biradical but a single zwitterion was in good accord with the chemical reactivities described above. Further investigations of the new intermediate sila-*m*-quinomethane are in progress.

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Configuration, Conformation, and Colligative Properties of a Phosphorus-Stabilized Anion

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As part of a general program to develop chiral, phosphorus-based anionic reagents,[1] we required an accurate model of the structure and bonding in these species to guide the design of auxiliaries.[2] Apart from the pioneering spectroscopic studies on Horner–Wittig reagents by Kirilov[3] and Seyden-Penne,[4a-c] the structure of phosphorus-stabilized anions (excluding ylides) has been little investigated.[4d-h,5]
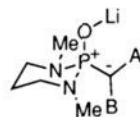
Li⁺1a⁻: A = H; B = Ph

Li⁺1b⁻: A = B = CH₃

We have recently reported the first X-ray crystal structure determination[6–8] of a phosphoryl-stabilized anion, Li⁺1a⁻, which

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(5) For a review on the structure of sulfur-stabilized anions: Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277.

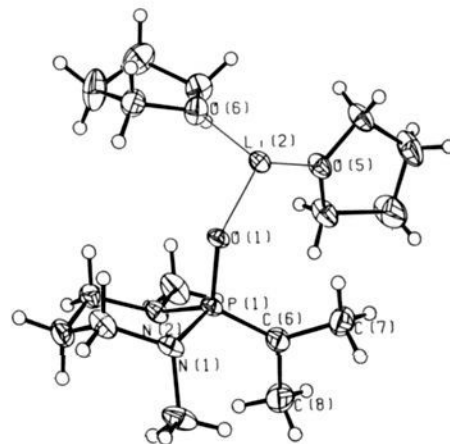(6) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864.

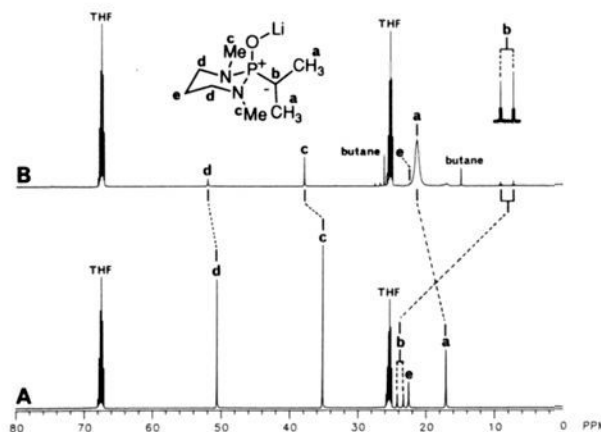**Figure 1.** Crystal structure of [Li⁺1b⁻]₂·4THF at −75 °C; monomer unit shown for clarity (35% thermal ellipsoids).

Figure 2. ¹³C NMR spectra (125.8 MHz) at −100 °C. Spectrum A: **1b** (neutral, natural abundance). Spectrum B: Li⁺1b⁻ (anion, 50% ¹³C-enriched in one *C*-methyl group).

Table I. Planarity Criteria for C(6) (Mean Values)[a]

anion	A	B	|α| + |β|, deg	Σ, deg	γ, deg	d, Å
Li⁺1a⁻	H	Ph	171.1 (35)	359.4 (60)	7.3	0.06
Li⁺1b⁻	CH₃	CH₃	165.4 (9)	358.5 (7)	11.6	0.11

[a] The sum of the torsion angles ($|\alpha| + |\beta|$); the sum of all angles about C(6) (Σ); the angle of the C(6)–P(1) vector to the C(6)–A–B plane (γ); the distance of C(6) to the A–P(1)–B plane (d).

established, inter alia, the planarity and preferred conformation of the carbanionic carbon. In this report we disclose crystallographic and NMR analyses of the related *P*-isopropyl anion Li⁺1b⁻

(7) Two other types of phosphorus-stabilized anions have been crystallographically defined: chelated Mg²⁺ and Cu²⁺ keto phosphonates[7a,b] and lithiophosphinomethides.[7c-e] (a) Weiss, E.; Kopf, J.; Gardein, T.; Corbelin, S.; Schümann, U.; Kirilov, M.; Petrov, G. *Chem. Ber.* **1985**, *118*, 3529. (b) Macicek, J.; Angelova, O.; Petrov, G.; Kirilov, M. *Acta Crystallogr.* **1988**, *C44*, 626. (c) Byrne, L. T.; Engelhardt, L. M.; Jacobsen, G. E.; Leung, W.-P.; Papasergio, R. I.; Raston, C. L.; Skelton, B. W.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 105. (d) Karsch, H. H.; Zellner, K.; Mikulcik, P.; Lachmann, J.; Müller, G. *Organometallics* **1990**, *9*, 190 and references cited. (e) Fraenkel, G.; Winchester, W. R.; Willard, P. G. *Organometallics* **1989**, *8*, 2308.

(8) The X-ray structure of a diethyl lithiobenzylphosphonate·DABCO complex has recently been reported. Zarges, W.; Marsch, M.; Harms, K.; Haller, F.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, *124*(4). We thank Professor Boche for a preprint of this manuscript.

which demonstrate that (1) the planarity of the carbanion in Li$^+$1a$^-$ is *not* primarily due to phenyl conjugation, (2) the barrier to rotation about the P(1)–C(6) bond is very low, (3) the preferred conformation of the anion is parallel, and (4) the anion exists as a dimer in THF solution.

The lithio anion Li$^+$1b$^-$ (derived from 1,3-dimethyl-2-isopropyl-1,3,2-diazaphosphorinane 2-oxide, 1b) readily crystallized from THF as a dimer with approximate C_s symmetry.[9] Each lithium atom is bonded to both phosphonyl oxygens and is solvated by two THF molecules. Half of the dimer unit is presented for clarity in Figure 1. Most of the important structural features of Li$^+$1b$^-$ are very similar to those from Li$^+$1a$^-$, e.g., the lack of an Li(2)–C(6) bond (3.778 (10) Å), the anion conformation (torsional angle O(1)–P(1)–C(6)–C(8) 164.4 (18)°, and the pyramidality of the nitrogens ($\sum$ angles N(1) 344.7 (7)°, N(2) 345.1 (20)°). Most striking, however, is the near planarity of the carbanionic carbon. The comparison between Li$^+$1a$^-$ and Li$^+$1b$^-$ by four criteria of planarity is summarized in Table I. While no single measure of planarity is best, the correlation between the two anions is remarkable and stands in striking contrast to the corresponding lithio sulfones.[10] In these structures (RSO$_2$CAB)$^-$, the carbanion is planar in the a series[10a] ($|\alpha| + |\beta| \approx 180°$) while in the b series it is highly pyramidalized ($|\alpha| + |\beta| = 139°$).[10b] The planarity of Li$^+$1a$^-$ and Li$^+$1b$^-$ persists in solution as indicated by the large increase in $^1J_{PC}$[11] upon lithiation (Δ^1J_{PC}:1a, 105.7 Hz; 1b, 125.8 Hz).

Both Li$^+$1a$^-$ and Li$^+$1b$^-$ display the same conformation of the anion, wherein the P(1)–O(1) bond is nearly coincident with the A–C(6)–B plane (torsion angles 12.9° and 15.2°, respectively). The deviation from ideality in Li$^+$1b$^-$ is noteworthy. Both the slight pyramidalization of C(6) and the torsion of the anionic plane are consistent with a hyperconjugative interaction with σ^*(P-(1)–N(1)).[12] The barrier to conformational change in solution could not be established in Li$^+$1a$^-$ since single resonances both for the *N*-methyl groups and for HC(6) were observed down to –76 °C. This has two limiting interpretations: (1) a high barrier in an anacomeric C_s-symmetric, parallel anion or (2) a low barrier. To distinguish these possibilities, a sample of 1b labeled with ^{13}C (50%) in one *C*-methyl group was lithiated and ^{13}C NMR spectra were recorded at low temperature, Figure 2. Upon lithiation of 1b (*n*-BuLi, THF, final concentration 0.21 M)[13] the carbanionic carbon (C(6)) moved dramatically upfield ($\Delta\delta$ –15.6 ppm). Further, at –100 °C, the methyl groups bonded to C(6) appeared as a *single broadened resonance* ($W_{1/2}$ = 75 Hz). This broadening confirms that the preferred conformation in solution is as shown in Figure 1 wherein the diastereotopic *C*-methyl groups should be anisochronous.[14] Although we cannot unambiguously rule out the possibility that the broadening is due to aggregation effects (vide infra), similar broadening was observed at –100 °C at lower concentration (0.03 M, $W_{1/2}$ = 74 Hz). The coalesced resonance for these nuclei indicates a small barrier to rotation with an estimated upper limit of ca. 8 kcal/mol.[15]

A low rotational barrier in these anions is consistent with the small $k_{exchange}/k_{racemization}$ observed for (+)-diethyl 2-octyl-phosphonate[16] and is again in contrast to the large ratio observed for sulfones.[17] Moreover, Gais has recently reported the rotational barriers for lithio sulfones ($\Delta G^{\ddagger}_{215}$ 9.6–9.7 kcal/mol) and triflones ($\Delta G^{\ddagger}_{215}$ 16.0–17.8 kcal/mol).[18] A low barrier would appear to be inconsistent with the significant double-bond character of the P(1)–C(6) bond (1.657 (3) Å).[19] However, the barrier to rotation will depend on the *splitting* between the orthogonal π-acceptor orbitals on the phosphorus unit.[20] This splitting is expected to be small for Li$^+$1a$^-$ and Li$^+$1b$^-$ where the ligands on phosphorus are all electronegative, resulting in effective overlap at all angles.

Finally, we have been able to establish the aggregation state of the anion in THF solution by the use of ^{6}Li NMR spectroscopy.[21] The lithio anion ^{6}Li$^+$1b$^-$ was generated in THF (0.15 M)[13] by deprotonation of 1b with *sec*-butyllithium-^{6}Li.[22] The appearance of a distinct triplet at –0.62 ppm (J = 1.1 Hz) in the ^{6}Li NMR spectrum at –100 °C requires that each lithium nucleus be coupled to two ($S = {}^1/_2$) ^{31}P nuclei, thus implicating a dimeric structure. *The ^{31}P-decoupled ^{6}Li NMR spectrum*[23] *showed the expected singlet, thus confirming the two-bond ^{6}Li–^{31}P coupling.* Two-bond coupling between lithium and phosphorus has recently been observed for HMPA solvates of lithium halides (^{7}Li),[24a] ate complexes (^{7}Li),[24b,c] phenyllithium (^{6}Li),[24c] and lithium amide bases (^{6}Li).[24d] The narrow ^{31}P resonance (202.5 MHz, –100 °C, $W_{1/2}$ = 8.6 Hz) and the ability to resolve a 1-Hz coupling in the ^{6}Li spectrum further support the conclusion that the broadening of the C(6)-methyl groups in the ^{13}C spectrum is not due to a bimolecular process.

The assignment of a dimeric solution structure for Li$^+$1b$^-$ by the ^{6}Li NMR method was corroborated by cryoscopic measurements in THF at –108 °C.[25] The degree of association (n) was found to be 2.00 ± 0.17 (151.6 mmol/kg).[26] A dimeric aggre-

(9) Space group *P*$\bar{1}$, *a* = 10.227 (3) Å, *b* = 11.852 (4) Å, *c* = 17.840 (8) Å, α = 80.74 (4)°, β = 77.76 (3)°, γ = 69.34 (3)°, *Z* = 2 (one dimer/asymmetric unit); *R* = 0.048 and R_w = 0.060 for 4152 reflections with *I* > 2.58σ(*I*). Selected distances (mean values) (Å) and bond angles (mean values) (deg) (the asymmetric unit has approximate C_s symmetry (Li(2), O(5), O(6) plane)): P(1)–C(6) 1.657 (3); P(1)–O(1) 1.525 (2); Li(2)–O(1) 1.922 (5); C(6)–CH$_3$ 1.510 (5); P(1)–N(1) 1.708 (7); P(1)–N(2) 1.697 (3); P(1)–C-(6)–C(7) 120.8 (2); P(1)–C(6)–C(8) 122.9 (8); C(6)–P(1)–O(1) 115.7 (2); P(1)–O(1)–Li(2) 134.5 (11); N(1)–P(1)–N(2) 99.6 (6). Torsional angles (mean absolute value) (deg): O(1)–P(1)–C(6)–C(8) ±164.4 (18); Li(2)–O-(1)–P(1)–C(6) ±48.6 (33).

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(13) The spectrum was taken on a sample of recrystallized anion. The final concentration was determined by integration against benzene as an internal standard.

(14) This situation would not obtain if the angle O(1)–P(1)–C(6)–C(8) were 90° in Li$^+$1b$^-$, i.e., a C_s orthogonal anion.

(15) This limit is based on the assumption that the observed linewidth is the *minimum* difference in chemical shift at the decoalescence limit ($W_{1/2} \ll \Delta\nu_0$). Allerhand, A.; Gutowsky, H. S.; Jonas, J.; Meinzer, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3185.

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(19) Compare: (a) C–P (Ph$_3$P=CH$_2$) = 1.661 Å (Bart, J. C. *J. J. Chem. Soc. B* **1969**, 350). (b) C–P (MesitylP=CPh$_2$) = 1.69 Å (van der Knaap, T. A.; Klebach, T. C.; Visser, F.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijn, M. *Tetrahedron* **1984**, *40*, 765). See also: (c) Ammon, H. L.; Wheeler, G. L.; Watts, P. L., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6158.

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(26) (a) Cryoscopy performed by Friederike Haller (Prof. G. Boche, Marburg). (b) Two other measurements were taken: *n* = 2.04 ± 0.55 (120.7 mmol/kg); *n* = 1.83 ± 0.21 (99.9 mmol/kg). All determinations take into account the ΔT due to the presence of a molal equivalent of *n*-butane from the *n*-BuLi.

gation state in Li⁺1b⁻ has also been found for an acyclic phosphonate[8] and is in contrast to the monomeric state found for sulfones[18] in THF solution. This disparate behavior may be ascribed to the enhanced basicity of the phosphonyl group[27] and the potential bidentate coordination of the lithium by the sulfonyl oxygens.

The intrinsic planarity and low rotational barrier for phosphonyl anions place stringent requirements on the design of chiral ligands for effective asymmetric reagents. The development of such chiral ligands along with further studies on the structure of related phosphorus-stabilized anions is in progress.

Supplementary Material Available: A listing of crystal and positional parameters, bond lengths and angles, and torsional angles for Li⁺1b⁻ (24 pages). Ordering information is given on any current masthead page.

(27) Compare −Δ$H°_{BF_3}$ (298 K): for tetramethylene sulfone, 12.3 kcal/mol; for trimethyl phosphate, 20.3 kcal/mol. Maria, P.-C.; Gal, J.-F. *J. Phys. Chem.* **1985**, *89*, 1296.

Iron(II) Organizes a Synthetic Peptide into Three-Helix Bundles

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Considerable efforts have been directed[1] toward the design and synthesis of small model proteins to elucidate interactions involved in protein folding. We[2] and other groups[3] have devised a strategy in which a rigid molecule acts as a template to assemble secondary structures in simple model proteins. The X-ray structures of tris-bipyridine metal complexes suggest that covalent attachment of an amphiphilic α-helical segment to the 4-position of bipyridine would allow the formation of a three α-helix bundle protein on addition of a metal ion such as Fe²⁺. Metal ions are known to play important roles in defining the three-dimensional structure of native metalloproteins such as DNA-binding zinc finger proteins.[4] Synthetic peptides bearing two metal binding sites at the *i* and *i* + 4 residues have been reported[5a–c] to form monomeric

* To whom correspondence should be addressed.
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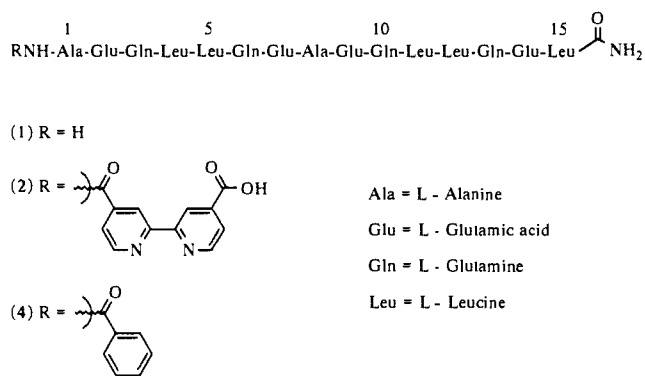

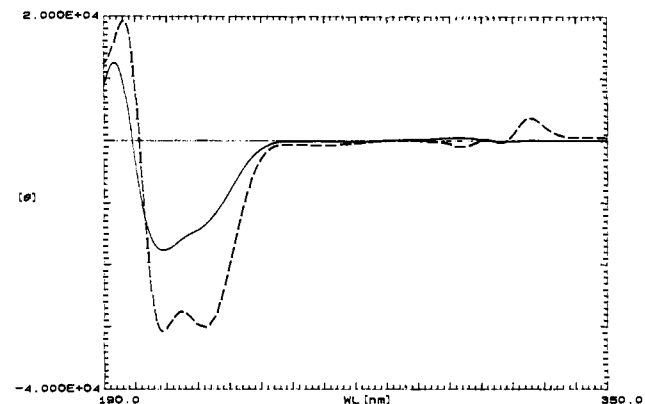**Figure 1.** Structure of synthetic peptides **1**, **2** (pepy), and **4**.

RNH-Ala-Glu-Gln-Leu-Leu-Gln-Glu-Ala-Glu-Gln-Leu-Leu-Gln-Glu-Leu—NH₂

(positions 1, 5, 10, 15)

(1) R = H

(2) R = [structure]

(4) R = [structure]

Ala = L - Alanine
Glu = L - Glutamic acid
Gln = L - Glutamine
Leu = L - Leucine

Figure 2. Circular dichroism spectra of pepy (—) and Feᴵᴵ(pepy)₃ (---). Obtained on a JASCO 700 CD spectrophotometer in 0.5-mm cells, 5 × 10⁻⁵ M solutions in 250 mM acetate buffer, pH = 4.8, 23 °C; *x*-axis, wavelength (nm); *y*-axis, molar ellipticity per residue (deg cm² dmol⁻¹).

Scheme I. Metal-Induced Formation of Three-α-Helix Bundle[a]
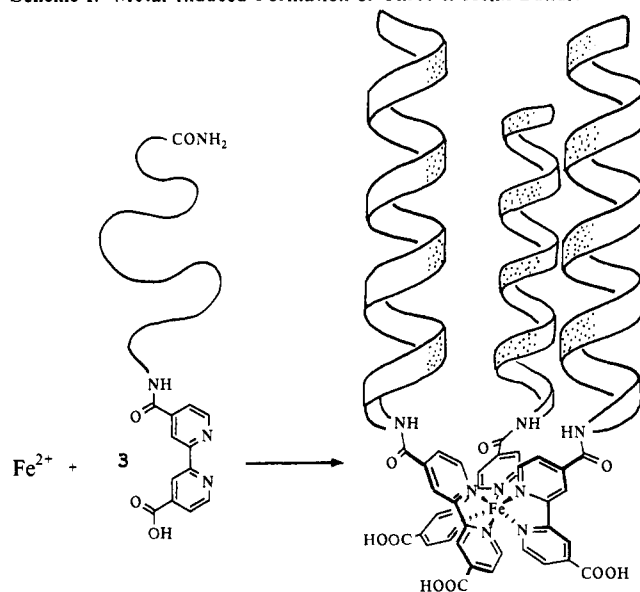
[a] The shaded regions of the helices represent hydrophobic residues.

α-helices in the presence of heavy metal ions. Recently, several Zn²⁺ binding proteins derived from a four-α-helix motif were also synthesized.[5d] We report here the synthesis of a three-α-helix-bundle protein using a tris-bipyridine metal complex as a template as depicted in Scheme I.

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