Synthesis and Crystal Structures of Lithium Salts of New Iminophosphide/Phosphinoamide Anions

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Aminodiphenylphosphines are deprotonated by alkyllithium reagents to give the corresponding iminophosphide/phosphinoamide ions: lithium (neopentyl)(diphenylphosphino)amide (**3**), lithium (isopropyl)(diphenylphosphino)-amide (**4**), and lithium (2,4,6-tri-*tert*-butylphenyl)(diphenylphosphino)amide (**5**). Derivative **3** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$, $a = 17.717(2)$ Å, $b = 11.167(2)$ Å, $c = 22.151(1)$ Å, $\beta = 104.35(1)°$, R1 = 0.064, and wR2 = 0.184 at −73 °C. Derivative **4** crystallizes in the orthorhombic space group $Pna2_1$ with $Z = 4$, $a = 20.557(4)$ Å, $b = 10.475(2)$ Å, $c = 17.982(4)$ Å, R1 = 0.044, and wR2 = 0.089 at −70 °C. Derivative **5** crystallizes in the monoclinic space group $C2/c$ with $Z = 8$, $a = 47.256(6)$ Å, $b = 9.126(2)$ Å, $c = 18.246(2)$ Å, $\beta = 104.67(1)°$, R1 = 0.064, and wR2 = 0.165 at −73 °C. The solid-state structures of compounds **3** and **4** consist of approximately centrosymmetric dimers containing a Li_2N_2 rhombus with each lithium ion bound by both anions through their nitrogen atoms and by an ether solvate to give approximate trigonal planar coordination geometry. In some cases, weak second-sphere dipole interactions are suggested by relatively short P···Li distances. The anions of **3** and **4** adopt *cis* conformations. In contrast, **5** is a monomer in the solid state. The anion of **5** adopts a *trans* conformation and the cation, which is bound by two ether solvates, exhibits approximately trigonal planar geometry.

Introduction

Phosphinoamides have been isolated as their transition metal adducts for nearly two decades,[3] but only relatively recently has an alkali metal salt been isolated.[4] The free anion could formally be described as a resonance hybrid of the phosphino-amide (**1a**) and iminophosphide (**1b**) anions:
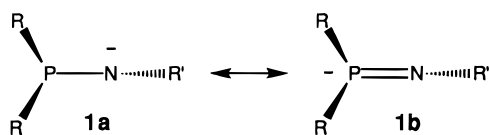
The phosphorus atom in both resonance forms is in the P(III) oxidation state; however, resonance form **1a** has a formal negative charge on the nitrogen atom, whereas for resonance form **1b** the negative charge is located on the phosphorus atom. Form **1a** is expected to predominate if the greater electronegativity of the nitrogen atom is the dominate factor; however, form **1b**, in which phosphorus has expanded its octet, results in additional stabilization due to resonance delocalization of the charge and P−N multiple bonding. A recent *ab initio* molecular

orbital study of phosphinoamide/iminophosphide anions suggested that hyperconjugation is not sufficient to describe most derivatives of **1** as iminophosphides (**1b**), although electron-withdrawing substituents at phosphorus strengthens the P−N bond and the iminophosphide form (**1b**) predominates for fluorine derivatives.[5] While most simple alkyl/aryl derivatives of **1** are best described as phosphinoamide anions (**1a**) with the negative charge located mainly on nitrogen, our calculations suggested that there is sufficient hyperconjugative bonding to enforce two ground-state conformations, *cis* (**1c**) and *trans* (**1d**):
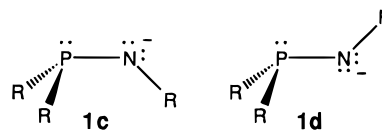
We have measured an experimental barrier for interconversion of the *cis* and *trans* isomers of [Ph₂PNPh]⁻ of 8 kcal/mol, and the barriers of other derivatives have been calculated to be in the range 7−32 kcal/mol, where the larger barriers are associated with derivatives with substituents that are relatively electron-withdrawing.[5] It is important to emphasize at this point that most of the molecular orbital calculations were carried out for the anion in the gas phase where interion interactions are absent, whereas the solid-state structures of phosphinoamides are presumably the result of a combination of effects: the inherent preference for *cis/trans* conformations about the P−N bonds of the anions, intramolecular steric interactions, electrostatic forces, and crystal packing. The previously reported crystal structure of [Li(Ph₂PNPh)(OEt₂)]₂ appears to exhibit a weak P···Li interaction that may reinforce the observed *cis* conformation.[4] However, our subsequent *ab initio* molecular orbital study

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(3) (a) Newton, M. G.; King, R. B.; Chang, M.; Gimeno, *J. Am. Chem. Soc.* **1978**, *100*, 1632. (b) Suss-Fink, G.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1987**, *320*, 101. (c) Hey, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *Polyhedron* **1988**, *7*, 2083. (d) Hey, E.; Muller, U., *Z. Naturforsch.*, *B* **1989**, *44*, 1538. (e) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R.; Dromzee, Y. *Organometallics* **1991**, *10*, 45. (f) Lindner, E.; Heckmann, M.; Fawzi, R.; Hiller, W. *Chem. Ber.* **1991**, *124*, 2171. (g) Mague, J. T.; Lin, Z. *Organometallics* **1992**, *11*, 4139. (h) Baranger, A. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7890. (i) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822.
(4) Ashby, M. T.; Li, Z. *Inorg. Chem.* **1992**, *31*, 1321.
(5) Trinquier, G.; Ashby, M. T. *Inorg. Chem.* **1994**, *33*, 1306.

Table 1. Crystal Data for Compounds **2**−**5**

	2	**3**	**4**	**5**
formula	$C_{30}H_{40}NP$	$C_{42}H_{62}Li_2N_2O_2P_2$	$C_{38}H_{54}Li_2N_2O_2P_2$	$C_{38}H_{59}LiNO_2P$
fw	445.60	702.76	646.65	599.77
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$C2/c$ (No. 15)
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
a, Å	14.428(1)	17.717(2)	20.557(4)	47.256(6)
b, Å	9.544(1)	11.167(2)	10.475(2)	9.126(2)
c, Å	19.879(1)	22.151(1)	17.982(4)	18.246(2)
β, deg	95.34(1)	104.35(1)		104.67(1)
V, Å^3	2725.5(4)	4245.7(9)	3872.1(14)	7612(2)
T, °C	−73(2)	−73(2)	−70(2)	−73(2)
Z	4	4	4	8
D_{calc}, g·cm^{-3}	1.086	1.099	1.109	1.047
λ, Å	Cu Kα (1.54178 Å)	Cu Kα (1.54178 Å)	Mo Kα (0.71073 Å)	Cu Kα (1.54178 Å)
μ, cm^{-1}	99.1	118.1	15.4	85.3
cryst size, mm^3	0.5 × 0.4 × 0.4	0.7 × 0.2 × 0.1	0.6 × 0.5 × 0.4	0.6 × 0.4 × 0.2
final R indices[a]	R1 = 0.062, wR2 = 0.165	R1 = 0.064, wR2 = 0.184	R1 = 0.044, wR2 = 0.089	R1 = 0.064, wR2 = 0.165
R indices [all data used in refinement]	R1 = 0.067, wR2 = 0.170	R1 = 0.087, wR2 = 0.206	R1 = 0.072, wR2 = 0.105	R1 = 0.081, wR2 = 0.181
GOF	1.03	1.11	1.04	1.04

[a] $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $wR2 = [\sum (w(F_o^2 - F_c^2)^2)/\sum (w(F_o^2)^2)]^{1/2}$; $w = 1/\sum [\sigma^2(F_o)^2 + (aP)^2 + (bP)]$, $P = (F_o)^2[^1/_3 + [2(F_o)^2/3]]$ for $F_o^2 \geq 0$ (otherwise zero). $GOF = [\sum (w(F_o^2 - F_c^2)/(n - m)]^{1/2}$, where n = number of reflections observed and m = number of parameters.

failed to locate an energy minimum with a Li···P contact for the model ion dimer $[Li(H_2PNH)]_2$.[5] Surprisingly, a more recent theoretical study of diphosphinoamides by Schleyer *et al.* that included some *ab initio* calculations of lithium/phosphinoamide ion pairs indicated the presence of a Li···P contact for a *cis* monomer, and some theoretical evidence was presented that the *cis* conformation is indeed reinforced by weak P···Li interactions.[6]

We report here the synthesis and solid-state structures of three new phosphinoamide anions. In the solid state, two of these derivatives are dimeric and exhibit *cis* conformations, like that of the previously reported phosphinoamide anion, but the third is monomeric and it exhibits the anticipated (but previously unobserved) *trans* conformation. The four known crystal structures of lithium phosphinoamides, the one previously reported and the three that are reported herein, all exhibit different P···Li contacts. Thus, these structures offer insight into the aforementioned conformational and electrostatic issues.

Experimental Section

All operations were performed under an atmosphere of purified argon using standard Schlenk techniques.[7] Diethyl ether was dried over Na/K alloy and distilled before use. All of the other reagents were used as received from Aldrich without further purification. ^{1}H and ^{31}P NMR spectra were recorded on either a Varian XL-500 or a Bruker AMX 300 spectrometer using residual solvent peaks and external 85% *o*-H$_3$PO$_4$ as references, respectively.

((2,4,6-Tri-*tert*-butylphenyl)amino)diphenylphosphine (2). To 3.80 g (15 mmol) of (2,4,6-tri-*tert*-butylphenyl)amine in 40 mL of diethyl ether at 0 °C was added dropwise a hexane solution of *n*-butyllithium (8.8 mL, 1.7 M). After 10 min, the mixture was warmed slowly to room temperature and heated to reflux for another 30 min. This solution was added to 3.21 g (15 mmol) of chlorodiphenylphosphine in 40 mL of diethyl ether at −78 °C. After 20 min, the mixture was warmed to room temperature. After removal of the lithium chloride precipitate by filtration and concentration under vacuum, compound **2** was obtained as colorless crystals (4.30 g, 64% yield). ^{31}P NMR (121.4 MHz, C$_6$D$_6$, 20 °C): δ 48.6 ppm. ^{1}H NMR (300.1 MHz, THF-d_6, 20 °C): δ 7.13−7.58 (m, 10H), 7.51 (s, 2H), 4.89 (br, 1H, NH), 1.54 (s, 18H), 1.48 (s, 9H) ppm.

Lithium (Neopentyl)(diphenylphosphino)amide (3). To 1.84 g (6.8 mmol) of (neopentylamino)diphenylphosphine in 40 mL of diethyl ether at −78 °C was added dropwise a hexane solution of *tert*-butyllithium (4.0 mL, 1.7 M). After 40 min, the mixture was warmed slowly to room temperature and stirred for another 40 min. Compound **3** was obtained as light yellow crystals at 4 °C after concentrating the solution (1.15 g, 81% yield). ^{31}P NMR (121.4 MHz, C$_6$D$_6$, 20 °C): δ 44.9 ppm. ^{1}H NMR (300.1 MHz, THF-d_6, 20 °C): δ 7.46−7.81 (m,

10H), 2.37 (br s, 2H), 1.25 (s, 9H) ppm. ^{1}H NMR resonances for 1 equiv of "free" diethyl ether were also observed at 3.41 (q, $^3J_{HH}$ = 2 Hz) and 1.14 (t) ppm.

Lithium (Isopropyl)(diphenylphosphino)amide (4). To 0.61 g (2.5 mmol) of (isopropylamino)diphenylphosphine in 20 mL of diethyl ether at −78 °C was added dropwise a hexane solution of *tert*-butyllithium (1.7 mL, 1.5 M). After 40 min, the mixture was warmed slowly to room temperature and stirred for another 40 min. Compound **4** was obtained as light yellow crystals at 4 °C after concentrating the solution (0.35 g, 57% yield). ^{31}P NMR (121.4 MHz, C$_6$D$_6$, 20 °C): δ 44.4 ppm. ^{1}H NMR (499.9 MHz, THF-d_6, 20 °C): δ 6.98−7.45 (m, 10H), 3.39 (d sept, 1H, $^3J_{HP}$ = 20 Hz, $^3J_{HH}$ = 6 Hz), 0.77 (d, 6H) ppm. ^{1}H resonances for 1 equiv of "free" diethyl ether were also observed at 3.41 (q, $^3J_{HH}$ = 2 Hz) and 1.14 (t) ppm.

Lithium (2,4,6-Tri-*tert*-butylphenyl)(diphenylphosphino)amide (5). To 2.15 g (4.8 mmol) of (2,4,6-tri-*tert*-butylphenyl)amino)diphenylphosphine (**2**) in 40 mL of diethyl ether at −78 °C was added dropwise a hexane solution of *tert*-butyllithium (2.8 mL, 1.7 M). After 40 min, the mixture was warmed slowly to room temperature and stirred for another 40 min. Compound **5** was obtained as light yellow crystals at 4 °C after concentrating the solution (1.57 g, 73% yield). ^{31}P NMR (121.4 MHz, C$_6$D$_6$, 20 °C): δ 63.2 ppm. ^{1}H NMR (300.1 MHz, THF-d_6, 20 °C): δ 7.43−7.67 (m, 10H), 7.65 (s, 2H), 1.54 (s, 18H) ppm. ^{1}H NMR resonances for 1 equiv of "free" diethyl ether were also observed at 3.41 (q, $^3J_{HH}$ = 2 Hz) and 1.14 (t) ppm.

General Procedures Employed in the Crystallographic Studies. X-ray data were collected for **2**, **3**, and **5** using an Enraf-Nonius CAD-4 diffractometers and monochromated Cu Kα radiation (λ = 1.541 78 Å).[8] The data for **4** were collected using a Siemens P4 diffractometer and Mo Kα radiation (λ = 0.710 73 Å).[9] The crystallographic data are summarized in Table 1. Selected atomic coordinates and equivalent isotropic displacement parameters are given for **2**−**5** in Table 2. Selected bond distances and angles for **2**−**5** are given in Tables 3−6, respectively. Table 7 compares selected metric data for **2**−**5** with that previously reported for $[Li(Ph_2PNPh)(OEt_2)]_2$. Other crystallographic data are available as Supporting Information. Automatic centering, indexing, and least-squares routines were employed to obtain the cell dimensions. The Laue symmetry and systematic absences of trial data sets were used to identify the space groups. The data were corrected for Lorentz and polarization effects. No absorption correction was

(6) Kremer, T.; Hampel, F.; Knoch, F. A.; Bauer, W.; Schmidt, A.; Gabold, P.; Schütz, M.; Ellermann, J.; Schleyer, P. v. R. *Organometallics* **1996**, *15*, 4776.
(7) *Organometallic Compounds*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.
(8) CAD4 Version 5.0, Enraf-Nonius, Delft, The Netherlands, 1988.
(9) Ashby, M. T.; Khan, M. A.; Halpern, J. *Organometallics* **1991**, *10*, 2011.

Table 2. Selected Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for Compounds **2**−**5**^{a}

atom	x	y	z	U_{eq}^{b}
		Compound **2**		
P	0.21093(4)	0.6319(6)	0.14753(3)	0.0447(3)
N	0.24787(14)	0.4801(2)	0.18936(9)	0.0431(5)
C(N)	0.2376(2)	0.3556(2)	0.14927(11)	0.0413(5)
C(P)	0.2274(2)	0.7566(2)	0.21728(12)	0.0452(6)
C′(P)	0.3105(2)	0.6732(2)	0.09929(12)	0.0463(6)
		Compound **3**		
P	0.16016(4)	0.46553(7)	0.13856(3)	0.0195(3)
	0.28987(5)	0.81531(7)	0.05636(4)	0.0235(3)
N	0.22688(13)	0.5679(2)	0.16859(11)	0.0170(6)
	0.27564(15)	0.6688(2)	0.04363(11)	0.0208(6)
C(N)	0.2568(2)	0.5699(3)	0.23730(13)	0.0186(7)
	0.2969(2)	0.6202(3)	−0.01175(15)	0.0307(8)
C(P)	0.0795(2)	0.4757(3)	0.17726(14)	0.0232(7)
	0.2427(2)	0.8959(3)	−0.01603(15)	0.0256(8)
C′(P)	0.1979(2)	0.3150(3)	0.1643(2)	0.0253(8)
	0.3928(2)	0.8504(3)	0.0609(2)	0.0325(8)
Li	0.3132(3)	0.5704(5)	0.1227(2)	0.0266(12)
	0.1865(3)	0.6717(5)	0.0898(3)	0.0275(12)
O	0.41216(13)	0.4862(2)	0.14962(12)	0.0410(7)
	0.09150(13)	0.7684(2)	0.06843(12)	0.0396(7)
		Compound **4**		
P	0.32337(5)	0.11525(11)	0.82934(6)	0.0282(2)
	0.38562(5)	−0.27610(11)	0.66502(6)	0.0322(3)
N	0.2937(2)	−0.0264(3)	0.8059(2)	0.0295(8)
	0.4124(2)	−0.1522(3)	0.7144(2)	0.0291(8)
C(N)	0.2285(2)	−0.0685(4)	0.8303(3)	0.0375(10)
	0.4820(2)	−0.1186(4)	0.7132(2)	0.0312(10)
C(P)	0.3293(2)	0.1372(4)	0.9313(2)	0.0314(10)
	0.4070(2)	−0.2490(5)	0.5662(2)	0.0342(11)
C′(P)	0.2620(2)	0.2399(4)	0.8095(2)	0.0307(10)
	0.4389(2)	−0.4160(4)	0.6839(2)	0.0356(11)
Li	0.3675(4)	−0.1543(7)	0.8147(4)	0.037(2)
	0.3397(4)	−0.0217(7)	0.7040(4)	0.033(2)
O	0.3963(2)	−0.2427(3)	0.9053(2)	0.0414(8)
	0.32328(15)	0.1047(3)	0.6231(2)	0.0406(8)
		Compound **5**		
P	0.090230(14)	0.12395(7)	0.05627(4)	0.0221(2)
N	0.11213(4)	0.2658(2)	0.05492(12)	0.0191(5)
C(N)	0.14293(5)	0.2319(3)	0.07756(14)	0.0178(6)
C(P)	0.06924(6)	0.1472(3)	0.1303(2)	0.0298(7)
C′(P)	0.05780(5)	0.1577(3)	−0.0231(2)	0.0257(6)
Li	0.11450(10)	0.4818(5)	0.0431(3)	0.0342(11)
O	0.08097(4)	0.6146(2)	0.00566(12)	0.0372(5)
O′	0.14964(4)	0.6177(2)	0.06343(12)	0.0342(5)

Multiple entires are for crystallographically independent anions. ^{b} The equivalent isotropic factor, U_{eq}, is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

applied to the data collected for **4** since absorption was judged to be negligible. However, empirical absorption corrections based upon ψ scans were applied to the data collected for **2** and **5**. For **3**, DIFABS was employed.[10] The structure of **4** was solved using a combination of the heavy atom and direct methods provided by the SHELX-86 program.[11] The structures of **2**, **3**, and **5** were solved using direct methods provided by the SHELXS-86 program. Neutral scattering factors were used for all atoms as included in the programs.[12] The models were refined on F^2 using all of the reflections with the SHELX-93 program and full-matrix methods.[13] The structure of **4** was solved using the Siemens SHELXL system,[14] and it was also refined by full-matrix least squares on F^2 using all of the reflections.

(10) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(11) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175−189.
(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.
(13) *SHELX-93. Program for Crystal Structure Determination.* University of Göttingen: Göttingen, Germany, 1993.
(14) SHELXTL Software Package for the Determination of Crystal Structures, Release 5.0, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1995.
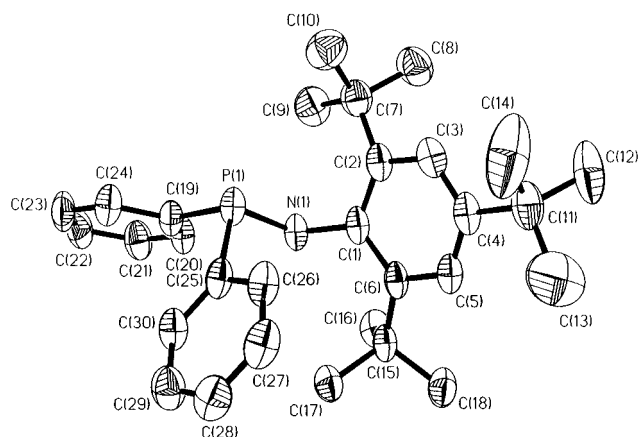
Figure 1. View of **2** showing the atom-labeling scheme and the thermal vibration ellipsoids (50% probability).
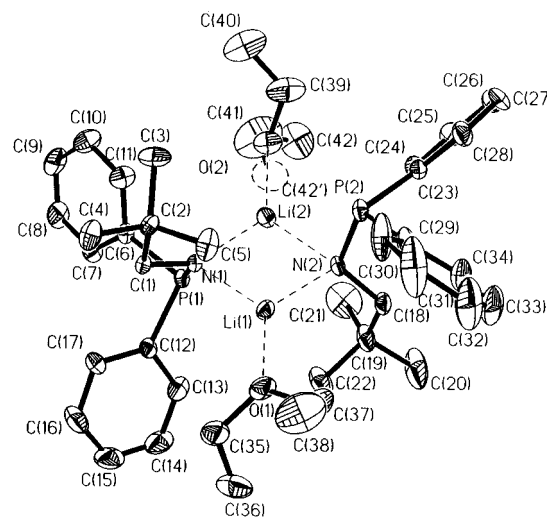
Figure 2. View of **3** showing the atom-labeling scheme and the thermal vibration ellipsoids (40% probability). Atoms C(42) [0.57(2) occupancy] and C(42′) [0.43(2) occupancy] are related by a two-site disorder model.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

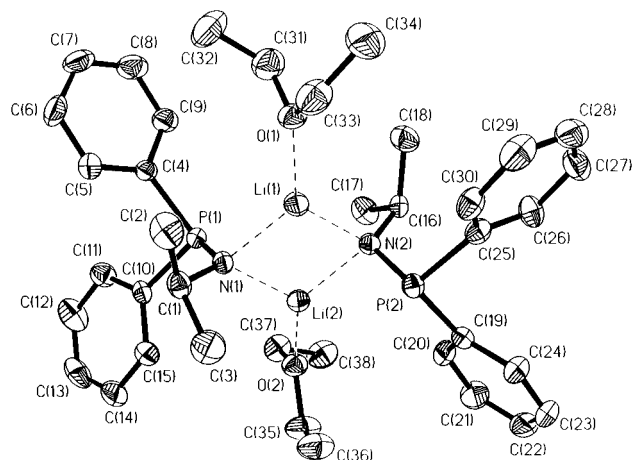|			
P(1)−N(1)	1.730(2)	P(1)−C(19)	1.826(2)
P(1)−C(25)	1.843(3)	N(1)−C(1)	1.431(3)
N(1)−P(1)−C(19)	99.7(1)	N(1)−P(1)−C(25)	102.1(1)
C(19)−P(1)−C(25)	101.7(1)	P(1)−N(1)−C(1)	114.6(1)

Crystal Data for 2. The crystallographic data for **2** are summarized in Table 1. The Laue symmetry and systematic absences of a trial data set unambiguously determined the cell to be monoclinic and the space group to be $P2_1/c$. A total of 4042 unique reflections were measured ($3 \leq \theta \leq 60°$). The positional and anisotropic thermal parameters for all the non-hydrogen atoms were included in the final refinement. An extinction correction was applied. The structure was refined by full-matrix least-squares methods using all of the reflections and 293 variables.

Crystal Data for 3. The crystallographic data for **3** are summarized in Table 1. The Laue symmetry and systematic absences of a trial data set unambiguously determined the cell to be monoclinic and the space group to be $P2_1/c$. A total of 6308 unique reflections were measured ($3 \leq \theta \leq 60°$). The positional and anisotropic thermal parameters for all the non-hydrogen atoms were included in the final refinement. A two-site disorder of one of the ethyl groups was observed. The structure was refined by full-matrix least-squares methods using all of the reflections and 467 variables.

Crystal Data for 4. The crystallographic data for **4** are summarized in Table 1. The Laue symmetry and systematic absences of a trial data set unambiguously determined the cell to be orthorhombic and the space group to be $Pna2_1$. A total of 3438 unique reflections were measured ($4 \leq 2\theta \leq 50°$). The positional and thermal parameters for

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

P(1)−N(1)	1.660(2)	P(1)−C(6)	1.843(4)
P(1)−C(12)	1.846(4)	P(1)−Li(2)	2.633(6)
P(2)−N(2)	1.669(2)	P(2)−C(23)	1.848(3)
P(2)−C(29)	1.843(4)	P(2)−Li(2)	2.673(6)
O(1)−Li(1)	1.948(6)	O(2)−Li(2)	1.957(6)
N(1)−C(1)	1.483(4)	N(1)−Li(1)	2.036(6)
N(1)−Li(2)	2.069(7)	N(2)−C(18)	1.473(4)
N(2)−Li(1)	2.035(5)	N(2)−Li(2)	2.084(6)
N(1)−P(1)−C(6)	109.2(1)	N(1)−P(1)−C(12)	109.6(2)
N(1)−P(1)−Li(2)	51.8(2)	C(6)−P(1)−C(12)	100.1(2)
C(6)−P(1)−Li(2)	111.9(2)	C(12)−P(1)−Li(2)	146.6(2)
N(2)−P(2)−C(23)	108.3(1)	N(2)−P(2)−C(29)	108.9(2)
N(2)−P(2)−Li(2)	51.2(2)	C(23)−P(2)−C(29)	99.9(2)
C(23)−P(2)−Li(2)	109.8(2)	C(29)−P(2)−Li(2)	148.1(2)
C(35)−O(1)−C(37)	118.7(4)	C(35)−O(1)−Li(1)	123.7(3)
C(37)−O(1)−Li(1)	117.5(3)	C(39)−O(2)−C(41)	115.6(4)
C(39)−O(2)−Li(2)	120.4(3)	C(41)−O(2)−Li(2)	123.6(4)
P(1)−N(1)−C(1)	117.4(2)	P(1)−N(1)−Li(1)	111.0(2)
P(1)−N(1)−Li(2)	89.1(2)	C(1)−N(1)−Li(1)	113.0(2)
C(1)−N(1)−Li(2)	144.9(3)	Li(1)−N(1)−Li(2)	73.5(2)
P(2)−N(2)−C(18)	116.3(2)	P(2)−N(2)−Li(1)	112.4(2)
P(2)−N(2)−Li(2)	90.2(2)	C(18)−N(2)−Li(1)	114.9(2)
C(18)−N(2)−Li(2)	142.7(3)	Li(1)−N(2)−Li(2)	73.3(2)
O(1)−Li(1)−N(1)	124.8(3)	O(1)−Li(1)−N(2)	127.0(3)
N(1)−Li(1)−N(2)	108.1(3)	P(1)−Li(2)−P(2)	147.3(2)
P(1)−Li(2)−O(2)	110.6(2)	P(1)−Li(2)−N(1)	39.1(1)
P(1)−Li(2)−N(2)	114.9(2)	P(2)−Li(2)−O(2)	102.1(2)
P(2)−Li(2)−N(1)	116.9(3)	P(2)−Li(2)−N(2)	38.6(1)
O(2)−Li(2)−N(1)	127.6(3)	O(2)−Li(2)−N(2)	126.9(3)
N(1)−Li(2)−N(2)	105.0(3)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

P(1)−N(1)	1.659(4)	P(1)−C(4)	1.852(4)
P(1)−C(10)	1.850(4)	P(1)−Li(2)	2.693(7)
P(2)−N(2)	1.666(4)	P(2)−C(19)	1.852(4)
P(2)−C(25)	1.861(4)	O(1)−Li(1)	1.965(8)
O(2)−Li(2)	1.996(8)	N(1)−C(1)	1.478(6)
N(1)−Li(1)	2.030(9)	N(1)−Li(2)	2.063(8)
N(2)−C(16)	1.474(6)	N(2)−Li(1)	2.026(8)
N(2)−Li(2)	2.034(9)		
N(1)−P(1)−C(4)	112.8(2)	N(1)−P(1)−C(10)	109.4(2)
N(1)−P(1)−Li(2)	50.0(2)	C(4)−P(1)−C(10)	98.5(2)
C(4)−P(1)−Li(2)	152.5(2)	C(10)−P(1)−Li(2)	107.4(2)
N(2)−P(2)−C(19)	108.3(2)	N(2)−P(2)−C(25)	108.8(2)
C(19)−P(2)−C(25)	99.0(2)	C(31)−O(1)−C(33)	115.6(4)
C(31)−O(1)−Li(1)	119.1(4)	C(33)−O(1)−Li(1)	125.4(4)
C(35)−O(2)−C(37)	113.2(4)	C(35)−O(2)−Li(2)	128.1(4)
C(37)−O(2)−Li(2)	118.5(4)	P(1)−N(1)−C(1)	121.7(3)
P(1)−N(1)−Li(1)	107.2(3)	P(1)−N(1)−Li(2)	92.1(3)
C(1)−N(1)−Li(1)	117.2(3)	C(1)−N(1)−Li(2)	133.4(4)
Li(1)−N(1)−Li(2)	75.1(3)	P(2)−N(2)−C(16)	119.9(3)
C(16)−N(2)−Li(1)	108.4(3)	P(2)−N(2)−Li(2)	103.4(3)
C(16)−N(2)−Li(1)	117.3(3)	C(16)−N(2)−Li(2)	123.5(3)
Li(1)−N(2)−Li(2)	75.8(3)	O(1)−Li(1)−N(1)	126.9(4)
O(1)−Li(1)−N(2)	127.3(4)	N(1)−Li(1)−N(2)	105.3(4)
P(1)−Li(2)−O(2)	103.6(3)	P(1)−Li(2)−N(1)	38.0(2)
P(1)−Li(2)−N(2)	111.9(3)	O(2)−Li(2)−N(1)	125.9(4)
O(2)−Li(2)−N(2)	129.6(4)	N(1)−Li(2)−N(2)	103.8(4)

Figure 3. View of **4** showing the atom-labeling scheme and the thermal vibration ellipsoids (40% probability).

Figure 4. View of **5** showing the atom-labeling scheme and the thermal vibration ellipsoids (40% probability). Atoms C(11)/C(12)/C(13) [0.670(6) occupancy] and C(11′)/C(12′)/C(13′) [0.330(6) occupancy] are related by a two-site disorder model.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **5**

P(1)−N(1)	1.661(2)	P(1)−C(19)	1.879(3)
P(1)−C(25)	1.848(3)	O(1)−Li(1)	1.974(5)
O(2)−Li(1)	2.030(5)	N(1)−C(1)	1.442(3)
N(1)−Li(1)	1.989(5)		
N(1)−P(1)−C(19)	111.5(1)	N(1)−P(1)−C(25)	104.8(1)
C(19)−P(1)−C(25)	93.5(1)	C(31)−O(1)−C(33)	112.5(2)
C(31)−O(1)−Li(1)	117.4(2)	C(33)−O(1)−Li(1)	128.0(2)
C(35)−O(2)−C(37)	113.3(2)	C(35)−O(2)−Li(1)	120.6(2)
C(37)−O(2)−Li(1)	126.0(2)	P(1)−N(1)−C(1)	114.6(2)
P(1)−N(1)−Li(1)	145.7(2)	C(1)−N(1)−Li(1)	99.4(2)
O(1)−Li(1)−O(2)	103.6(2)	O(1)−Li(1)−N(1)	125.7(3)
O(2)−Li(1)−N(1)	130.7(3)		

all the non-hydrogen atoms and the positional parameters for the hydrogen atoms were included in the final refinement. All of the heavy atoms of the **4** were refined anisotropically. The structure was refined by full-matrix least-squares methods using all of the reflections and 415 variables. The absolute structure was determined by Flack's *x*-refinement ($x = 0.02(12)$).
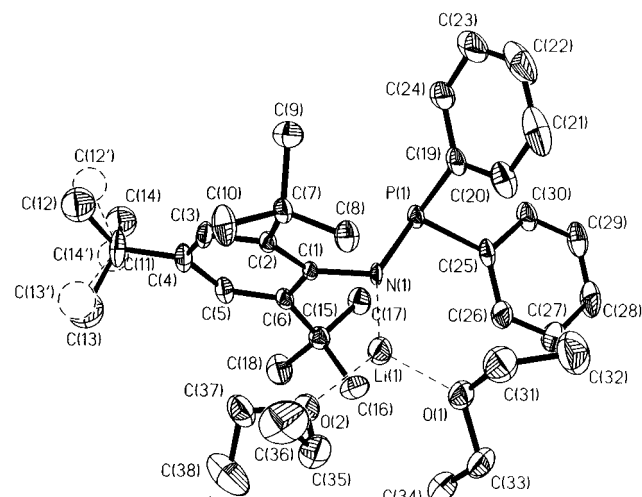
Crystal Data for 5. The crystallographic data for **5** are summarized in Table 1. The Laue symmetry and systematic absences of a trial data set determined the cell to be monoclinic and the space group to be *C2/c*. A total of 5644 unique reflections were measured ($4 \leq \theta \leq 60°$). The positional and thermal parameters for all the non-hydrogen atoms and the positional parameters for the hydrogen atoms were included in the final refinement. A two-site disorder model was applied to one of the *tert*-butyl groups. An extinction correction was applied. The structure was refined by full-matrix least-squares methods using all of the reflections and 394 variables.

Results and Discussion

Aminophosphine **2** was synthesized using a conventional approach, reaction of chlorodiphenylphosphine with the corre-

sponding amide. The lithium phosphinoamides **3**−**5** were synthesized using the same approach that was used to synthesize the previously reported [Li(Ph₂PNPh)(OEt₂)]₂,[4] deprotonation of the corresponding aminophosphine by alkyllithium reagents in diethyl ether solvent. X-ray-quality crystals of **3**−**5** were grown from the reaction mixtures. Because the phosphino-amides are highly sensitive to moisture and oxygen and the

Table 7. Selected Interatomic Distances (Å), Angles (deg), and Torsion Angles (deg) for $(C_6H_5)_2PNHR$ and $[(C_6H_5)_2PNR]^-$ ^{a}

	$(C_6H_5)_2PNHR$	$[(C_6H_5)_2PNR]^-$			
	R = $C_6H_2(C(CH_3)_3)_3$ (**2**)	R = C_6H_5 (*cis*)	R = $CH_2C(CH_3)_3$ (**3**, *cis*)	R = $CH(CH_3)_2$ (**4**, *cis*)	R = $C_6H_2(C(CH_3)_3)_3$ (**5**, *trans*)
P–N	1.730(2)	1.672(2)	1.660(2) [1.669(2)]	1.659(4) [1.666(4)]	1.661(2)
P···Li		2.684(3)	2.633(6) [2.673(6)]	2.693(7) [2.913(8)]	3.490(5)
P···Li′		3.004(4)	3.053(6) [3.084(5)]	2.977(8) [3.002(7)]	
P–C$_{ipso}$	1.826(2)	1.843(2)	1.848(3) [1.843(4)]	1.861(4) [1.852(4)]	1.879(3)
P–C$_{ipso}$′	1.843(3)	1.845(2)	1.843(4) [1.846(4)]	1.852(4) [1.850(4)]	1.848(3)
N–C	1.431(3)	1.41(1)	1.473(4) [1.483(4)]	1.474(6) [1.478(6)]	1.442(3)
C$_{ipso}$–P–N	99.7(1)	110.04(9)	108.30(14) [109.2(1)]	108.8(2) [112.8(2)]	111.5(1)
C$_{ipso}$′–P–N	102.1(1)	108.9(1)	108.9(2) [109.6(2)]	108.3(2) [109.4(2)]	104.8(1)
P–N–C	99.7(1)	126.7(1)	116.3(2) [117.4(2)]	119.9(3) [121.7(3)]	114.6(2)
C$_{ipso}$–P–N–C	175.7(2)	68.5(3)	51.7(3) [52.7(2)]	48.7(3) [59.3(4)]	114.0(2)
C$_{ipso}$′–P–N–C	−80.0(2)	−44.3(3)	−56.1(3) [−56.0(3)]	−57.9(3) [−49.2(4)]	−146.2(2)
ref	this study	4	this study	this study	this study

^{a} The numbers in brackets are for crystallographically independent anions. Note: $[(C_6H_5)_2PN(C_6H_5)]^-$ is a centrosymmetric dimer.

transparent crystals become opaque in the absence of solvent (presumably as a result of loss of the volatile diethyl ether solvate), no attempt was made to obtain combustion analyses. Chemical purity of the crystalline compounds was assessed through the use of ^1H and ^{31}P NMR. In general, small amounts of the corresponding aminophosphines were observed in the NMR samples, presumably resulting from trace amounts of water that could not be removed from the NMR solvent.

Single-crystal X-ray structure analyses were carried out on **3**−**5**. Conformational disorders of some of the side chains were observed for **3** (an ethyl group of one of the diethyl ether solvate molecules) and **5** (the 4-*tert*-butyl group of the 2,4,6-tri-*tert*-butylbenzene substituent of the amine); however, neither of these disorder problems compromise the precision of the metric parameters of interest, and both disorders were reasonably fit by two-site disorder models. When compound **5** proved to have a molecular structure very different from the structures of the other three phosphinoamides, the X-ray crystal structure of the parent aminophosphine **2** was determined for the sake of comparison.

Molecular and Electronic Structures of Aminophosphines. There are surprisingly few examples of aminophosphines that have been characterized by single-crystal X-ray crystallography. None of these bear simple alkyl or aryl substituents at the amino nitrogen atom.[15] Several structures of organic derivatives of diphosphinoamines have been determined.[16] Figure 1 illustrates the molecular structure of **2**. Selected bond lengths and angles for **2** are given in Table 3. Significant bond distances, bond angles, and torsion angle for the aminophosphine and the phosphinoamides of this study are compared in Table 7. Compound **2** is monomeric with no significant intermolecular

contacts. The hydrogen atom bound to N(1) was clearly located in the final difference map. N(1) exhibits a shallow pyramidal geometry (the sum of the angles about N(1) equals 114.6 + 111.2 + 112.8 = 338.6°). The nitrogen atoms of aminophosphines typically exhibit trigonal planar geometry at the nitrogen atom or very shallow pyramidal geometry. Large bond angles can be explained by a relatively low inversion barrier at the nitrogen atom and that fact that such a geometry minimizes steric interactions between the substituents of the nitrogen atom.[17] Furthermore, hyperconjugative mixing of the nitrogen lone pair favors large bond angles about the nitrogen atom (*vide infra*). It is noteworthy that the molecular structure of **2** has no symmetry in the solid state, either crystallographically-imposed or approximate, and the conformation about the P−N bond is *gauche*. This conformation renders the lone pair on nitrogen approximately *trans* to the P(1)−C(25) bond
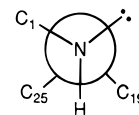
an orientation that favors $N(n_\sigma) \rightarrow P(1)-C(25)\sigma^*$ negative hyperconjugation[18] (and to a much less extent, donation into a phosphorus d orbital):

(15) Triphenylsilyl: Schmidbaur, H.; Schier, A.; Lauteschlager, S.; Riede, J.; Muller, G. *Organometallics* **1984**, *3*, 1906. 1-Pyrole: Nifantév, E. E.; Grachev, M. K.; Burmistrov, S. Y.; Bekker, A. R.; Vasyanina, L. K.; Antipin, M. Y.; Struchkov, Y. T. *Zh. Obshch. Khim.* **1992**, *62*, 1461. A borane compound: Noth, H.; Stolpmann, H.; Thomann, M. *Chem. Ber.* **1994**, *127*, 81. A 2-pyrimidine compound: Florke, U.; Haupt, H.-J. *Z. Kristallogr.* **1993**, *205*, 127.

(16) For structures of free organic derivatives of diphosphinoamines see: (a) Keat, R.; Manojlovic-Muir, L.; Muir, K. W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2192. (b) Noth, H.; Fluck, E. *Z. Naturforsch., B* **1984**, *39*, 744. (c) Faught, J. B. *Can. J. Chem.* **1976**, *54*, 738. (d) Ellerman, J.; Kock, E.; Zimmermann, H.; Gomm, M. *Acta Crystallogr. C* **1987**, *43*, 1795. (e) Babu, R. P. K.; Krishnamurthy, S. S.; Nethaji, M. *Heteroatom Chem.* **1991**, *2*, 477. (f) Babu, R. P. K.; Krishnamurthy, S. S.; Nethaji, M. *Tetrahedron: Asymmetry* **1995**, *6*, 427. For structures of metal complexes of diphosphinoamines see: (a) Steil, P.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1989**, *366*, 313. (b) Vogt, R.; Jones, P. G.; Kolbe, A.; Schmutzler, R. *Chem. Ber.* **1991**, *124*, 2705. (c) Reddy, V. S.; Katti, K. V.; Barnes, C. L. *J. Chem. Soc., Chem. Commun.* **1995**, 317. For structures of that contain the P−N−P skeleton and bear inorganic substituents see: Prout, T. R.; Imiolczyk, T. W.; Barthelemy, F.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. *Inorg. Chem.* **1994**, *33*, 1783 and references therein.
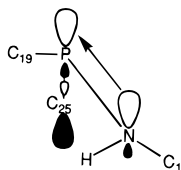
Such a donation is evidenced by the relatively long P(1)−C(25) = 1.843(2) Å bond as compared to the P(1)−C(19) = 1.826(2) Å bond. Since approximate C_s symmetry is observed for the aminophosphines that have been previously characterized by X-ray crystallography,[4] we believe this is the first time that negative hyperconjugation has been evidenced in the structure of an aminophosphine. It is unlikely that electronic factors dictate the observed conformation of **2**. Instead, intramolecular and intermolecular (crystal packing) steric effects are likely the cause. We note that similar negative hyperconjugative bonding is evidenced by the geometries of phosphorus ylides, and in one case three independent molecules were located in the asymmetric unit, each with a different conformation about the P−C(ylide) bond and correspondingly different bond lengths about the phosphorus atom.[19]

Molecular and Electronic Structures of Phosphinoamides. The molecular structure of the phosphinoamide [Ph$_2$PNPh]$^-$ has been determined by single-crystal X-ray diffraction in an earlier study.[4] The structure consists of a dimer with a Li$_2$N$_2$ rhombus (**I**) that is frequently observed for lithium salts of simple
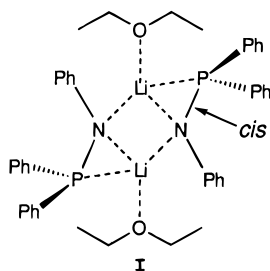

organoamides.[20] The anion exhibits a *cis* conformation about the P−N bond and a weak Li···P interaction is indicated by the orientation of the phosphorus lone pair toward one of the lithium ions of the dimer and a corresponding short Li−P interatomic distance. Since the dimer sits on a crystallographic center of symmetry, the phosphorus atoms of the two anions of the dimer are oriented toward different lithium ions. As discussed in the introduction to this paper, our previous efforts to perform high-level *ab initio* calculations on the model dimer [Li(H$_2$PNH)]$_2$ failed to show a P···Li contact or even the C_i distortion observed in the solid-state structure of [Li(Ph$_2$PNPh)-(OEt$_2$)]$_2$.[4] Indeed, when we tried to detect an energy minimum corresponding to a C_i-distorted structure, with the experimentally-determined geometry of [Li(Ph$_2$PNPh)(OEt$_2$)]$_2$ being assigned

to the [LiNP]$_2$ moiety of the model [Li(H$_2$PNH)]$_2$, the geometry relaxed to one of C_{2h} symmetry that did not have close P···Li contacts. We concluded from these earlier studies that the disagreement between the η^2 binding found experimentally for [Ph$_2$PNPh]$^-$ and the η^1 binding determined computationally for [Li(H$_2$PNH)]$_2$ may be due to delocalization of the negative charge of the real system (not as important for the model anion) or crystal packing effects. We were particularly interested therefore in learning whether P···Li interactions were indicated in the structures of this study.

Compounds [Li(Ph$_2$PNCH$_2$C(CH$_3$)$_3$)(OEt$_2$)]$_2$ (**3**) and [Li(Ph$_2$-PNCH(CH$_3$)$_2$)(OEt$_2$)]$_2$ (**4**) have molecular structures that are very similar to that previously determined for [Li(Ph$_2$PNPh)-(OEt$_2$)]$_2$ (Figures 2 and 3). All three compounds are dimers of *cis* anions that form Li$_2$N$_2$ rhombi. However, whereas [Li(Ph$_2$-PNPh)(OEt$_2$)]$_2$ is centrosymmetric with one apparent P···Li contact per lithium ion (i.e. **I**), compound **4** is best described by structure **II** with two P···Li contacts with the same lithium
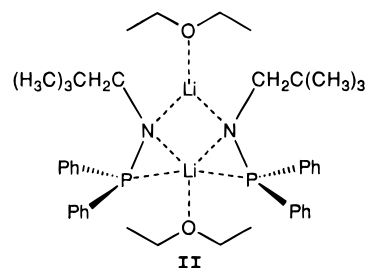
ion, and compound **5** is best described by structure **III** with
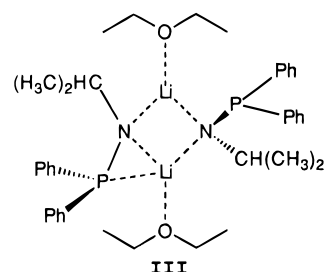
one P···Li contact with one of the lithium ions (Table 7). We conclude from the known dimeric structures that the P−Li dipolar interaction (if there is one at all) must be very weak. While this experimental observation is consistent with our earlier calculations,[5] it does contrast with more recent calculations that indicate P−Li dipolar interactions are important for monomeric complexes of lithium and *cis*-phosphinoamides.[6] However, we cannot test this point at present since there are no known monomeric complexes of lithium and *cis*-phosphinoamides.

(17) For *ab initio* calculations on aminophosphine and derivatives, see ref 5 and the following: (a) Cowley, A. H.; Mitchell, D. J.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224. (b) Gonbeau, D.; Liotard, D.; Pfister-Guillouzo, G. *Nouv. J. Chim.* **1980**, *4*, 228. (c) Barthelat, M.; Mathis, R.; Mathis, F. *J. Mol. Struct.* **1981**, *85*, 351. (d) Galasso, V. *J. Electron Spectrosc. Rel. Phenom.* **1983**, *32*, 359. (e) Magnusson, E. *J. Comput. Chem.* **1984**, *5*, 612. (f) Galasso, V. *J. Chem. Phys.* **1984**, *80*, 365. (g) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969. (h) Sudhakar, P. V.; Lammertsma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1899.

(18) The term "hyperconjugation" was originally coined to denote $\sigma \rightarrow \pi^*$ delocalization, where the symbols σ and π describe the symmetry of localized orbitals. The term "negative hyperconjugation" has been used to denote $\pi \rightarrow \sigma^*$ delocalization. For a discussion of negative hyperconjugation effects see: Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434 and references therein.

(19) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed., Engl.* **1992**, *31*, 99.

(20) (a) Wanat, R. A.; Collum, D. B.; van Duyne, G.; Clardy, J.; DePue, R. T. *J. Am. Chem. Soc.* **1986**, *108*, 3415. (b) Williard, P. G.; Salvino, J. M. *J. Org. Chem.* **1993**, *58*, 1. (c) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1987**, 716. (d) Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 6058. (e) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q.; Williard, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 5100. (f) Setzer, W. N.; Schleyer, P. v. R.; Mahdi, W.; Dietrich, H. *Tetrahedron* **1988**, *44*, 3339. (g) Barr, D.; Berrisford, D. J.; Jones, R. V. H.; Slawin, A. M. Z.; Snaith, R.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1044. (h) Sato, D.; Kawasaki, H.; Shimada, I.; Arata, Y.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 761. (i) Andrews, P. C.; Armstrong, D. R.; Baker, D. R.; Mulvey, R. E.; Clegg, W.; Horsburgh, L.; O'Neil, P. A.; Reed, D. *Organometallics* **1995**, *14*, 427. (j) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285. (k) Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R.; Clegg, W.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1988**, 617.

In contrast to the dimeric structures discussed above, compound **5** is a monomer in the solid state with a *trans* configuration about the P—N bond (Figure 4, **IV**). Monomeric


IV
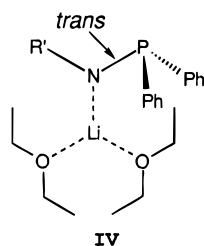
lithium amides are less common than the dimers discussed above, but they can be promoted by employing the following: (1) sterically demanding substituents (as in the case of **5**);[21] (2) ancillary ligands that saturate the coordination environment of the cation;[22] (3) amides that bear nitrogen substituents that can chelate the cation;[23] (4) nitrogen substuents that tie up the nitrogen lone pair.[24] Compound **5** represents the first *trans* phosphinoamide to be isolated and characterized by X-ray crystallography. As expected, there is no short P···Li contact in the structure of **5**. Molecular orbital calculations on the free anions indicate that *trans*-phosphinoamides should have somewhat longer P—N bonds as compared to *cis*-phosphinoamides bonds.[25] According to Schleyer *et al.*, this trend should be preserved for the lithium—phosphinoamide ion pair for which the *cis* isomer appears to have a P···Li contact and the *trans* isomer does not.[26] Since phosphinoamide anions exhibit short P—N bonds as compared to aminophosphine P—N bonds (the result of more extensive negative hyperconjugation for phosphinoamides compared with aminophosphines), the calculations predict ion pairing of lithium ions and the phosphinoamides will result in a lengthening of the P—N bonds as a result of charge localization on the nitrogen atoms (so as to maximize the Li^+N^- coulombic interaction). Table 7 summarizes the P—N bond lengths for all four structurally-characterized phosphinoamides (three of which are *cis* and the fourth is *trans*). While all four compounds bear the same PPh_2 acceptor, they all bear different NR donor groups. Since we do not know the substituent effects of the R-groups on the hyperconjugative interaction and we do not have structures of *cis* and *trans* isomers that bear the same substituent, it is impossible to test the above hypothesis. It is noteworthy, however, that the deviation of the P—N bond lengths for a given complex that has crystallographically-independent (but essentially chemically equivalent) anions and the crystallographic statistical errors are

both greater than the difference in P—N lengths that are predicted for the *cis* and *trans* isomers (ca. 0.01—0.02 Å). So even if *cis* and *trans* isomers of the same compound could be characterized structurally, it is unlikely that a statistically-significant difference in the P—N bond lengths would be observed.

Though a comparison of P—N bond lengths is problematic (*vide supra*), the P—C bond lengths of **5** do indeed evidence $Nn_\sigma \rightarrow P-C\sigma^*$ negative hyperconjugation (cf. the discussion of **2** above). The observed $|C(1)-N(1)-P(1)-C(19)| = 114°$ and $|C(1)-N(1)-P(1)-C(25)| = 146°$ torsion angles, a difference of 32°, indicate the p-type lone pair on the nitrogen (the sum of the angles about N(1) equals $145.7 + 114.6 + 99.4 = 359.7°$) is better oriented for $Nn_\pi \rightarrow P-C(19)\sigma^*$ donation than $Nn_\pi \rightarrow P-C(25)\sigma^*$ donation:
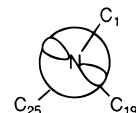
And, this is evidenced by the relatively long $P(1)-C(19) = 1.879(3)$ Å bond length compared to the $P(1)-C(25) = 1.848(3)$ Å bond length. One should note that for compounds **3** and **4** $|C-N-P-C'| \approx |C-N-P-C''|$ (i.e., the anion exhibits local approximate C_s symmetry). For $[Li(Ph_2PNPh)(OEt_2)]_2$, $|C-N-P-C'| = 69°$ and $|C-N-P-C''| = 44°$, a difference of 25°, but the P—C bond lengths are statistically equivalent. However, in the case of $[Li(Ph_2PNPh)(OEt_2)]_2$, the nitrogen atom is not trigonal planar (it is coordinated by P, C, Li, and Li′) but rather exhibits irregular tetrahedral geometry. Interpretation is further complicated by the apparent interactions between the phosphorus and lithium atoms in this compound. Therefore, it is difficult to say in this case whether the orbitals on the nitrogen atom optimally mix with one P—C σ^* orbital or the other.

Conclusion

The earlier report of the first isolated phosphinoamide/iminophosphide anion[4] and the theoretical studies that followed[5,6] raised several questions concerning the influence of negative hyperconjugation on the electronic and molecular structures of the anion. In the present study, we describe the synthesis and crystal structures of three new phosphinoamide/iminophosphide anions. Importantly, one of the (now) four characterized anions exhibits the illusive *trans* geometry. We conclude from a detailed comparison of the molecular structures of these four compounds (together with the molecular structure of an aminophosphine that is also reported herein) that negative hyperconjugation does indeed influence the molecular structures of phosphinoamide/iminophosphide anions. Specifically, P—C bond lengths are shortened and sterically unfavorable *cis* conformations about the P—N bond can be enforced by such orbital interactions (although *trans* conformations are also possible). Dipolar interactions between the phosphine moiety and the lithium ions (as indicated in the earlier structure of a phosphinoamide/iminophosphide anion and predicted by some molecular orbital calculations) do not appear to be significant.

Supporting Information Available: Tables of crystallographic data including data collection and refinement details, all atom parameters, calculated coordinates of the hydrogen atoms, thermal parameters of the non-hydrogen atoms, and distances and angles of the bonded atoms of **2**—**5** (35 pages). Ordering information is given on any current masthead page.

(21) (a) Boese, R.; Klingebeil, U. *J. Organomet. Chem.* **1986**, *315*, C17. (b) Stalke, D.; Klingebeil, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1457. (c) Chen, H.; Bartlett, R. A.; Dias, H. V. R.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1989**, *111*, 4338.

(22) (a) Power, P. P.; Xiaojie, X. *J. Chem. Soc., Chem. Commun.* **1984**, 358. (b) Bartlett, R. A.; Dias, H. V. R.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6921. (c) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1987**, 716.

(23) (a) Engelhardt, L. M.; Jacobsen, G. E.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1011. (b) Klingebeil, U.; Stalke, D.; Vollbrecht, S. *Z. Naturforsch., B* **1992**, *47*, 27.

(24) In this example there is a coordinatively unsaturated (6-electron) borane (σ/π bound to the nitrogen) that ties up the nitrogen lone pair thereby making it an ineffectual donor to the lithium ion: Chen, H.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1990**, *112*, 1048.

(25) For the free anions, we calculate for *trans*-$[H_2PNH]^-$ P—N = 1.649 Å and for *cis*-$[H_2PNH]^-$ P—N = 1.638 Å (see ref 5). Schleyer *et al.* obtain similar numbers (see ref 6): for *trans*-$[H_2PNH]^-$ P—N = 1.674 Å and for *cis*-$[H_2PNH]^-$ P—N = 1.661 Å.

(26) For the ion pairs, Schleyer *et al.* calculate for *trans*-$[H_2PNH]^-$ P—N = 1.707 Å and for *cis*-$[H_2PNH]^-$ P—N = 1.685 Å (see ref 6).