanes are known to undergo a reversible [2 + 1] cycloaddition with P−P bond formation to give the corresponding azadiphosphiridene. Since compounds of this type are known to exist in equilibrium with the iminophosphane monomer,[23] only one resonance would be observed in the ^{31}P NMR spectrum. Unfortunately, we have been unable to obtain crystals of the 210 ppm species for structural determination. Hence, we cannot rule out the possibility of [2 + 2] cycloaddition of the iminophosphane to give a cyclodiphosphetidene. In that case, however, P−P bond formation would have to occur via a rearrangement process upon reaction of this four-membered P$_2$N$_2$ ring with the organometallic reagent.

Synthesis and X-ray Structure of {Li[DippNPhP(O)P(^{n}Bu)PhNDipp]}$_2$ (7). Storage of a solution of **3** in Et$_2$O and *n*-hexane at −18 °C for 1 week yielded further crystalline material. The crystals were shown by X-ray crystallography to be the oxidation product {Li[DippNPhP(O)P(^{n}Bu)PhNDipp]}$_2$ (**7**) (Figure 6). Formation of **7** is presumably due to the presence of trace amounts of air present in the sample vial. This was confirmed when a solution of **3** in hexane and Et$_2$O was briefly exposed to air. The volume of the resulting orange solution was reduced, and colorless crystals of **7** were isolated in 50% yield. Under these conditions the oxidation of **3** to **7** is quantitative by ^{31}P NMR. Selected bond lengths and bond angles for **7** are shown in Table 4.

Complex **7** has a dimeric structure in the solid state and is the result of oxidation of a phosphorus center in complex **3**, Li[DippNPhP−P(^{n}Bu)PhNDipp]·Et$_2$O. The addition of an oxygen at one phosphorus center provides the ligand with two possible modes of coordination. In the case of oxophilic lithium, the ligand becomes N,O-chelated to the metal center, with an exocyclic =NDipp

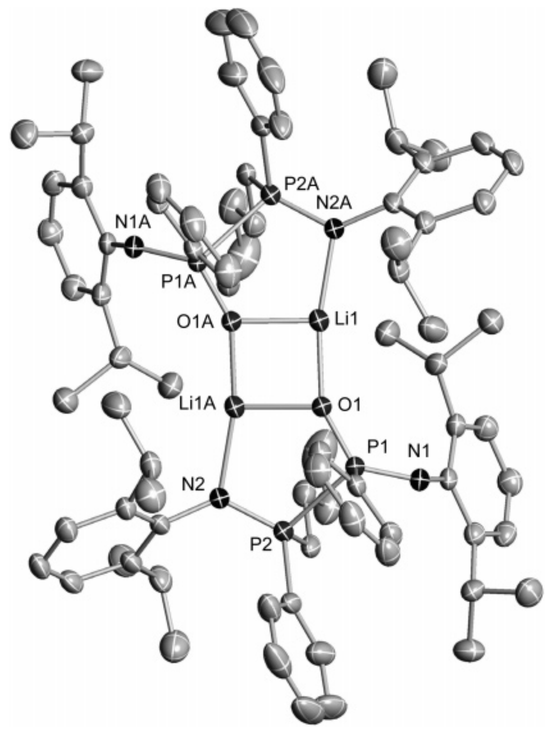


Figure 6. Molecular structure of$\{Li[DippNPhP(O)P(^nBu)PhNDipp]\}_2$ (**7**) (30% thermal ellipsoids are shown). Hydrogen atoms and lattice solvent have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $\{Li[DippNPhP(O)P(^nBu)PhNDipp]\}_2$ (7)

Bond Lengths			
P(1)−N(1)	1.546(3)	N(1)−C(7)	1.410(6)
P(1)−O(1)	1.523(3)	N(2)−C(19)	1.439(6)
P(1)−C(1)	1.798(5)	N(2)−Li(1A)	2.044(8)
P(1)−P(2)	2.263(2)	Li(1)−O(1)	1.902(8)
P(2)−N(2)	1.595(4)	Li(1)−O(1A)	1.923(8)
P(2)−C(37)	1.788(5)	Li(1)−N(2A)	2.044(8)
P(2)−C(31)	1.792(5)	O(1)−Li(1A)	1.923(8)
Bond Angles			
O(1)−P(1)−N(1)	124.0(2)	C(31)−P(2)−P(1)	108.8(2)
O(1)−P(1)−C(1)	108.8(2)	C(7)−N(1)−P(1)	136.5(3)
N(1)−P(1)−C(1)	106.9(2)	C(19)−N(2)−P(2)	128.9(3)
O(1)−P(1)−P(2)	99.8(1)	C(19)−N(2)−Li(1A)	122.3(3)
N(1)−P(1)−P(2)	113.2(2)	P(2)−N(2)−Li(1A)	108.6(3)
C(1)−P(1)−P(2)	102.2(2)	O(1)−Li(1)−O(1A)	91.1(3)
N(2)−P(2)−C(37)	119.8(2)	O(1)−Li(1)−N(2A)	168.3(4)
N(2)−P(2)−C(31)	115.2(2)	O(1A)−Li(1)−N(2A)	100.0(4)
C(37)−P(2)−C(31)	103.8(2)	P(1)−O(1)−Li(1)	152.9(3)
N(2)−P(2)−P(1)	106.1(1)	P(1)−O(1)−Li(1A)	119.4(3)
C(37)−P(2)−P(1)	102.1(2)	Li(1)−O(1)−Li(1A)	87.8(3)

fragment. Two LiOPPN metallacycles are linked together through a Li_2O_2 ring, removing the requirement for coordination of an ether molecule (cf. complex **3**). This dimeric structure would be unlikely in the case of a N,N-chelated ligand, due to the considerable steric bulk of the diisopropylphenyl substituents on nitrogen. The observed bond lengths reflect the change in coordination mode; P(1)−N(1) at 1.546(3) Å is now indicative of a formal double bond, more than 0.1 Å shorter than the length observed when N(1) is coordinated to the metal center in complex **3**. There is no appreciable difference in the length of the P−N bond (P(2)−N(2) = 1.595(4) Å) on the opposite side of the ligand. As expected, the lithium center is more strongly coordinated to the oxygen than to the nitrogen center, due to a greater difference in electronegativity. The P−P bond length of 2.263(2) Å is only slightly longer than that observed in the parent complex **3**. This is most likely to compensate for the decrease in bond lengths (from P(1)−N(1) in **3** to P(1)−O(1) in **7**) as a result of changing from N,N′ to N,O coordination. Both phosphorus centers have distorted-tetrahedral geometries with bond angles in the range 99.8(1)−124.0(2)° for P(1) and 102.1(2)−119.8(2)° for P(2).

Complex **7** crystallizes in the centrosymmetric space group *Pccn*, with both the *R*,*R* and the *S*,*S* enantiomers observed in the solid state. No diastereomers of **7** are observed in the solution NMR spectra. The ^{31}P NMR spectrum exhibits the expected two mutually coupled doublets with a one-bond $^{31}P-^{31}P$ coupling of 197 Hz (cf. 298 Hz for **3**).

Conclusions

The preparation and the first structural characterization of a mono(amino)chlorophosphine, PhP(Cl)N(H)-Dipp, has led to the synthesis of a new class of species adopting an acyclic NPNCN backbone. These species have the potential to act as bidentate nitrogen coordinating ligands, similar to the family of β-diketiminate (nacnac) ligands. Deprotonation reactions using organolithium, -magnesium, and -aluminum reagents have shown that these neutral species are susceptible to nucleophilic attack at the phosphorus center by the metalating agent, resulting in the cleavage of the P−N bond, driven by the formation of the corresponding metal amidinate as a byproduct. A direct route to complexes of the type $Li[DippNPhP(R)PPhNDipp]\cdot Et_2O$ (R = ^nBu, Me) has been developed. The presence of a phosphenium center in these ligands offers the possibility of additional metal coordination via this Lewis basic site.

Experimental Section

Reagents and General Procedures. All reactions and the manipulation of products were carried out by using standard inert-atmosphere techniques under an atmosphere of argon. The compounds $PhPCl_2$, 1,3-di-*tert*-butylcarbodiimide (99%), 1,3-dicyclohexylcarbodiimide, ^nBuLi (2.5 M solution in hexanes), ^tBuLi (1.7 M solution in pentane), Bu_2Mg (1.0 M solution in heptane), and MeLi (1.6 M solution in diethyl ether) were obtained commercially (Aldrich) and used as received. 2,6-Diisopropylphenylaniline (97%, Aldrich) was purified by distillation (110 °C, 10^{-2} Torr). The lithiated carbodiimides $Li[^nBuC(N^tBu)_2]$, $Li[^nBuC(NCy)_2]$, and $Li[^tBuC(NCy)_2]$ were prepared according to literature procedures.[24] Filtrations were performed by using either a PTFE filter disk (Acrodisc syringe filter; diameter 25 mm; pore size 0.45 μm) or a sintered-glass frit (8 μm). Solvents were dried with appropriate drying agents and distilled onto molecular sieves before use.

Instrumentation. ^1H, ^{31}P, ^{13}C, and ^7Li NMR spectra were measured at 25 °C in C_6D_6 on a Bruker DRX 400 MHz spectrometer using a 5 mm broadband probe (BBO probe). ^1H and ^{31}P spectra for complex **7** were measured on a Bruker 300 MHz spectrometer using a BBi5 probe. Chemical shifts are reported relative to Me_4Si in $CDCl_3$ (^1H and ^{13}C), 85% H_3PO_4 in D_2O (^{31}P), and 1.0 M LiCl in D_2O (^7Li). Infrared spectra were

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(24) (a) Chivers, T.; Downard, A.; Yap, G. P. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2603. (b) Zhou, Y.; Richeson, D. S. *J. Am. Chem. Soc.* **1996**, *118*, 10850. (c) Boeré, R. T.; Masuda, J.; Wolmershäuser, G. *Can. J. Chem.* **2000**, *78*, 1613.

obtained as Nujol mulls between KBr plates on a Nicolet Nexus 470 FT-IR spectrometer. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

Preparation of PhP(Cl)N(H)Dipp (1). A solution of $DippNH_2$ (3.77 mL, 20.0 mmol) in diethyl ether (30 mL) was added slowly to a solution of $PhPCl_2$ (1.36 mL, 10.0 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was warmed to 23 °C and stirred for 3 h. $[DippNH_3]Cl$ was removed as a white precipitate by filtration to give a clear pale yellow solution. The solvent was removed in vacuo, and the resulting oil was washed with *n*-hexane (2 × 20 mL) to give a white powder (2.95 g, 9.23 mmol, 92%). Anal. Calcd for $C_{18}H_{23}NPCl$: C, 67.60; H, 7.25; N, 4.38. Found: C, 67.54; H, 7.36; N, 4.55. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 7.91 (m, 2H, C_6H_5 and C_6H_3), 7.19 (m, 6H, C_6H_5 and C_6H_3), 4.70 (d, $^3J_{H,H} = 8$ Hz, 1H, N*H*), 3.36 (septet, $^3J_{H,H} = 7$ Hz, 2H, $-CH(CH_3)_2$), 1.28 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.20 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$). ^{13}C NMR (C_6D_6, 25 °C, 100.594 MHz): δ 144.7 (C_1 of 2,6-Dipp), 135.4 (C_1 of phenyl), 130.4 (C_2 and C_6 of 2,6-Dipp), 130.1 (C_2 and C_6 of phenyl), 129.9 (C_3 and C_5 of 2,6-Dipp), 128.8 (C_3 and C_5 of phenyl), 126.8 (C_4 of 2,6-Dipp), 124.1 (C_4 of phenyl), 28.4 ($-CH(CH_3)_2$), 23.7 ($-CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 123.4 (s). IR data (Nujol, cm^{-1}): 3366 (ν(N−H)). Mp: 94−97 °C. Colorless X-ray-quality crystals were grown from a saturated solution in acetonitrile at −15 °C.

Preparation of DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (2a). A solution of Li[^{n}BuC(N^{t}Bu)$_2$] (2.18 g, 10.0 mmol) in *n*-hexane (30 mL) was added dropwise to a solution of PhP(Cl)N(H)Dipp (3.20 g, 10.0 mmol) in *n*-hexane (30 mL) at −78 °C. The reaction mixture was warmed to 23 °C and stirred for 3 h. LiCl was removed by filtration to give a clear yellow solution. The solution was reduced to dryness in vacuo to give a yellow powder (3.64 g, 7.34 mmol, 73%). Yellow crystals were obtained from an acetonitrile solution after 24 h at −15 °C. Anal. Calcd for $C_{31}H_{50}N_3P$: C, 75.11; H, 10.17; N, 8.48. Found: C, 75.08; H, 9.70; N, 8.25. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 7.88−7.95 (m, 2H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 7.08−7.22 (m, 6H, C_6H_5 and $-C_6H_3(^iPr)_2$), 3.65 (septet, $^3J_{H,H} = 7$ Hz, 2H, $-CH(CH_3)_2$), 1.85−2.15 (m, 2H, $-CCH_2CH_2CH_2CH_3$), 1.46 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.43 (s, 9H, $-C(CH_3)_3$), 1.39 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.22 (s, 9H, $-C(CH_3)_3$), 1.10−1.30 (m, 4H, $-CH_2CH_2CH_2CH_3$), 0.86 (t, 3H, $-CCH_2CH_2CH_2CH_3$), $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 74.1 (s).

Preparation of DippN(H)PhPNCyC^{t}BuNCy (2b). A solution of Li[^{t}BuC(NCy)$_2$] (2.70 g, 10.0 mmol) in *n*-hexane (30 mL) was added dropwise to a solution of PhP(Cl)N(H)Dipp (3.20 g, 10.0 mmol) in *n*-hexane (30 mL) at −78 °C. The reaction mixture was stirred at 23 °C for 3 h, resulting in a cloudy yellow solution. LiCl was removed by filtration, and the clear yellow filtrate was reduced to dryness in vacuo to give a white powder (4.16 g, 7.59 mmol, 76%). Colorless crystalline blocks were obtained from a saturated solution in diethyl ether after storage at −15 °C for 24 h. Anal. Calcd for $C_{35}H_{54}N_3P$: C, 76.74; H, 9.94; N, 7.67. Found: C, 76.66; H, 10.26; N, 7.77. ^1H NMR data (C_6D_6, 25 °C, 399.731 MHz): δ 8.02 (m, 2H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 7.14−7.38 (m, 6H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 3.78 (septet, $^3J_{H,H} = 7$ Hz, 2H, $-CH(CH_3)_2$), 2.87 (m, 1H, $-C_6H_{11}$), 2.37−2.44 (m, 2H, $-C_6H_{11}$), 2.02−2.06 (m, 1H, $-C_6H_{11}$), 1.60−1.78 (m, 10H, $-C_6H_{11}$), 1.54 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.37 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.13−1.25 (m, 7H, $-C_6H_{11}$), 0.74−0.77 (m, 1H, $-C_6H_{11}$), 0.93 (s, 9H, $-C(CH_3)_3$). ^{13}C NMR (C_6D_6, 25 °C, 100.594 MHz): 12 resonances in the range δ 163.2−125.3 (phenyl and aryl 2,6-Dipp), 16 resonances in the range δ 38.7−25.1 (C_4H_9 and C_6H_{11}). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 69.1 (s).

Preparation of DippN(H)PhPNCy^{n}BuCNCy (2c). A solution of Li[^{n}BuC(NCy)$_2$] (2.70 g, 10.0 mmol) in *n*-hexane (30 mL) was added dropwise to a solution of PhP(Cl)N(H)Dipp (3.20 g, 10.0 mmol) in *n*-hexane (30 mL) at −78 °C. The reaction mixture was warmed to 23 °C and stirred for 3 h. LiCl was removed by filtration to give a clear yellow solution. The solvent was removed in vacuo to give a yellow oily residue (3.94 g, 7.20 mmol, 72% yield). Anal. Calcd for $C_{35}H_{54}N_3P$: C, 76.74; H, 9.94; N, 7.67. Found: C, 76.97; H, 10.20; N, 7.84. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 7.82−7.85 (m, 2H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 7.04−7.26 (m, 6H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 3.63 (septet, $^3J_{H,H} = 7$ Hz, 2H, $-CH(CH_3)_2$), 3.20 (m, 1H, $-NCH(CH_2)_5$), 2.94 (m, 1H, $-NCH(CH_2)_5$), 1.41−2.12 (series of overlapping m, 14H, $-NCH(CH_2)_5$), 1.42 and 1.40 (2 overlapping doublets, $^3J_{H,H} = 7$ Hz, 12H, $-CH(CH_3)_2$), 1.31 (m, 2H, $-CH_2CH_2CH_2CH_3$), 1.12−1.23 (m, 4H, $-CH_2CH_2CH_2CH_3$), 1.05−1.11 (m, 4H, $-NCH(CH_2)_5$), 0.82 (m, 3H, $-CH_2CH_2CH_2CH_3$), 0.65−0.74 (m, 2H, $-CH(CH_2)_5$). ^{13}C NMR (C_6D_6, 25 °C, 100.594 MHz): δ 161.3 (d, $^2J_{P-C} = 8.5$ Hz, $-CC_4H_9$), 145.7 (C_2 and C_6 of 2,6-Dipp), 141.4 (d, $^2J_{P-C}$ 12.9 Hz, C1 of 2,6-Dipp), 130.4 (d, $^1J_{P-C}$ 17.4 Hz, C1 of phenyl), 144.0 (C_3 and C_5 of 2,6-Dipp), 128.3 (d, $^2J_{P-C} = 3.8$ Hz, C_2 and C_6 of phenyl), 127.5 (C_3 and C_5 of phenyl), 124.2 (C_4 of 2,6-Dipp), 123.7 (C_4 of phenyl), 57.3 ($-CH(CH_2)_5$), 57.1 ($-CH(CH_2)_5$), 13 resonances in the range 23.4−37.8 ($-NCH(CH_2)$, $CH(CH_3)_2$, and $-C_4H_9$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 72.3 (s).

Preparation of Li[DippNPhP(^{n}Bu)PPhNDipp]·OEt$_2$ (3). ^{n}BuLi (9.38 mL, 1.6 M solution in hexanes, 15.0 mmol) was added dropwise to a solution of PhP(Cl)N(H)Dipp (**1**; 3.195 g, 10.0 mmol) in *n*-hexane (50 mL) at −78 °C, producing a cloudy yellow solution. The solution was warmed to 23 °C, and diethyl ether (20 mL) was added. The reaction mixture was stirred for 2 h. The remaining white precipitate was removed by filtration to give a clear yellow solution. Concentration of the reaction mixture and storage at −15 °C for 24 h yielded colorless crystalline blocks (2.19 g, 62% yield). Anal. Calcd for $C_{44}H_{63}LiN_2OP_2$: C, 74.97; H, 9.01; N, 3.97. Found: C, 74.67; H, 9.15; N, 4.28. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 8.01−8.06 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 7.66−7.70 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 6.98−7.43 (m, 12H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 3.81 (septet, $^3J_{H-H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 3.29 (septet, $^3J_{H-H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 3.16 (q, $^3J_{H-H} = 7.0$ Hz, 4H, $-O(CH_2CH_3)_2$), 1.88−1.91 (m, 2H, $-CH_2CH_2CH_2CH_3$), 1.37 (d, $^3J_{H-H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 1.26, (d, $^3J_{H-H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 1.10 (d, $^3J_{H-H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 1.05 (d, $^3J_{H-H} = 6.2$ Hz, 6H, $-CH(CH_3)_2$), 0.87−0.95 (m, 4H, $-CH_2CH_2CH_2CH_3$), 0.73 (t, $^3J_{H-H} = 7.0$ Hz, 6H, $-O(CH_2CH_3)_2$), 0.54 (t, $^3J_{H-H} = 7.3$ Hz, 3H, $-CH_2CH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 59.8 (d, $^1J_{P-P} = 298$ Hz), 26.9 (d, $^1J_{P-P} = 298$ Hz). ^7Li NMR (C_6D_6, 25 °C, 155.459 MHz): δ 2.17 (s). Mp: decomposes at 130 °C, orange oil at 150 °C.

Preparation of Al(Me)$_2$[DippNPhP(Me)PPhNDipp] (4). Me_3Al (1 mL, 2.0 M solution in heptane, 2.0 mmol) was added dropwise to a stirred solution of DippN(H)PhPNCyCBu^{t}NCy (**2b**; 1.094 g, 2.0 mmol) in *n*-hexane (30 mL) at −78 °C, resulting in a pale yellow solution. The solution was stirred for 2 h at 25 °C. The volume of solvent was reduced to approximately 10 mL and the solution was stored at −15 °C for 24 h. This yielded colorless crystalline blocks which were identified as Me$_2$Al[CyNCBu^{t}NCy]^{25} by ^1H NMR spectroscopy and elemental analysis (0.19 g, 30% yield). The yellow solution was decanted and further reduced in volume to a yellow oil. Storage at −18 °C for 24 h yielded colorless crystalline blocks (0.23 g, 48% yield). Anal. Calcd for $C_{39}H_{53}AlN_2P_2$: C, 73.33; H, 8.36; N, 4.39. Found: C, 73.15; H, 8.60; N, 4.22. ^1H NMR (C_6D_6, 25 °C, 300.138 MHz): δ 7.95−8.00 (m, 2H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 7.48−7.54 (m, 2H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 7.30−7.32 (m, 1H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 6.92−7.19 (m, 11H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 4.54 (septet, $^3J_{H,H} = 6.8$ Hz, 1H, $-CH(CH_3)_2$), 4.00 (septet, $^3J_{H,H} = 6.7$ Hz, 1H, $-CH(CH_3)_2$), 3.73 (septet, $^3J_{H,H} = 6.6$ Hz, 1H, $-CH(CH_3)_2$), 3.37 (septet, $^3J_{H,H} = 6.7$ Hz, 1H, $-CH(CH_3)_2$), 1.79 (d, $^3J_{H,H} = 6.8$ Hz, 3H, −CH-

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(25) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183.

Table 5. Selected Crystal Data for PhP(Cl)N(H)Dipp (1), DippN(H)PhPN^{t}BuC^{n}BuN^{t}Bu (2a), DippN(H)PhPNCyC^{t}BuNCy (2b), Mg[DippNPPh^{n}Bu)(NCyC^{n}BuNCy)]·OEt$_2$ (5), Li[DippNPhP(Me)PPhNDipp]·OEt$_2$ (6), and {Li[DippNPhP(O)P(^{n}Bu)PhNDipp]}$_2$ (7)

	1	**2a**	**2b**	**5**	**6**	**7**
formula	$C_{18}H_{23}ClNP$	$C_{31}H_{50}N_3P$	$C_{35}H_{54}N_3P$	$C_{43}H_{72}MgN_3OP$	$C_{41}H_{57}LiN_2OP_2$	$C_{41.5}H_{56.5}LiN_2OP_2$
fw	319.79	495.71	547.78	702.32	662.77	668.27
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*Pbca*	*Pccn*
a (Å)	8.274(2)	14.263(3)	10.3660(10)	10.637(2)	18.489(4)	12.560(3)
b (Å)	11.254(3)	12.312(3)	17.230(2)	10.744(2)	18.933(4)	20.652(4)
c (Å)	18.689(5)	18.094(6)	19.646(3)	20.461(4)	22.152(4)	33.098(7)
α (deg)	90	90	77.429(4)	74.795(7)	90	90
β (deg)	99.764(14)	105.215(9)	81.670(5)	84.401(6)	90	90
γ (deg)	90	90	75.900(7)	75.178(6)	90	90
V (Å^3)	1715.0(8)	3066.0(14)	3305.9(7)	2180.3(7)	7754(3)	8586(3)
Z	4	4	4	2	8	8
T (K)	173(2)	123(2)	173(2)	173(2)	123(2)	123(2)
d_{calcd} (g cm^{-3})	1.239	1.074	1.101	1.070	1.135	1.034
μ (mm^{-1})	0.31	0.112	0.109	0.111	0.145	0.131
F(000)	680	1088	1200	772	2864	2884
R^a	0.041	0.047	0.045	0.052	0.052	0.0723
$R_w{}^b$	0.105	0.131	0.110	0.152	0.1413	0.2501

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $(I > 2.00\sigma(I))$. ^{b} $R_w = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$ (all data).

$(CH_3)_2$), 1.48−1.52 (2 overlapping doublets, 6H, $-CH(CH_3)_2$), 1.32 (d, $^3J_{H,H} = 6.5$ Hz, 3H, $-CH(CH_3)_2$), 1.17 (d, $^3J_{H,H} = 6.6$ Hz, 3H, $-CH(CH_3)_2$), 1.13 (d, $^3J_{H,H} = 6.8$ Hz, 3H, $-CH(CH_3)_2$), 0.99 (d, $^2J_{P,H} = 11.3$ Hz, 3H, $-PCH_3$), 0.91 (d, $^3J_{H,H} = 6.5$ Hz, 3H, $-CH(CH_3)_2$), 0.15 (s, 3H, $-Al(CH_3)_2$), 0.08 (d, $^3J_{H,H} = 6.7$ Hz, 3H, $-CH(CH_3)_2$), −0.61 (s, 3H, $-Al(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 45.9 (d, $^1J_{P-P} = 264$ Hz), 40.2 (d, $^1J_{P-P} = 264$ Hz).

Preparation of Mg[DippNPPh(^{n}Bu)(NCyC^{n}BuNCy)]·OEt$_2$ (5). Bu_2Mg (2 mL, 1.0 M solution in heptane, 2.0 mmol) was added dropwise to a solution of DippN(H)PhPNCyC^{n}BuNCy (**2c**; 1.094 g, 2.0 mmol) in *n*-hexane (30 mL) at −78 °C, resulting in a clear yellow solution. The solution was warmed to 23 °C, and stirred for 2 h. The solvent was removed in vacuo, and the resulting yellow solid was washed with diethyl ether (3 × 15 mL). Colorless crystalline blocks were grown from a saturated solution in diethyl ether stored at −15 °C for several days (0.97 g, 1.38 mmol, 69% yield). Anal. Calcd for $C_{43}H_{72}MgN_3OP$: C, 73.54; H, 10.33; N, 5.98. Found: C, 73.11; H, 9.88; N, 6.17. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 7.13−7.52 (m, 8H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 3.70 (m, 2H, $-CH(CH_2)_5$), 3.43 (septet, $^3J_{H,H} = 7$ Hz, 2H, $-CH(CH_3)_2$), 2.37 (m, 2H, $-CH(CH_2)_5$), 2.24 (m, 2H, $-PCH_2CH_2CH_2CH_3$), 2.20 (m, 2H, $-CH(CH_2)_5$), 1.76−1.29 (m, 24H, $-CH(CH_2)_5$, $-PCH_2CH_2CH_2CH_3$ and $-CCH_2CH_2CH_2CH_3$), 1.27 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.17 (d, $^3J_{H,H} = 7$ Hz, 6H, $-CH(CH_3)_2$), 1.06 (m, 4H, $-PCH_2CH_2CH_2CH_3$ and $-CCH_2CH_2CH_2CH_3$), 0.85 and 0.89 (2 overlapping triplets, 6H, $-PCH_2CH_2CH_2CH_3$ and $-CCH_2CH_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 43.0 (s). Mp: decomposes at 82 °C, yellow oil at 118 °C.

Preparation of Li[DippNPhP(Me)PPhNDipp]·OEt$_2$ (6). MeLi (9.38 mL, 1.6 M solution in diethyl ether, 15.0 mmol) was slowly added to a slurry of PhP(Cl)NHDipp (**1**; 3.195 g, 10.0 mmol) in *n*-hexane (50 mL) at −78 °C to give a pale yellow suspension. The reaction mixture was warmed to 23 °C and stirred for 2 h. Diethyl ether (20 mL) was added, and the remaining white precipitate was removed by filtration. Reduction of the volume of the reaction mixture in vacuo to approximately 10 mL and storage at −15 °C for 24 h resulted in pale yellow crystalline blocks (1.76 g, 53% yield). Anal. Calcd for $C_{41}H_{57}LiN_2OP_2$: C, 74.30; H, 8.67; N, 4.23. Found: C, 74.31; H, 9.13; N, 4.19. ^1H NMR (C_6D_6, 25 °C, 399.731 MHz): δ 7.88−6.96 (m, 16H, $-C_6H_5$ and $-C_6H_3(^iPr)_2$), 3.87 (septet, $^3J_{H,H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 3.16 (septet, $^3J_{H,H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 3.07 (q, $^3J_{H,H} = 7$ Hz, 4H, $O(CH_2CH_3)_2$), 1.35 (d, $^3J_{H,H} = 6.9$ Hz, 6H, $-CH(CH_3)_2$), 1.30 (d, $^3J_{H,H} = 6.7$ Hz, 6H, $-CH(CH_3)_2$), 1.04 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 0.89 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 0.86 (d, $^2J_{P,H} = 9$ Hz, 3H, $-PCH_3$), 0.71 (t, $^3J_{H,H} = 7$ Hz, 6H, $O(CH_2CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 161.821 MHz): δ 67.3 (d, $^1J_{P,P} = 285$ Hz), 19.0 (d, $^1J_{P,P} = 285$ Hz), ^7Li NMR (C_6D_6, 25 °C, 155.459 MHz): δ 2.19 (s). Mp: decomposes at 75 °C, orange oil at 92 °C.

Preparation of {Li[DippNPhP(O)P(^{n}Bu)PhNDipp]}$_2$ (7). A sample of **3** (0.50 g, 0.71 mmol) was dissolved in hexane (20 mL) and diethyl ether (20 mL). Air was introduced to the flask through a needle for approximately 5 s. The reaction mixture was stirred for 1 h, resulting in a clear orange solution. The volume of solvent was reduced to approximately 20 mL and the solution was stored at −18 °C for 24 h yielding colorless crystals (0.23 g, 50%). Anal. Calcd for $C_{40}H_{53}LiN_2OP_2$: C, 74.28; H, 8.26; N, 4.33. Found: C, 74.31; H, 8.02; N, 4.40. ^1H NMR (C_4D_8O, 25 °C, 300.136 MHz): δ 8.00−7.93 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 7.35−7.16 (m, 6H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 7.09−7.06 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 6.83−6.81 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 6.70−6.68 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 6.54−6.51 (m, 2H, $-C_6H_5$ and $C_6H_3(^iPr)_2$), 3.94 (septet, $^3J_{H,H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 3.55 (septet, $^3J_{H,H} = 6.8$ Hz, 2H, $-CH(CH_3)_2$), 1.98−2.30 (m, 2H, $-CH_2CH_2CH_2CH_3$), 1.70−1.43 (m, 4H, $-CH_2CH_2CH_2CH_3$), 1.30 (s, 3H, $-CH_2CH_2CH_2CH_3$), 1.13 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 1.05 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 0.88 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$), 0.65 (d, $^3J_{H,H} = 6.8$ Hz, 6H, $-CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (C_4D_8O, 25 °C, 121.498 MHz): δ 5.3 (d, $^1J_{P,P} = 197$ Hz), −10.2 (d, $^1J_{P,P} = 197$ Hz), ^7Li NMR (C_4D_8O, 25 °C, 116.645 MHz): δ −1.70 (s).

X-ray Analyses. Single crystals of **1**, **2a**,**b**, and **5**−**7** were coated with Paratone 8277 oil (Exxon), mounted onto thin glass fibers, and quickly frozen in the cold nitrogen stream of the goniometer. Measurements were made on a Nonius CCD four-circle Kappa FR540C diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were measured using φ and ω scans. Data reduction was performed by using the HKL DENZO and SCALEPACK software.[26] A multiscan absorption correction was applied to the data (SCALEPACK).[26] Relevant parameters for the data collections and crystallographic data are summarized in Table 5. The structures were solved by direct methods and Patterson (SIR-92[27] and SHELXS-97[28a]) and refined by a full-matrix least-squares method based on F^2 using SHELXL-97.[28b] The non-hydrogen atoms were

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(26) HKL DENZO and SCALEPACK v1.96: Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: San Diego, CA, 1997; Vol. 276 (Macromolecular Crystallography, Part A), pp 307−326.

(27) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. SIR-92, a package for crystal structure solution by direct methods and refinement. *J. Appl. Crystallogr.* **1993**, *26*, 343.

refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The N−H hydrogen atoms were initially located in the difference Fourier map and then included at geometrically idealized positions. The positions of the phosphorus and chlorine atoms in **1** are disordered over two sites (P(1), P(1′), Cl(1), and Cl(1′)) with partial occupancy factors. P(1′) and Cl(1′) contribute 9.34% to the occupancy and are not shown in Figure 2. The asymmetric unit of **2b** consists of two independent molecules of $C_{35}H_{54}N_3P$. Since the structural features for both molecules are very similar, selected bond lengths and bond angles for only one molecule are reported (Table 2). In the case of **7**, data could only be collected with a θ(max) of 23.1°, due to poor diffraction. Low-temperature measurements were made to improve the diffraction. Repeated attempts to grow better crystals have proved unsuccessful. Thermal ellipsoid plots were generated using the program XSHELL (SHELXTL-97).[28]

Acknowledgment. We gratefully acknowledge NSERC (Canada) for financial support.

Supporting Information Available: Crystallographic data as CIF files for **1**, **2a**,**b**, and **5**−**7**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM0492045

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(28) (a) Sheldrick, G. M. SHELXS 97-2: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997. (b) Sheldrick, G. M. SHELXL 97-2: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.