Organometallics **2001,** *20,* 1451−1455 1451

Monomeric Alkali Metal (Li, Na, K) Complexes of Bis(iminophosphorano)methanides

Ruppa P. Kamalesh Babu, Kasani Aparna, Robert McDonald,[†] and
Ronald G. Cavell*

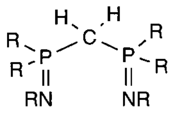
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received November 20, 2000

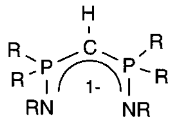
The reaction of the bis(iminophosphorano)methane, $\mathrm{CH_2(Cy_2P{=}NSMe_3)_2}$ (**1**), with methyllithium (even with excess of the latter) gave the monomeric methanide complex $[\mathrm{Li\{HC(Cy_2P{=}NSiMe_3)_2}\text{-}\kappa C,\kappa N,\kappa N'\}(\mathrm{OEt_2})]$ (**2**) in a good yield. The reaction of $\mathrm{H_2C(Ph_2P{=}NSiMe_3)_2}$ (**2**) with equimolar equivalents of NaH or KH in THF solvent yielded monomeric $[\mathrm{M\{HC(Ph_2P{=}NSiMe_3)_2}\text{-}\kappa N,\kappa N'\}(\mathrm{THF})_2]$ (M = Na, **4**; K, **5**) with evolution of hydrogen gas. The crystal structures of each complex show the development of a unique coordination sphere around each alkali metal. In the lithium complex, **3**, the central carbon atom of the ligand is bound to the metal, but such interaction does not occur in the case of either the Na, **4**, or the K, **5**, complexes. However in the potassium complex, one of the phenyl rings of the ligand is π-coordinated to the metal.

Introduction

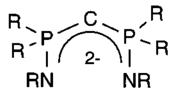
Alkali metal organometallic compounds exhibit a pronounced tendency to form oligomeric aggregates, and as a result few monomeric structures have been observed in comparison with the large number of oligomeric species. Dimeric, trimeric, tetrameric, and ladder type structures are found throughout the group depending on the spatial demands of the substituent organic groups, the ionic radius of the metal ion, and the extent of solvation.[1] Herein we report monomeric lithium, sodium, and potassium complexes of bis(iminophosphorano)methane ligands. A rich and diverse transition metal chemistry has been developed for these bis(iminophosphorano)methane ligands, which may bind as neutral (**A**) or monoanionic (**B**) species.[2−9] Recently we have reported an interesting series of transition metal and lanthanide complexes wherein the backbone methylene linkage of these ligand systems has been doubly deprotonated (e.g., as **C**), and so the ligand is formally dianionic.[10−15] This dianionic form of the ligands either yields a terminal multiple metal−carbon (carbene) bond from the metal to the central carbon[10,11,13−15] or, alternatively, forms carbene complexes in which the central carbon bridges two metals.[12]



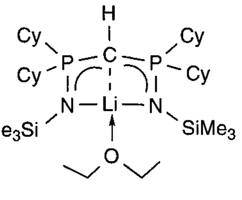
A



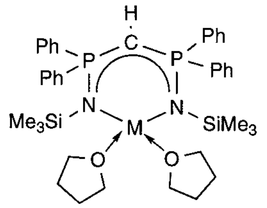
B



C



3



M = Na **4**, K **5**

Several routes have been used to prepare transition metal complexes of the anionic members of this ligand

---

[†] University of Alberta X-ray structure determination laboratory.

* To whom correspondence should be addressed. Tel: 780-492-5310. Fax: 780-492-8231. E-mail: Ron.Cavell@ualberta.ca.

(1) (a) Beswick, M. A.; Wright, D. S. In *Comprehensive Organometallic Chemistry (II)*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 1; pp 1−34. (b) Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339−346. (c) Hoffmann, D.; Bauer, W.; Hampel, F.; Hommes, N. J. R. v. E.; Schleyer, P. v. R.; Otto, P.; Pieper, U.; Stalke, D.; Wright, D. S.; Snaith, R. *J. Am. Chem. Soc.* **1994**, *116*, 528−536. (d) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47−142. (e) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169−278. (f) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353−451. (g) Lucht, B. L.; Bernstein, M. P.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 10707−10718.

(2) Avis, M. W.; van der Boom, M. E.; Elsevier: C. J.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1997**, *527*, 263−276.

(3) Imhoff, P.; Gülpen, J. H.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Elsevier, C. J. *Inorg. Chim. Acta* **1995**, *235*, 77−88.

(4) Avis, M. W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Spek, A. L.; Elsevier, C. J. *Inorg. Chem.* **1995**, *34*, 4092−4105.

(5) Imhoff, P.; Elsevier, C. J. *J. Organomet. Chem.* **1989**, *361*, C61−C65.

(6) Imhoff, P.; van Asselt, R.; Elsevier, C. J.; Zoutberg, M. C.; Stam, C. H. *Inorg. Chim. Acta* **1991**, *184*, 73−87.

(7) Avis, M. W.; Vrieze, K.; Ernsting, J. M.; Elsevier, C. J.; Veldman, N.; Spek, A. L.; Katti, K. V.; Barnes, C. L. *Organometallics* **1996**, *15*, 2376−2392.

(8) Imhoff, P.; van Asselt, R.; Ernsting, J. M.; Vrieze, K.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Kentgens, A. P. M. *Organometallics* **1993**, *12*, 1523−1536.

(9) Avis, M. W.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chem.* **1996**, *35*, 1518−1528.

(10) Cavell, R. G.; Kamalesh Babu, R. P.; Kasani, A.; McDonald, R. *J. Am. Chem. Soc.* **1999**, *121*, 5805−5806.

(11) Kamalesh Babu, R. P.; McDonald, R.; Decker, S. A.; Klobukowski, M.; Cavell, R. G. *Organometallics* **1999**, *18*, 4226−4229.

(12) Kasani, A.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **1999**, 1993−1994.

(13) Aparna, K.; Ferguson, M.; Cavell, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 726−727.

(14) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Chem. Commun.* **2000**, 481−482.

(15) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Organometallics* **2000**, *19*, 3462−3465.

10.1021/om000982g CCC: $20.00
Publication on Web 03/08/2001

system. In general, the most common avenue is the preliminary, in situ, preparation of the deprotonated (generally lithiated) backbone species, which is then reacted, without isolation, with metal halides. Rarely, therefore, have the structures of the intermediate alkali metal bis(iminophosphorano)methane compounds themselves been characterized. The structural details of a few alkali metal monoanionic bis-phosphine derivatives of the type $M\{R_2PC(H)PR_2\}$ wherein the phosphorus atom is trivalent have been reported.[16] We and others have recently reported the structure of the dilithium salt $Li_2\{C(Ph_2P{=}NSiMe_3)_2\}$,[17,18] and we also recently reported the structures of the diverse, dimeric, Li and Na bis(phosphoranimine) complexes.[19]

Herein, we report a detailed study of the deprotonation of the methylene backbone in bis(iminophosphorano)methane compounds and the first crystal structures of monomeric lithium, sodium, and potassium complexes of the monoanionic forms of the bis(iminophosphorano)methanide ligands, $\{HC\{R_2P{=}NSiMe_3\}_2{}^-\}$ (R = Cy or Ph). The structural trends for these alkali metals are discussed and compared with the previous dimeric derivatives of these same systems,[19] the dianionic, dimeric Li complex,[17,18] and also with the free ligand structures. These compounds represent the first examples of structural characterization of monomeric group-1A metal complexes of the entire $H_2C(R_2P{=}X)_2$ (X = O, S, Se, NR) series of ligand systems.

Experimental Section

All experimental manipulations were performed under rigorously anaerobic conditions using Schlenk techniques or an argon-filled glovebox. Solvents were dried and distilled under argon prior to use. Hexane, THF, and toluene were distilled from Na−K alloy and Na, respectively. NMR solvents benzene-d_6 and toluene-d_8 were freshly vacuum transferred from Na−K alloy. Commercial (Aldrich) supplies of dppm and MeLi were used as obtained. Sodium and potassium hydrides obtained as mineral oil dispersions were washed with hexane and dried before use. The preparation of $H_2C\{Cy_2P{=}NSiMe_3\}_2$ (**1**) is analogous to the preparation of the phenyl-substituted ligand $H_2C\{Ph_2P{=}NSiMe_3\}_2$ **2**.[20] NMR chemical shifts were determined with reference to the deuterium signal of the solvent employed. The ^1H 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 reflect downfield shifts. Infrared spectra were recorded on a Nicolet 7199 infrared spectrometer.

$[Li\{HC(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa N'\}(OEt_2)]$, 3. Methyllithium (1.4 M solution in diethyl ether, 0.49 mL, 0.69 mmol) was added to a solution of $H_2C\{Cy_2P{=}NSiMe_3\}_2$ (**1**) (0.2 g, 0.34 mmol) in 5 mL of toluene at room temperature with stirring. After 3 days stirring the volume of the solution was reduced to nearly half of the original volume by evaporation under vacuum, and the flask was allowed to stand at −15 °C for 48 h, whereupon colorless crystals formed. Yield: 0.145 g, 63.8%. IR (Nujol mull): 1269 m, 1242 s, 1223 s, 1211 s, 1197 s, 1167 s, 1151 s, 1113 m, 1071 w, 1007 m, 987 s, 893 m, 875 m, 850 s, 822s, 777 m, 752 s, 730 w, 666 m, 641 w, 601 m, 562 s. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 3.39 (q, 4 H, CH_2, ether), 2.05−1.24 (m, 44 H, CH_2 and CH, cyclohexyl), 1.09 (t, 6 H, CH_3, ether), 0.03 (s, 18 H, CH_3, CH_3Si), −0.02 (s, 1 H, CH, P−CH−P). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 65.2 (s, 2 C, CH_2, ether), 41.2 (d, $^1J_{PC}$ = 63.0 Hz, 4 C, *ipso* cyclohexyl), 27.5 (m, 12 C, *ortho* and *para* cyclohexyl), 27.0 (s, 8 C, *meta* cyclohexyl), 15.1(s, 2 C, CH_3, ether), 5.3 (t, $^1J_{PC}$=128.6 Hz, 1 C, CH, P−CH−P), 5.08 (s, 6 C, CH_3Si). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 36.7 (2 P). Anal. Calcd for $C_{35}H_{73}LiN_2OP_2Si_2$: C, 63.43; H, 11.10; N, 4.23. Found: C, 63.19; H, 10.97 N, 4.30.

$[M\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N'\}(THF)_2]$ (M = Na, **4**; K, **5**). To a solution of $H_2C(Ph_2P{=}NSiMe_3)_2$ (**2**) (0.54 mmol) in 10 mL of THF was added 1 equiv of MH (0.54 mmol) with stirring. The reaction mixture slowly became a clear solution. After 24 h, the solution was filtered and concentrated to a low volume. The resultant solution was then cooled to −15 °C for 2 days, whereupon colorless crystals deposited, which were isolated by filtration and dried. When stored, these crystals slowly lost solvent and became opaque.

$[Na\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N\}(THF)_2]$, 4. Yield: 0.31 g, 80%. IR (Nujol mull): 1434 s, 1251 s, 1193 s, 1120 m, 1104 s, 1050 s, 1030 m, 1000 w, 967 s, 894 m, 851 s, 821 s, 739 s, 707 s, 696 s, 667 m, 595 m, 557 m, 530 s, 513 s, 488 s. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.92 (m, phenyl), 7.08 (m, phenyl), 3.50 (m, 8H, CH_2-THF), 1.95 (b.s, 1 H, CH, P−CH−P), 1.30 (m, 8H, CH_2-THF), 0.15 (s, 18 H, CH_3, CH_3Si). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 143.0 (m, 4 C, *ipso* phenyl), 131.8 (s, 8 C, *ortho* phenyl), 129.0 (s, 4 C, *para* phenyl), 128.2 (s, 8 C, *meta* phenyl), 68.0 (s, 4 C, CH_2-THF), 26.6 (t, 1 C, $^1J_{PC}$ = 131.1 Hz, CH, P−CH−P), 25.6 (s, 4 C, CH_2-THF), 4.5 (s, 6 C, CH_3, CH_3Si). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 15.2 (2 P). Anal. Calcd for $Na\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N'\}(THF)_2$, $C_{39}H_{55}N_2NaO_2P_2Si_2$: C, 64.61; H, 7.65; N, 3.84. Found: C, 63.98; H, 7.39; N, 3.82.

$[K\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N'\}(THF)_2]$, 5. Yield: 0.29 g, 72%. IR (Nujol mull): 1434 m, 1258 s, 1241 s, 1209 m, 1173 s, 1161 s, 1098 m, 1069 w, 1028 w, 1002 w, 978 m, 861 m, 844 m, 828 s, 777 w, 746 m, 737 m, 712 m, 699 s, 666 w, 647 w, 590 m, 557 m, 511 m. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 7.95 (m, phenyl), 7.16 (m, phenyl), 7.08 (m, phenyl), 3.54 (m, 8H, CH_2-THF), 1.82 (t, $^2J_{PH}$ = 2.8 Hz, 1 H, CH, P−CH−P), 1.40 (m, 8H, CH_2-THF), 0.06 (s, 18 H, CH_3, CH_3Si). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 144.0 (m, 4 C, *ipso* phenyl), 131.5 (t, $^2J_{PC}$ = 5.0 Hz, 8 C, *ortho* phenyl), 128.9 (s, 8 C, *meta* phenyl), 127.7 (s, 4 C, *para* phenyl), 67.8 (s, 4 C, CH_2-THF), 25.7 (s, 4 C, CH_2-THF), 24.1 (t, 1 C, $^1J_{PC}$ = 134.0 Hz, CH, P−CH−P), 4.6 (s, 6 C, CH_3, CH_3Si). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 12.6 (2 P). Anal. Calcd for $K\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N'\}\cdot THF$, $C_{35}H_{47}KN_2OP_2Si_2$: C, 62.84; H, 7.08; N, 4.19. Found: C, 62.44; H, 7.10; N, 3.93.

X-ray Crystallography. The diffraction data for **3** were collected on a Siemans P4/RA diffractometer, and those for **4** and **5** on a Bruker P4/RA/SMART1000 diffractometer system. The structure solutions were obtained using SHELX-86[21] and DIRDIC-96 direct methods analysis and refined using full-matrix least-squares on F^2 using SHELX-93.[22] All the non-hydrogen atoms were refined anisotropically. The hydrogen

---

(16) (a) Issleib, v. K.; Abicht, H. P.; Winkelmann, H. *Z. Anorg. Allg. Chem.* **1972**, *388*, 89−96. (b) Brauer, D. J.; Hietkamp, S.; Stelzer, O. *J. Organomet. Chem.* **1986**, *299*, 137−142. (c) Karsch, H. H.; Deubelly, B.; Müller, G. *J. Organomet. Chem.* **1988**, *352*, 47−59. (d) Karsch, H. H.; Grauvogl, G.; Mikulcik, P.; Bissinger, P.; Müller, G. *J. Organomet. Chem.* **1994**, *465*, 65−71.

(17) Kasani, A.; Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1483−1484.

(18) Ong, C. M.; Stephan, D. W. *J. Am. Chem. Soc.* **1999**, *121*, 2939−2940.

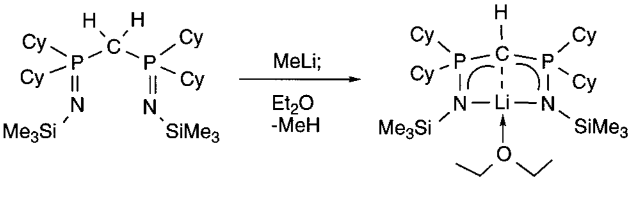
(19) Kamalesh Babu, R. P.; Aparna, K.; McDonald, R.; Cavell, R. G. *Inorg. Chem.* **2000**, *39*, 4981−4984.

(20) Appel, R.; Ruppert, I. *Z. Anorg. Allg. Chem.* **1974**, *406*, 131−144.

(21) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(22) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen: Germany, 1993. Refinement on $F_o{}^2$ for all reflections (all of these having $F_o{}^2 \geq -3\sigma(F_o{}^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on $F_o{}^2$; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative $F_o{}^2$. The observed criterion of $F_o{}^2 \geq 2\sigma(F_o{}^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. *R*-factors based on $F_o{}^2$ are statistically about twice as large as those based on F_o, and *R*-factors based on all data will be even larger.

Scheme 1



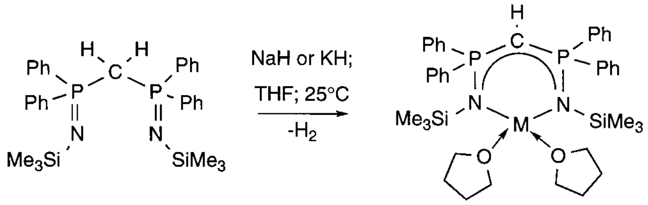
1 **3**

atoms were placed in calculated positions. Experimental details are listed in Table 1, and full data are provided as Supporting Information.

Results and Discussion

Syntheses. The reaction of the cyclohexyl ligand $H_2C(Cy_2P{=}NSiMe_3)_2$, **1**, with excess MeLi in ether, consumed only 1 equiv of MeLi to give the air- and moisture-sensitive bis(di(cyclohexyl)trimethylsilyliminophosphorano)methanide lithium complex, $[Li\{HC(Cy_2P{=}NSiMe_3)_2\text{-}\kappa C,\kappa N,\kappa N'\}(OEt_2)]$, **2**, in good yield (Scheme 1). No evidence for further deprotonation of this ligand was observed in contrast to the phenyl-substituted ligand, $H_2C(Ph_2P{=}NSiMe_3)_2$, **2**, which gave, with a 2-fold ratio of MeLi, $Li_2\{C(Ph_2P{=}NSiMe_3)_2\}$.[17,18] Restricting the quantity of LiMe to an equimolar ratio with the phenyl ligand **2** gave the expected $Li\{HC(Ph_2P{=}NSiMe_3)_2$, which was recently reported elsewhere,[18] supported in that case by NMR evidence but with no crystal structure. The two ligands $H_2C(Cy_2P{=}NSMe_3)_2$, **1**, and $H_2C(Ph_2P{=}NSiMe_3)_2$, **2**, thus display contrasting deprotonation chemistry with the alkali metal in that the former cannot be doubly deprotonated with the lithium reagent (even under more severe conditions than those used here), whereas the latter yielded both protons to the lithiation. We infer that the likely reason for this difference arises because of the reduced relative acidity of the protons on the methylene unit on the backbone of **1** due to the electron-donating action of the cyclohexyl groups on the phosphorus centers.

Scheme 2



2

M = Na **4**, K **5**

Previously we had found dimeric bis((diphenyl)trimethylsilylphosphoranimido)methanide complexes of Li and Na which were derived from reactions of ligand **2** with amides of these alkali metals.[19] Treating $H_2C(Ph_2P{=}NSiMe_3)_2$, **2**, with equimolar ratios of the alternate, readily available, deprotonating reagents such as sodium or potassium hydride in THF gave high yields of the monomeric monomethanide complexes $[M\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa N,\kappa N'\}(THF)_2]$ (M = Na, **4**; K, **5**) accompanied by evolution of hydrogen gas (Scheme 2). When the reaction of **2** was carried out with an excess (3 equiv) of sodium hydride in THF, only the monomethanide compound formed and the excess reagent had no further effect on this product, even under prolonged reflux conditions (higher temperatures). Under similar conditions however, potassium hydride reacted further; the solution gradually turned from clear to a deep red color, and several products were formed, as indicated by ^{31}P NMR spectroscopy; however we have not yet been able to identify these products.

All the alkali metal complexes were characterized by analytical, infrared, and multinuclear NMR spectroscopic techniques. Infrared spectra of the monomethanide alkali metal compounds showed the P−N stretch absorption at slightly lower wavenumber values (1165−1260 cm^{-1}) than those observed for the free bis(iminophosphorano)methane compounds. This suggested a lengthening and weakening of the P=N bond, which was confirmed by X-ray diffraction studies (vide infra). This bond order reduction is presumably the result of π-electron delocalization within the framework.

All the singly deprotonated alkali metal compounds show ^{31}P resonances shifted (by about 15−20 ppm) downfield relative to the parent bis(iminophosphorano)methanes. Although a triplet signal was expected in the ^1H NMR for the single methine proton present on the P−C−P backbone because of coupling to two equivalent phosphorus nuclei, the methine ^1H signals for both the lithium (**3**) and sodium (**4**) compounds were somewhat broader ($\nu_{1/2}$ = 5−9 Hz) than all the other ^1H signals in

Table 1. Crystallographic Experimental Details for 3−5

	3	4	5
empirical formula	$C_{35}H_{73}LiN_2OP_2Si_2$	$C_{39}H_{55}N_2NaO_2P_2Si_2$	$C_{39}H_{55}KN_2O_2P_2Si_2$
fw	663.01	724.96	741.07
space group	$P2_1/n$ (a nonstandard setting of $P2_1/c$ [No. 14])	$I2/a$ (a nonstandard setting of $C2/c$ [No. 15])	$P2_1/n$ (a nonstandard setting of $P2_1/c$ [No. 14])
unit cell params			
a (Å)	10.4393(12)	20.412(14)	10.5559(5)
b (Å)	18.457(2)	10.276(6)	17.5139(9)
c (Å)	21.421(2)	19.489(14)	22.8781(10)
β (deg)	95.089(8)	96.104(18)	93.7960(10)
V (Å^3)	4111.0(7)	4065(5)	4220.3(3)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.071	1.185	1.166
μ (mm^{-1})	0.191	0.211	0.292
(λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp (°C)	−80	−80	−80
indep reflns	7258	3878	8004
final R indices[a]			
$F_o^2 \geq 2\sigma(F_o^2)$	$R_1 = 0.0587$, $wR_2 = 0.1213$	$R_1 = 0.0593$, $wR_2 = 0.1317$	$R_1 = 0.0470$, $wR_2 = 0.1196$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

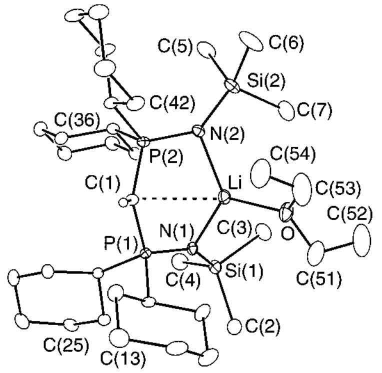


Figure 1. Perspective ORTEP[24] view of [Li{HC(Cy$_2$P=NSiMe$_3$)$_2$-κ*C*,κ*N*,κ*N*′}(OEt$_2$)] (**3**) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity except for the methine hydrogen. Non-hydrogen atoms are represented by Gaussian ellipsoids at 20% probability level.

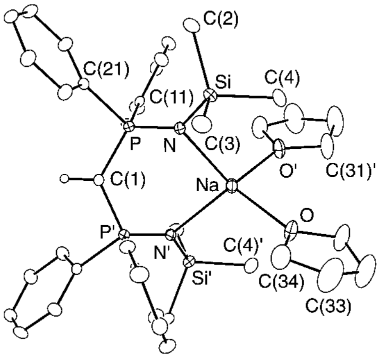


Figure 2. ORTEP[24] view of Na{HC(Ph$_2$P=NSiMe$_3$)-κ*N*,κ*N*′}(THF)$_2$ (**4**) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity except for the methine hydrogen. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

these complexes. The potassium compound **5**, however, had a much sharper ^{1}H methine carbon signal, which showed clearly the expected triplet signal. In all complexes the ^{13}C{^{1}H} NMR spectrum for the methine carbon atom was a triplet with $^1J_{PC}$ values of 125−135 Hz. Assignments were confirmed by ^{13}C APT and ^{1}H−^{13}C HMQC NMR experiments.[23]

The molecular structures of **3**, **4**, and **5**, illustrated as ORTEP[24] plots in Figures 1, 2, and 3, were deduced from X-ray crystal analysis. Selected bond distances and angles are listed in Table 2, and further metrical data are given in the Supporting Information. In addition to the monomeric nature of the complexes, which is rare for alkali metal complexes,[1] the complexes display a unique coordination sphere around each alkali metal and the heavier congeners differ markedly from the behavior illustrated by lithium. The core structure in all three cases, however, consists of a twisted six-membered metallacycle (Figure 4) formed by chelation of the two trimethylsilylimine groups to the metal. The differences occur mainly at the backbone carbanion center of the ligand. In the case of lithium, the metal center is bound to the central carbon, consistent with the propensity displayed by this element to bind to carbon. The resultant tridentate coordination mode of the monoanionic bis(phosphoranimine)methanide ligand is rare[3,25,26] and has only been previously demonstrated by [Ir(I){HC(Ph$_2$P=N−C$_6$H$_4$-4-CH$_3$)$_2$}(cod)]I.[3] The Li−C(1) distance of 2.633(7) Å in **3** is only slightly longer than the Li−C distances that appeared in the dilithium cluster (2.31−2.45 Å (range)), wherein the carbanions are bridging the lithium centers,[17,18] but is similar to the average of the two Li−C distances (2.76(1), 2.47(1) Å) found in the previously reported dimer.[19] The Li−C(1) distance in **3** is also slightly longer than those found in the usual oligomeric aggregates such as [PhLi·TMEDA]$_2$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and [PhLi·OEt$_2$]$_4$.[27] Notably, also, the central framework of complex **3** is folded about the C(1)−Li vector to form two rather strained four-membered metallacycles sharing the Li−C(1) edge.

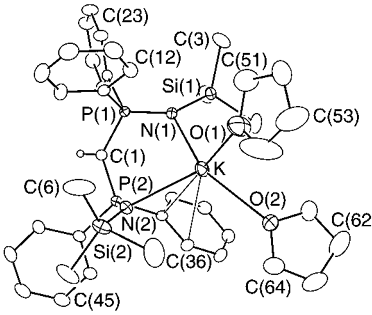


Figure 3. Perspective ORTEP[24] view of [K{HC(Ph$_2$P=NSiMe$_3$)$_2$-κ*N*,κ*N*′}(THF)$_2$] (**5**) showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity except for the methine hydrogen. Non-hydrogen atoms are represented by Gaussian ellipsoids at 20% probability level.

Table 2. Selected Metrical Parameters for Complexes 3−5

	M = Li (**3**)	M = Na (**4**)^a	M = K (**5**)
A. Bond Distances (Å)			
M- - -C(1)^{b,c}	2.633(7)	3.739(7)	4.145(2)
M−N(1)	2.033(6)	2.416(4)	2.798(2)
M−N(2)	2.012(7)	2.416(4)	2.731(2)
M−O (or O(1))	2.001(6)	2.346(4)	2.677(3)
M−O(2) (**4** and **5**)		2.346(4)	2.731(2)
endocyclic P−C: P(1)−C(1)	1.726(3)	1.708(3)	1.711(2)
P(2)−C(1)	1.731(3)	1.708(3)	1.712(2)
exocyclic P−C (mean)	1.848(3)	1.828(4)	1.830(2)
P(1)−N(1)	1.589(3)	1.582(3)	1.572(2)
P(2)−N(2)	1.593(3)	1.582(3)	1.571(2)
Si−N (mean)	1.690(3)	1.681(3)	1.671(2)
B. Bond Angles (deg)			
P(1)−C(1)−P(2)	131.0(2)	126.3(3)	121.2(1)
P(1)−N(1)−M	97.6(2)	111.4(2)	114.0(1)
P(2)−N(2)−M	98.8(2)	111.4(2)	107.1(1)
N(1)−M−N(2)	118.6(3)	96.8(2)	84.6(1)
N(1)−P(1)−C(1)	110.5(2)	116.4(2)	116.8(1)
N(2)−P(2)−C(1)	113.2(2)	116.4(2)	118.8(1)

[a] Symmetrically equivalent lengths and angles are given twice. This more symmetric complex is labeled differently: N(1) = N, N(2) = N′, P(1) = P, P(2) = P′, O(1) = O, O(2) = O′. [b] Intraatomic distances between the metal atom and the central methanide carbon. [c] In complex **5**, longer range metal−carbon and metal−hydrogen interactions are K···C(31) = 3.456(3) Å and K···C(36) = 3.416(3) Å and, with methyl hydrogens on Si(2), K···H(4A) = 2.73 Å, K···H(7C) = 2.92 Å, K···H(5A′) = 3.15 Å (not shown).

---

(23) Braun, S.; Kalinowski, H.; Berger, S. *150 and More Basic NMR Experiments; A Practical Course*; Wiley-VCH: New York, 1998.

(24) Johnson, C. K. *ORTEP*; Report ORNL No. 5138; Oak Ridge Nat. Labs: Oak Ridge, TN, 1976.

(25) Valderrama, M.; Contreras, R.; Bascuñan, M.; Alegria, S.; Boys, D. *Polyhedron* **1995**, *14*, 2239−2246.

(26) Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552−554.

(27) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320−5324.

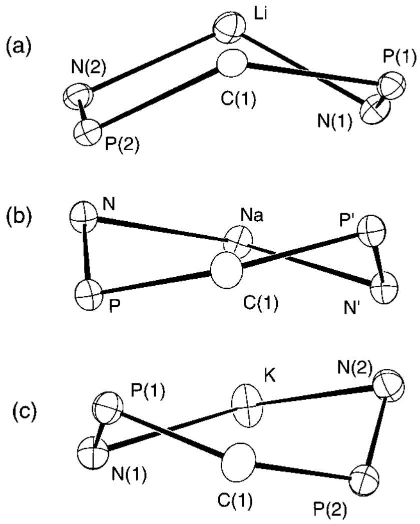


Figure 4. Views of six-membered M, N(1), P(1), C(1), P(2), N(2) metallacycle rings in complexes **3**, **4**, and **5** approximately along the M−C(1) axis.

The sodium (**4**) and potassium (**5**) complexes have 2 mol of coordinated THF and have generally similar structural features in that, in contrast to the lithium complex (**3**), these complexes show the carbanion to be well separated from the metal center (the nonbonded Na to C(1) distance is 3.7 Å and the nonbonded K to C(1) distance is even larger at 4.1 Å). The separation between the central carbanion carbon and Na is even greater than that observed (2.9−3.0 Å) in the sodium dimer complex reported previously.[19]

The sodium complex crystallizes in a highly symmetric space group; thus the two Na−N and Na−O distances (Table 2) are equal by symmetry. The potassium complex, **5**, interestingly, however, shows an additional π-acid coordination interaction between the alkali metal and two carbon atoms of one of the phenyl rings of the ligand {K···C(31) = 3.456(3) Å, K···C(36) = 3.416(3) Å} and also agostic interactions with the trimethylsilyl methyl group protons on Si(2) {K···H(4A) = 2.73 Å, K···H(7C) = 2.92 Å, K···H(5A′) = 3.15 Å} These interactions distort the molecular structure such that the potassium complex does not yield a symmetric space group nor symmetrically equivalent M−N and M−O bond lengths. The P−C bond lengths to the carbanion center are essentially identical, as they are relatively remote from the distortion center.

The Li−N distances {Li(1)−N(1) = 2.033(6) Å, Li(1)−N(2) = 2.012(7) Å} lie in the range generally observed for lithium amides,[28] lithium monophosphinimines,[29] and lithium aminidinates.[30] The sodium−nitrogen distances in **4** are shorter than the Na−N bond distances observed in normal neutral amine-coordinated complexes[31] and lie in the range reported for sodium amide derivatives.[28] The potassium−nitrogen distances in **5** are, as expected, longer than other alkali metal−nitrogen distances and lie in the range observed for amidinate complexes of potassium.[32]

The bis(iminophosphorano)methanide ligands fully encapsulate the alkali metal cations, and so there are no intermolecular interactions observed in these crystal lattices.

In all three complexes, **3**, **4**, and **5**, the exocylic P−C bond distances are normal, but the endocyclic P−C bond distances overall are significantly shortened, suggesting that there is a considerable delocalization throughout the N−P−C−P−N backbone of the ligand in all cases. The P−C−P bond angles (131.0(2)° for **3**, 126.3(3)° for **4**, 121.2(1)° for **5**) are significantly expanded relative to the corresponding values in the parent ligands, $H_2C\{Ph_2P{=}NSiMe_3\}_2$ (112.4(2)° [33]) and $H_2C\{Cy_2P{=}NSiMe_3\}_2$ (117.4(1)°).[34]

Conclusion

Monomeric lithium, sodium, and potassium bisphosphinimine methanide salts can be obtained as well-defined crystalline materials. These compounds, which represent the first examples of monomeric group-1A metal complex of the complete $H_2C(R_2P{=}E)_2$ (E = O, S, Se, NR) ligand system to be structurally characterized, show a unique coordination geometry about each of the alkali metal centers. Only the lithium derivative shows significant binding to the carbanionic center. The sodium and potassium complexes do not show significant metal−carbanion interaction, but the potassium complex shows π-acid and agostic interactions with the other parts of the ligand which do not appear in the sodium system. The potassium complex thus has a lower molecular (and crystal) symmetry than the sodium complex. In all cases the structures also show evidence of extensive delocalization within the internal metallacyclic ring structure.

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

Supporting Information Available: Tables of X-ray crystallographic information in cif format for **3**, **4**, and **5** and an ORTEP[24] diagram of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000982G

---

(28) See for instance: (a) 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*, 427−439. (b) Andrews, P. C.; Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A.; Barr, D.; Cowton, L.; Dawson, A. J.; Wakefield, B. J. *J. Organomet. Chem.* **1996**, *518*, 85−95. (c) Clegg, W.; Henderson, K. W.; Horsburgh, L.; Mackenzie, F. M.; Mulvey, R. E. *Chem. Eur. J.* **1998**, *4*, 53−56. (d) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 11855−11863. (e) Knizek, J.; Krossing, I.; Nöth, H.; Schwenk, H.; Seifert, T. *Chem. Ber.* **1997**, *130*, 1053−1062.

(29) See for instance: Müller, A.; Neumüller, B.; Dehnicke, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2350−2352. (b) Hitchcock, P. B.; Lappert, M. F.; Wang, Z.-X. *J. Chem. Soc., Chem. Commun.* **1997**, 1113−1114. (c) Steiner, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1752−1755.

(30) Chivers, T.; Downard, A.; Parvez, M. *Inorg. Chem.* **1999**, *38*, 4347−4353.

(31) See for instance: (a) Schümann, U.; Behrens, U.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 476−477. (b) Besten, R.; Brandsma, L.; Spek, A. L.; Kanters, J. A.; Veldman, N. *J. Organomet. Chem.* **1995**, *498*, C6−C9. (c) Ellermann, J.; Schütz, M.; Heinemann, F. W.; Moll, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 257−262.

(32) Whitener, G. D.; Hagadorn, J. R.; Arnold, J. *J. Chem. Soc., Dalton. Trans.* **1999**, 1249−1255.

(33) Müller, A.; Möhlen, M.; Neumüller, B.; Faza, N.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1748−1751.

(34) Kamalesh Babu, R. P.; McDonald, R.; Cavell, R. G. Unpublished results. X-ray structure of $H_2C\{Cy_2P{=}NSiMe_3\}_2$, University of Alberta Structure Report RGC 9802 (important bond parameters are mean endocyclic P−C = 1.819(2) Å, exocyclic P−C = 1.837(2) Å, P−N = 1.547(2) Å, and P−C−P = 117.4(1)°.