Inorg. Chem. **2000,** *39,* 4981−4984

Dimeric Bridged and Chelated Alkali Metal (Li and Na) Bis(iminophosphorano)methanide Complexes with Contrasting Structures

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Received November 24, 1999

Introduction

The coordination chemistry of the alkali metal elements continues to attract considerable attention because of the extensive synthetic utility of such compounds.[1] Recent interest has focused on the structural aspects, providing detailed metrical parameters to contribute to our understanding of structure and bonding in these species.[2] While group 1 complexes of bisphosphinomethanide ligands are well-known,[3] related complexes of their doubly oxidized derivatives, $CH_2(R_2P{=}E)_2$ (E = NR, O, S, Se, Te), are scarce,[4,5] despite the extensive transition metal chemistry of this latter system.[6] There are therefore few structural reports of alkali metal complexes of the type $[MCH(R_2P{=}E)_2]$ (where M is a group 1 element and E = NR, O, S, Se, Te) containing singly deprotonated ligands, but this is perhaps understandable because they are generally prepared in situ for subsequent use in transmetalation reactions. Recently, however, we and others have characterized the doubly deprotonated methylenebis(phosphinimine) ligand in the form of the dilithiated salt[5,7] and we have further developed the transition metal chemistry of deprotonated $CH_2(R_2P{=}NR)_2$ ligands.[8] In this context we describe herein the synthetic and structural details of the dimeric lithium and sodium bis(iminophosphorano)methanide complexes. These display two different and contrasting bridging modes of coordination of the monoanionic ligand $CH(R_2P{=}NR)_2^-$, illustrating the differences in character between Li and Na. These complexes represent the first structurally characterized examples of group 1 complexes of the monomethanide series of ligands $CH(R_2P{=}E)_2^-$ (E = NR, O, S, Se, Te).

Experimental Section

General Methods. All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox with an efficient recirculator. The bisphosphinimine, $CH_2(Ph_2P{=}NSiMe_3)_2$,[9] was prepared according to the literature procedure, and $MN(SiMe_3)_2$ (M = Li and Na) compounds were obtained from Aldrich. Solvents were dried and distilled under argon prior to use. Hexane and toluene were distilled from Na−K alloy and Na, respectively. NMR solvents benzene-d_6 and toluene-d_8 were freshly transferred from Na−K alloy under vacuum. Shifts were determined with reference to the deuterium signal of the solvent employed. The ^{1}H NMR chemical shifts are reported in ppm from external Me_4Si, and the ^{31}P NMR spectra are reported in ppm from external 85% H_3PO_4. Positive values indicate downfield shifts. Infrared spectra were recorded on a Nicolet 7199 infrared spectrometer.

Preparation of $[Li\{\mu_2\text{-}\kappa N,\kappa C,\kappa N'\text{-}CH(Ph_2P{=}NSiMe_3)_2\}]_2$, 2. To a colorless solution of $CH_2(Ph_2P{=}NSiMe_3)_2$, **1** (0.200 g, 0.36 mmol), in 10 mL of toluene was added $LiN(SiMe_3)_2$ (0.060 g, 0.36 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 h, and then the solution was concentrated to a small volume and stored at room temperature. The colorless crystals that grew over 2 days were then collected by filtration and washed with a few milliliters of hexane. Yield, calculated for **2**·toluene: 0.162 g, 0.13 mmol, 74.0%. The transparent crystals gradually lost solvent and became opaque when dried under vacuum. IR (Nujol mull), cm^{-1}: 1437 m, 1242 m, 1166 bs, 1145 s, 1097 s, 1004 w, 991 m, 853 s, 829 s, 774 w, 746 s, 716 m, 696 s, 603 w, 517 s. ^{1}H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.67 (m, *o*-phenyl), 7.05 (m, *m*-phenyl and *p*-phenyl), 1.68 (bt, P−CH−P methine), 0.09 (s, CH_3Si methyl). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6,

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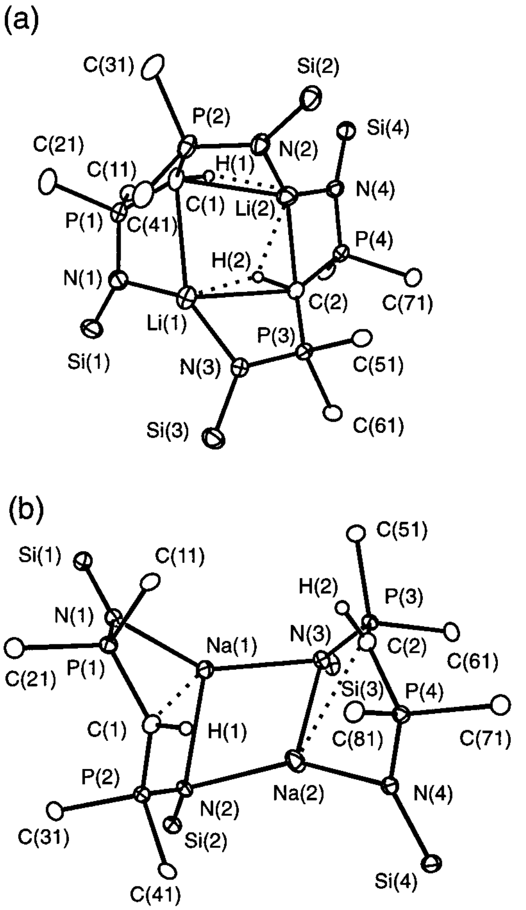


Figure 1. Perspective ORTEP[24] plots of (a) $[\mathrm{Li}\{\mu_2\text{-}\kappa N,\kappa C,\kappa N'\text{-CH}(\mathrm{Ph_2P{=}NSiMe_3})_2\}]_2$, **2**, and (b) $[\mathrm{Na}\{\mu_2\text{-}\kappa N,\kappa N'\text{-CH}(\mathrm{Ph_2P{=}NSiMe_3})_2\}]_2$, **3**, showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The phenyl (except the *ipso*-phenyl) carbon atoms, the methyl groups on silicon, and all hydrogen atoms (except the methine hydrogen atoms) have been omitted for clarity. The methine hydrogen atoms are shown with arbitrarily small thermal parameters.

298 K): δ 141.0 (m, *ipso*-phenyl), 131.3 (t, $^2J_{\mathrm{PC}} = 5.1$ Hz, *o*-phenyl), 129.5 (s, *p*-phenyl), 127.8 (t, $^3J_{\mathrm{PC}} = 5.0$ Hz, *m*-phenyl), 22.9 (t, $^1J_{\mathrm{PC}} = 125.1$ Hz, P−CH−P methine), 4.2 (s, $\mathrm{CH_3Si}$ methyl). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.9 MHz, $\mathrm{C_6D_6}$, 298 K): δ 17.4. $^7\mathrm{Li}\{^1\mathrm{H}\}$ NMR (155.5 MHz, $\mathrm{C_6D_6}$, 298 K): δ 0.70 s (with reference to 0.1 M LiCl in $\mathrm{D_2O}$). Anal. Calcd for $[\mathrm{Li}\{\mu^2\text{-CH}(\mathrm{R_2P{=}NSiMe_3})_2\text{-}\kappa^3 C,N,N'\}]_2$, $\mathrm{C_{62}H_{78}Li_2N_4P_4Si_4}$: C, 65.93; H, 6.96; N, 4.96. Found: C, 65.50; H, 7.06; N, 4.91.

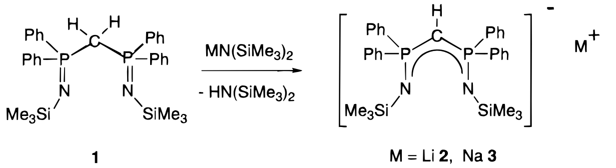
Preparation of $[\mathrm{Na}\{\mu_2\text{-}\kappa N,\kappa N'\text{-CH}(\mathrm{Ph_2P{=}NSiMe_3})_2\}]_2$, 3. To a colorless solution of $\mathrm{CH_2(Ph_2P{=}NSiMe_3)_2}$, **1** (0.300 g, 0.54 mmol), in 10 mL of toluene was added $\mathrm{NaN(SiMe_3)_2}$ (0.098 g, 0.54 mmol) at room temperature. The reaction mixture was stirred at room temperature for 3 h, and then the solution was concentrated to half of the original volume. The solution was stored at −15 °C, and in 2 days pale-yellow crystals were grown. These were collected by filtration, washed with a few milliliters of hexane and dried under vacuum. Yield, calculated for **3**·toluene: 0.210 g, 0.17 mmol, 64.8%. The crystals slowly lost solvent when stored. IR (Nujol mull), cm^{-1}: 1434 s, 1256 s, 1243 s, 1218 bs, 1173 m, 1120 s, 1093 s, 1070 m, 1029 w, 1001 w, 970 s, 863 s, 833 s, 779 m, 745 s, 738 s, 716 s, 700 s, 671 w, 649 m, 599 m, 587 w, 557 s, 512 s, 500 m. ^{1}H NMR (400.1 MHz, $\mathrm{C_6D_6}$, 298 K): δ 7.70 (m, *o*-phenyl), 7.05 (m, *m*-phenyl and *p*-phenyl), 7.1−6.9 (m, toluene phenyl), 2.10 (s, toluene methyl), 1.69 (t, $^2J_{\mathrm{PH}} = 5.0$ Hz, P−CH−P methine), 0.15 (s, $\mathrm{CH_3Si}$ methyl). $^{13}\mathrm{C}\ \{^1\mathrm{H}\}$ NMR (100.6 MHz, $\mathrm{C_6D_6}$, 298 K): δ 142.2 (m, *ipso*-phenyl), 137.8 (s, toluene *ipso*-phenyl), 131.3 (b. s, *o*-phenyl), 129.2 (s, toluene *o*-phenyl), 129.1 (s, *p*-phenyl), 128.5 (s, toluene *m*-phenyl), 127.7 (b. s, *m*-phenyl), 125.6 (s, toluene *p*-phenyl), 27.5 (t, $^1J_{\mathrm{PC}} = 128.8$ Hz, P−CH−P methine), 20.8 (s, toluene methyl), 4.7 (s, $\mathrm{CH_3Si}$ methyl). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (161.9 MHz, $\mathrm{C_6D_6}$, 298 K): δ 15.1. Anal. Calcd for $[\mathrm{Na}\{\mu^2\text{-CH}(\mathrm{R_2P{=}NSiMe_3})_2\text{-}\kappa^3 N,N,N'\}]_2\cdot$0.5 toluene, $\mathrm{C_{65.5}H_{82}Na_2N_4P_4Si_4}$: C, 65.15; H, 6.84; N, 4.64. Found: C, 65.01; H, 7.07; N, 4.75.

Table 1. Crystallographic Data for **2**·Toluene and **3**·Toluene

	2·Toluene		
chemical formula	$\mathrm{C_{69}H_{86}Li_2N_4P_4Si_4}$	fw	1221.54
a, Å	13.5173(12)	space group	$P2_1/n$ (No. 14)
b, Å	21.335(2)	temp, °C	−80
c, Å	24.581(2)	λ (Mo Kα), Å	0.71073^a
β, deg	91.086(2)	ρ_{calc}, g cm^{-3}	1.145
V, Å^3	7087.7(11)	μ (M$_\mathrm{o}$), mm^{-1}	0.215
Z	4	R1 [$F_\mathrm{o}^2 \geq 2\sigma(F_\mathrm{o}^2)$]	0.0807
		wR2 [$F_\mathrm{o}^2 \geq -3\sigma(F_\mathrm{o}^2)$]	0.2281
	3·Toluene		
chemical formula	$\mathrm{C_{69}H_{86}N_4Na_2P_4Si_4}$	fw	1253.64
a, Å	12.3907(10)	space group	$P\bar{1}$ (No. 2)
b, Å	14.5179(11)	temp, °C	−80
c, Å	21.3739(14)	λ (Mo Kα), Å	0.71073^a
α, deg	76.1521(15)	ρ_{calc}, g cm^{-3}	1.164
β, deg	86.5411(16)	μ (M$_\mathrm{o}$), mm^{-1}	0.226
γ, deg	73.2969(13)	R1 [$F_\mathrm{o}^2 \geq 2\sigma(F_\mathrm{o}^2)$]^b	0.0656
V, Å^3	3575.5(5)	wR2 [$F_\mathrm{o}^2 \geq -3\sigma(F_\mathrm{o}^2)$]^b	0.1861
Z	2		

^{a} Graphite-monochromated. ^{b} $R_1 = \Sigma||F_\mathrm{o}| - |F_\mathrm{c}||/\Sigma|F_\mathrm{o}|$; $\mathrm{wR}_2 = [\Sigma w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2/\Sigma w(F_\mathrm{o}^4)]^{1/2}$.

Scheme 1



X-ray Crystallography. The structures of **2**·toluene and **3**·toluene were determined by single-crystal X-ray analysis. The X-ray data were collected on a Bruker P4/RA/SMART1000 diffractometer. The structure solutions were obtained using SHELX-86[10] and DIRDIC-96 direct methods analysis and refined using full-matrix least-squares on F^2 using SHELX-93.[11] All the non-hydrogen atoms were refined anisitropically. The hydrogen atoms were assigned calculated positions. Experimental details are listed in Table 1.

Results and Discussion

Treatment of the bis(iminophosphorano)methane, $\mathrm{CH_2(Ph_2P{=}NSiMe_3)_2}$, **1**,[9] with 1 equiv of $\mathrm{MN(SiMe_3)_2}$ (M = Li or Na) in toluene at room temperature gave the respective bis(iminophosphorano)methanide complex $[\mathrm{Li}\{\mu_2\text{-}\kappa N,\kappa C,\kappa N'\text{-CH}(\mathrm{Ph_2P{=}NSiMe_3})_2\}]_2$, **2**, or $[\mathrm{Na}\{\mu_2\text{-}\kappa N,\kappa N'\text{-CH}(\mathrm{Ph_2P{=}NSiMe_3})_2\}]_2$, **3**, as a result of elimination of bis(trimethylsilyl)amine (Scheme 1). The products were obtained in good yields as colorless (**2**) or pale-yellow (**3**) crystals. It is noteworthy that the reaction of **1** with 2 equiv of the same alkali metal amide reagents (Li or Na) in toluene did not, in either case, yield the doubly deprotonated methandiide complex (NMR evidence) even using long (4 days) reflux conditions. These conditions were more severe than those

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used earlier to prepare $Li_2C(Ph_2P{=}NSiMe_3)_2$ from alkyllithium reagents,[5,7] and we attribute the difference in behavior to the less basic nature of the alkali metal amide reagents.

Analytical, infrared, and multinuclear NMR spectroscopic data of **2** and **3** were consistent with the formation of bis(iminophosphorano)methanide complexes. The X-ray structural analysis revealed the dimeric nature of the products each with a different mode of coordination of the ligand (vide infra). Solution NMR measurements, however, showed only minor differences in the chemical shift values and multiplicity patterns for the methine group of the P−C−P backbone, suggesting the possibility of almost identical, dynamically averaged structures in solution.

The solid-state IR spectra show intense $\nu_{P=N}$ absorptions around 1166 cm^{-1} for **2** and 1218 cm^{-1} for **3**. These absorptions occur at a lower energy than those in the parent compound **1** (1270 cm^{-1}), as is to be expected given the slightly elongated, delocalized phosphorus−nitrogen bond that is present in the anion. In solution the $\nu_{P=N}$ absorptions are shifted from the solid-state values (one increases and one decreases) so that the solution IR $\nu_{P=N}$ bands (1195 cm^{-1} (**2**), 1206 cm^{-1} (**3**)) ultimately become quite similar to each other. These differences also suggest that the solid-state structures are not preserved in solution as was implied by the NMR behavior and also that the averaged structures in solution are similar to each other in contrast to the structural differences observed in the solid state. The methine proton ^1H NMR resonances ($\delta \approx 1.68$ ppm) are observed as triplets due to the coupling of two equivalent phosphorus atoms. The corresponding methine carbon resonances in the $^{13}C\{^1H\}$ APT[12] NMR spectra appear as negative triplet signals, clearly indicating that these carbon atoms carry only one proton. The chemical shifts {at δ 22.9 (**2**) and 27.5 (**3**)} are slightly shifted upfield from the corresponding methylene carbon signal of **1** (δ 37.7). Complexes **2** and **3** each show one sharp singlet in the $^{31}P\{^1H\}$ NMR spectrum shifted downfield by about 15−20 ppm relative to **1**, showing that the phosphorus centers in each case are chemically equivalent in solution.

The molecular structures of $[Li\{\mu_2\text{-}\kappa N,\kappa C,\kappa N'\text{-}CH(Ph_2P{=}NSiMe_3)_2\}]_2$, **2**, and $[Na\{\mu_2\text{-}\kappa N,\kappa N'\text{-}CH(Ph_2P{=}NSiMe_3)_2\}]_2$, **3**, are shown in parts a and b of Figure 1, respectively, and selected bond distances and angles are listed in Table 2. The structures are, in each case, dimeric. In **2**, each central methanide carbon bridges two lithium atoms to form a twisted four-membered ring core structure that contains two tetracoordinated lithium atoms {Li(1) and Li(2)} and two pentacoordinated methanide carbon bridging atoms {C(1) and C(2)}. Each of the four edges are further extended to form four nearly planar four-membered rings containing carbon, phosphorus, nitrogen, and lithium. One opposing set of planes projects upward, and the other projects downward relative to the central plane. The planar Li−C−P−N four-membered ring structures are comparable to similar frames formed by the closely related monophosphinimine lithium complex $[Li(SiMe_3N{=}P(Ph_2){-}CHSiMe_3)(Et_2O)_2]$[13] but with slightly different bond parameters. In particular, in the present case (**2**), the Li−C bond distances found are longer and not uniform throughout the rings. Also, perhaps surprisingly, one of the lithium atoms shows longer lithium−carbon bond distances {Li(1)−C(1) = 2.737(11), Li(1)−C(2) = 2.784(10) Å} than for the other {Li(2)−C(1) = 2.569(10), Li(2)−C(2) = 2.370(9) Å}. The methine hydrogen atoms lie close to the lithium atoms {the nonbonded distances are Li(1)···H(2) = 2.11 Å, Li(1)···H(1) = 3.02 Å, Li(2)···H(2) = 2.21 Å, Li(2)···H(1) = 2.02 Å; and the angles are Li(1)−C(2)−H(2) = 37.7°, Li(1)−C(1)−H(1) = 97.7°, Li(2)−C(2)−H(2) = 68.5°, Li(2)−C(1)−H(1) = 45.5°}. These distances and angles indicate strong agostic interactions between Li and C−H.[14] The fact that Li(2) has two strong agostic interactions and Li(1) only one rationalizes the difference in Li−C bond lengths. Both of these Li−C bond length values are longer than the usual Li−C distances in alkyllithium complexes[15] and slightly longer than the values observed for phosphorus-substituted carbanions.[16] The Li−N distances {Li(1)−N(1) = 2.000(10) Å, Li(1)−N(3) = 1.999(9) Å, Li(2)−N(2) = 1.997(9) Å, Li(2)−N(4) = 2.050(9) Å} lie in the range generally observed for lithium amides[17] and for delocalized systems such as the alkyllithium complexes of monophosphinimines,[18] lithium aminidinates,[19] and lithium guanidinates.[20]

Table 2. Selected Metrical Parameters for Complexes **2** and **3**

atoms	distances (Å)	atoms	angles (deg)
(a) $[Li\{\mu_2\text{-}\kappa N,\kappa C,\kappa N'\text{-}CH(Ph_2P{=}NSiMe_3)_2\}]_2$, **2**			
C(1)−Li(1)	2.737(11)	P(1)−C(1)−P(2)	133.7(3)
C(1)−Li(2)	2.569(10)	P(3)−C(2)−P(4)	133.8(3)
C(2)−Li(1)	2.784(10)	P(1)−N(1)−Li(1)	102.7(4)
C(2)−Li(2)	2.370(9)	P(2)−N(2)−Li(2)	102.3(3)
N(1)−Li(1)	2.000(10)	P(3)−N(3)−Li(1)	108.1(3)
N(2)−Li(2)	1.997(9)	P(4)−N(4)−Li(2)	94.6(3)
N(3)−Li(1)	1.999(9)		
N(4)−Li(2)	2.050(9)		
P(1)−C(1)	1.730(5)		
P(3)−C(2)	1.743(5)		
P(1)−C(11)	1.812(5)		
P(3)−C(51)	1.818(5)		
P(1)−N(1)	1.583(4)		
P(3)−N(3)	1.593(4)		
(b) $[Na\{\mu_2\text{-}\kappa N,\kappa N'\text{-}CH(Ph_2P{=}NSiMe_3)_2\}]_2$, **3**			
C(1)···Na(1)	2.966(4)	P(1)−C(1)−P(2)	128.0(2)
C(2)···Na(2)	3.017(4)	P(3)−C(2)−P(4)	132.1(2)
N(1)−Na(1)	2.338(4)	P(1)−N(1)−Na(1)	103.4(2)
N(2)−Na(1)	2.524(3)	P(2)−N(2)−Na(1)	100.0(1)
N(3)−Na(1)	2.483(4)	P(3)−N(3)−Na(2)	98.3(2)
N(2)−Na(2)	2.534(4)	P(4)−N(4)−Na(2)	103.3(2)
N(3)−Na(2)	2.535(4)	P(2)−N(2)−Na(2)	97.0(2)
N(4)−Na(2)	2.334(4)	P(3)−N(3)−Na(1)	124.1(2)
P(1)−C(1)	1.725(4)		
P(3)−C(2)	1.716(4)		
P(1)−C(11)	1.829(4)		
P(3)−C(51)	1.822(4)		
P(1)−N(1)	1.573(3)		
P(3)−N(3)	1.604(3)		

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The contrasting structure of **3** derives from the fact that the sodium atoms are bridged by nitrogen rather than carbon as in **2**, thereby reflecting the chemical difference between Li and Na. The core of **3** consists of a twisted four-membered ring containing two tricoordinated sodium atoms and two imine nitrogen bridging atoms {N(2) and N(3)}. Two of the opposite edges of this central ring are further extended to form two six-membered ring structures (in contrast to the four-membered rings formed in **2**) that occur in twisted boat conformations containing the Na(2), N(3), P(3), C(2), P(4), N(4) atoms and the Na(1), N(2), P(2), C(1), P(1), N(1) atoms. The distances between the sodium and the carbon atoms {Na(1)···C(1) = 2.966(4) Å, Na(2)···C(2) = 3.017(4) Å} are longer than the normal Na−C distances observed for alkyl or aryl complexes;[21] however, the folding of the six-membered ring edge atoms {C(1), C(2)} toward the sodium suggests the presence of weak interactions between them. Also, in contrast to the lithium complex **2**, the M−C−H angles in **3** are much wider, and therefore, the hydrogen atoms of the methine centers point away from the sodium atoms {Na(1)···H(1) = 3.46 Å, Na(2)···H(2) = 3.60 Å; Na(1)−C(1)−H(1) = 113.6°, Na(2)−C(2)−H(2) = 120.7°}. As a result, there are no significant agostic interactions. The bridging Na−N distances {Na(1)−N(2) = 2.524(3) Å, Na(2)−N(2) = 2.534(4) Å, Na(1)−N(3) = 2.483(4) Å, Na(2)−N(3) = 2.535(4) Å} are slightly longer than the terminal Na−N distances {Na(1)−N(1) = 2.338(4) Å, Na(2)−N(4) = 2.334(4) Å}. The terminal distances are shorter than the Na−N bond distances observed in normal neutral amine coordinated complexes[22] and lie in the range as reported for sodium amide derivatives.[17]

In both complexes (**2** and **3**), the P−C bond distances of the P−C−P backbone are shortened and the P−N bonds are lengthened compared to those of the free ligand, **1**.[23] In addition, a shorter than expected M−N bond for a neutral amine coordination suggests partial π-electron delocalization in both the four-membered C, P, N, Li rings of **2** and the six-membered Na, N, P, C, P, N rings of **3**.

Thus, we have two novel dimeric bis(iminophosphorano)methanide complexes, one of lithium and one of sodium with unique coordination geometries. In both cases the structure shows evidence of extensive electron delocalization within the metallacyclic ring. These complexes are the first examples of structurally defined, singly deprotonated alkali metal complexes of methanide ligands $[\mathrm{CH(R_2P{=}E)_2}]^-$ (E = NR, O, S, Se, Te). Our current studies are exploring the chemical applications of these species.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, NOVA Chemicals Corp., and the University of Alberta for financial support.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[\mathrm{Li}\{\mu_2\text{-}\kappa N,\kappa C,\kappa N\text{-}\mathrm{CH(Ph_2P{=}NSiMe_3)_2}\}]_2$, **2**, and $[\mathrm{Na}\{\mu_2\text{-}\kappa N,\kappa N\text{-}\mathrm{CH(Ph_2P{=}NSiMe_3)_2}\}]_2$, **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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