Organometallics **1994,** *13,* 4578–4585

Solution Structure of Lithium Benzeneselenolate and Lithium Diphenylphosphide: NMR Identification of Cyclic Dimers and Mixed Dimers[1]

Hans J. Reich* and Robert R. Dykstra

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received July 11, 1994[⊗]

The solution structures of lithium benzeneselenoate (PhSeLi) and lithium diphenylphosphide (Ph_2PLi) in ether, THF, and mixtures with HMPA were studied by multinuclear NMR techniques. Lithium benzeneselenoate is aggregated in ether, as established by observation of ^{7}Li—^{77}Se coupling in both the ^{7}Li and ^{77}Se NMR spectra (J_{Li-Se} = 18 Hz). It is probably dimeric, although a cyclic trimer could not be definitively excluded. The titration of PhSeLi with HMPA in ether produces initially a triply bridged dimer **1a** ($(PhSeLi)_2(HMPA)_3$) and eventually (with excess HMPA) a separated ion pair. In THF the reagent is likely a contact monomeric species, as judged by Li and Se δ values and the sequence of ion pair formation during an HMPA titration. A mono HMPA contact ion pair and then a separated ion pair species is formed. Lithium diphenylphosphide is also dimeric in ether. Higher cyclic oligomers could be definitively ruled out by the analysis of the virtually coupled multiplet for the *ipso* phenyl carbon signal, resulting from large (>120 Hz) P—P J coupling between the lithium-bridged phosphorus nuclei. In THF, Ph_2PLi appears to be monomeric; treatment with HMPA leads to formation of a mono HMPA contact ion pair, followed by ion separation. When PhSeLi and Ph_2PLi are mixed in ether, a statistical mixture of a heterodimer and the two homodimers is formed. The heterodimer ($PhSeLi{\cdot}Ph_2PLi$) was characterized by ^{13}C, ^{31}P, ^{7}Li, and ^{77}Se NMR spectroscopy. It shows coupling between Li and P ($^1J_{Li-P}$ = 46 Hz), between Li and Se ($^1J_{Se-Li}$ = 18 Hz), and between the lithium-bridged Se and P nuclei ($^2J_{Se-P}$ = 91 Hz). Higher cyclic oligomers can be strictly ruled out for the mixed oligomer on the basis of the NMR spectra.

Introduction

The solution structure and reactivity of lithium salts is profoundly affected by interactions between the solvent and the lithium cation. Competition between solvent (or solvent additives) and the anionic counterion for coordination sites on lithium control aggregation phenomena and the formation of contact and/or separated ion pairs for monomers.

Although aggregation can be detected by colligative measurements, J-coupling between lithium and attached nuclei is a more convenient and less error-prone technique, although subject to significant limitations. Coupling to carbon was first detected for the more abundant Li isotope, ^{7}Li,[2] and this nucleus usually works quite well for monomers (which show larger coupling than aggregates).[3,4a,1a–e] However, reagents enriched in ^{6}Li allow more general detection of the characteristic multiplets resulting from the multicenter bonding in lithium aggregates.[3,5,6] In favorable cases multinuclear NMR techniques using lithium chemical shifts and J-coupling of ^{6}Li or ^{7}Li with NMR-active anionic atoms (such as ^{13}C in carbanions,[1a–e,4a,b,5,6] ^{15}N in amides,[7–9] ^{119}Sn in lithium organostannates,[1e,10] ^{31}P in phosphides,[11,12] or ^{29}Si in (trialkylsilyl)lithium reagents[3]) can allow the determination of solution structure in considerable detail. Coupling with such atoms in coordinating solvents such as HMPA, or in chelating

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) (a) Reich, H. J.; Reich, I. L.; Yelm, K. E.; Holladay, J. E.; Gschneidner, D. *J. Am. Chem. Soc.* **1993**, *115*, 6625. (b) Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1835. (c) Reich, H. J.; Dykstra, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 7041. (d) Reich, H. J.; Dykstra, R. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1469. (e) Reich, H. J.; Borst, J. P.; Dykstra, R. R. *Organometallics* **1994**, *13*, 1. (f) Reich, H. J.; Borst, J. P.; Dykstra, R. R.; Green, D. P. *J. Am. Chem. Soc.* **1993**, *115*, 8728. (g) Reich, H. J.; Green, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 8729. (h) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. (i) Reich, H. J.; Bowe, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 8994. Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414. Reich, H. J.; Green, D. P.; Phillips, N. H.; Borst, J. P.; Reich, I. L. *Phosphorus Sulfur* **1992**, *67*, 63. Reich, H. J.; Gudmundsson, B. Ö.; Dykstra, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7937. (j) Reich, H. J.; Cohen, M. L. *J. Org. Chem.* **1979**, *44*, 3148.

(2) McKeever, L. D.; Waack, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 3244.

(3) Edlund, U.; Lejon, T.; Venkatachalam, T. K.; Buncel, E. *J. Am. Chem. Soc.* **1985**, *107*, 6408.

(4) Seebach, D.; Siegel, H.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1980**, *63*, 2046.

(5) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745.

(6) Günther, H.; Moskau, D.; Bast, P.; Schmalz, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1212.

(7) (a) De Pue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 5524. (b) Romesburg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 2112. (c) Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 794. (d) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227. Romesburg, F. E.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751.

(8) (a) Jackman, L. M.; Scarmoutzos, L. M.; Porter, W. *J. Am. Chem. Soc.* **1987**, *109*, 6524. (b) Jackman, L. M.; Scarmoutzos, L. M.; Smith, B. D.; Williard, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 6058. (c) Jackman, L. M.; Chen, X. *J. Am. Chem. Soc.* **1992**, *114*, 403.

(9) Sato, D.; Kawasaki, H.; Shimada, I.; Arata, Y.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 761.

(10) Reed, D.; Stalke, D.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1459.

(11) (a) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. *J. Chem. Soc., Chem. Commun.* **1982**, 220. (b) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. *Phosphorus Sulfur* **1983**, *18*, 61.

(12) Hitchcock, P. B.; Lappert, M. F.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1669.

0276-7333/94/2313-4578$04.50/0

groups (such as ^{15}N in enriched amine or amide groups[12]), can be used to define the lithium coordination sphere beyond contacts to the counterion. In addition to these techniques, isotopic shift patterns can provide direct information about aggregation state.[13]

For lithium bonded to electronegative heteroatoms, dimers and tetramers are often found in THF (R_2NLi,[7,8a,b] ROLi,[8c] LiCl,[1f] MeSLi[1f]) unless charge is well delocalized and/or there is steric hindrance. For other heteroatom-bonded lithium salts such as Ph_2PLi,[11] R_3SiLi,[3] and Bu_3SnLi[1e] monomeric structures are observed (R_3SnLi is monomeric even in ether[1e,10]). In more strongly coordinating media (THF–HMPA) a few such lithium species maintain aggregated structures (phenoxides,[8c] lithium amides[7d]), but many undergo ion separation (e.g., LiCl,[1f] LiBr,[1g,1f] LiI,[1f] MeSLi,[1f] MeSeLi[1f]).

We report here the results of NMR studies of Ph_2PLi and PhSeLi in THF, ether, and mixtures with HMPA. Both are easily prepared nucleophilic reagents valuable for the preparation of phosphines and selenides, which have significant uses in organic synthesis.[14–16] These reagents provide an especially favorable situation for NMR studies since both ^{31}P (100% abundance) and ^{77}Se (7.7% natural abundance) are spin-$^{1}/_{2}$ nuclei. We demonstrate NMR techniques which allow the difficult distinction between cyclic dimers and higher cyclic oligomers to be made.

Lithium Benzeneselenolate has been little studied; neither aggregation state nor ion pair structure (CIP/SIP) in ether or THF is known. Various methods for the preparation of metal selenolates produce reagents of widely different reactivity.[16] We reported recently the characterization by HMPA titration in THF of related salts MeSeLi and MeSLi.[1f] The aggregation state for MeSeLi was not determined; MeSLi was found to be dimeric in THF. Both form separated ions in THF–HMPA, consistent with the finding that highly nucleophilic thiolate and selenolate species are formed in HMPA.[16,17]

X-ray crystal structures of THF-solvated monomeric lithium 2,4,6-tri-*tert*-butylbenzeneselenolate[18] and a mixed dimeric lithium–lutetium benzeneselenolate[19] have been reported.

Lithium Diphenylphosphides. A number of investigations have provided considerable insight into the chemistry[14] and solution structure of Ph_2PLi.[11,20–22] A ^{31}P and ^{7}Li NMR study showed that lithium was coupled to two phosphorus nuclei, and vice versa, so that a cyclic oligomer (probably a dimer) is formed in ether at low temperature.[11] These workers also examined PhHPLi by NMR and found a cyclic trimer structure. A tetrameric structure has been claimed for Ph_2PLi in THF solution, but this is probably in error.[20] In addition, the equilibrium between solvated monomeric ion pairs and solvated dimers was found by ^{13}C NMR to be solvent dependent,[21] with the monomer CIP favored in THF and the SIP in the presence of added cryptand (C 2.1.1). A number of X-ray structures of Ph_2PLi with different complexing ligands have been reported: polymeric $Ph_2PLi(Et_2O)$ and $Ph_2PLi(THF)_2$,[23] a TMEDA-complexed dimer,[24] lutetium–lithium mixed dimer,[25] PMDTA-complexed monomer,[24] and a 12-crown-4-complexed separated ion pair.[22] An X-ray structure of lithium di-2-pyridylphosphide shows that the contact ion pair lacks a Li–P contact owing to coordination of the lithium to the nitrogen atoms of the pyridyl rings.[26]

HMPA Titration Technique for Determining Ion Pair Structure. We have reported that Li–P coupling could be observed in low-temperature ^{31}P, ^{7}Li, and ^{6}Li NMR spectra of HMPA-complexed organolithium reagents[1b–d,1f] (also discovered independently by Snaith[27a]). Under these conditions individual solvated species having one to four HMPA molecules attached to lithium can be detected and quantified, and the CIP/SIP transition reliably identified.[28] As a result, properties of lithium reagents long recognized as crucial in understanding reactivity, but for which experimental techniques were lacking or difficult, can be determined. Published work in this area has included principally studies in THF solution and mixtures of THF with dimethyl and diethyl ether. The systems studied have included organolithium reagents,[1b–d,1f] lithium ate complexes,[1f–i] lithium halides,[1f–g,27a] lithium amides,[7,8ab] lithium chalcogenides,[1b,1f] and lithium phenoxides.[8c,27b]

Low-temperature work in ether is complicated by the poorer solubility of many lithium reagents and lithium reagent–HMPA complexes and by the generally higher aggregates found in ether than in THF. Only three compounds have been reported: lithium fluorenide,[1f] (trimethylstannyl)lithium,[1e] and (tributylstannyl)lithium.[1e] For the first two compounds, insoluble materials formed at >1 equiv of HMPA. Interesting HMPA-bridged dimers ($(Bu_3SnLi)_2(HMPA)_3$) were observed for the two stannyllithium reagents.[1e] Snaith and coworkers have crystallized a number of lithium salt–HMPA clusters from nonpolar media, including an HMPA-bridged LiBr dimer analogous to $(Bu_3SnLi)_2(HMPA)_3$.[27a] We report here additional examples in diethyl ether.

---

(13) Eppers, O.; Günther, H. *Helv. Chim. Acta* **1990**, *73*, 2071. Eppers, O.; Günther, H. *Helv. Chim. Acta* **1992**, *75*, 2553.

(14) Ashby, E. C.; Gurumurthy, R.; Ridlehuber, R. W. *J. Org. Chem.* **1993**, *58*, 5832.

(15) (a) Vedejs, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **1973**, *85*, 822. (b) Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 1178.

(16) Liotta, D.; Markiewicz, W.; Santiesteban, H. *Tetrahedron Lett.* **1977**, 4365. Cosford, N. D. P.; Schinazi, R. F. *J. Org. Chem.* **1991**, *56*, 2161. Evers, M.; Christiaens, L. *Tetrahedron Lett.* **1983**, *24*, 377.

(17) Kelly, T. R.; Dali, H. M.; Tsang, W.-G. *Tetrahedron Lett.* **1977**, 3859. Scarborough, R. M., Jr.; Toder, B. H.; Smith, A. B., III. *J. Am. Chem. Soc.* **1980**, *102*, 3904.

(18) (d) Du Mont, W.-W.; Kubiniok, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem. Ber.* **1991**, *124*, 1315. (b) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683.

(19) Schumann, H.; Albrecht, I.; Gallagher, M.; Hahn, E.; Muchmore, C.; Pickardt, J. *J. Organomet. Chem.* **1988**, *349*, 103.

(20) Zschunke, A.; Bauer, E.; Schmidt, E.; Issleib, K. *Z. Anorg. Allg. Chem.* **1982**, *495*, 115.

(21) Zschunke, A.; Riemer, M.; Schmidt, H.; Issleib, K. *Phosphorus Sulfur* **1983**, *17*, 237.

(22) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819.

(23) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243.

(24) Mulvey, R. E.; Wade, K.; Armstrong, D. R.; Walker, G. T.; Snaith, R.; Clegg, W.; Reed, D. *Polyhedron* **1987**, *6*, 987.

(25) Schumann, H.; Palamidis, E.; Schmid, G.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 718.

(26) Steiner, A.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1993**, 444.

(27) (a) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318. (b) Raitby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1011.

(28) Lithium–phosphorus coupling has also been detected in an α-lithiophosphoryl compound: Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 1468.

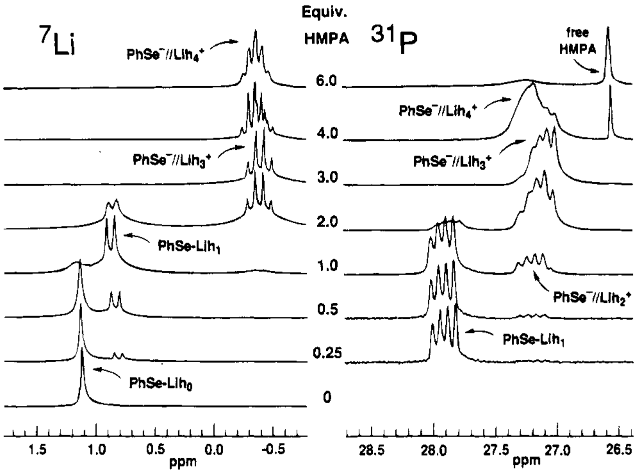


Figure 1. ^{7}Li and ^{31}P NMR spectra of an HMPA titration of 0.16 M PhSeLi in 3:2 THF−ether at −133 °C (h = HMPA).

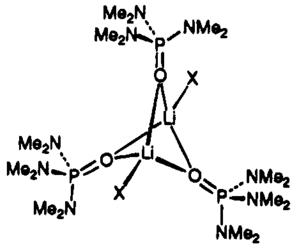
Results and Discussion

Lithium Benzeneselenolate in THF. The ^{7}Li and ^{77}Se NMR spectra of PhSeLi (formed by the reaction of diphenyl diselenide with *n*-BuLi) in THF or mixtures of THF and ether are singlets. Although no J_{Li-Se} coupling could be detected to provide direct information about aggregation or CIP/SIP status, the chemical shifts are informative. The selenium shift at δ 87.3 is more consistent with a monomeric CIP structure, since it is 52.3 ppm downfield of the known dimer in ether (see below) and 123.7 ppm upfield of the SIP formed during the HMPA titration discussed below. Similarly, since the ^{7}Li shift at δ 1.12 is upfield of the dimer in ether (δ 1.5) and downfield of typical SIP's in THF (δ −0.6), a monomeric CIP structure in THF−ether is indicated. Separated ions usually appear in a very narrow region between −0.35 and −1 ppm (exceptions are strongly magnetically anisotropic SIP's such as lithium fluorenide, which appears at δ −1.5).[1f]

The assignment of structure of the THF species is supported by the results of an HMPA titration in 3:2 THF−ether (Figure 1; see Table 1 for data). The PhSeLi(HMPA) complex (d, δ_{Li} 0.85; 1:1:1:1 quartet, δ_P 27.94, J_{Li-P} = 8.5 Hz) formed at 1 equiv of HMPA is also a CIP, as indicated by the ^{7}Li and ^{31}P chemical shifts and proven by the jump in coordination to form PhSe⁻//Li(HMPA)$_3$$^+$. The simultaneous appearance of mono and tris HMPA coordinated lithium (with little or no bis HMPA complexed material) is diagnostic of the CIP to SIP transition.[1f] Additional HMPA produces the typical ^{7}Li quintet of PhSe⁻//Li(HMPA)$_4$$^+$. The ease of SIP formation observed during the HMPA titration of PhSeLi is similar to that seen for LiBr, MeSeLi, (2-(trimethylsilyl)dithianyl)lithium,[1b] ((phenyldimethylsilyl)(phenylthio)methyl)lithium, and others,[1c,d] as well as that of Ph$_2$PLi reported below.

Lithium Benzeneselenolate in Ether. Although the spectra of PhSeLi in THF were fully consistent with a monomeric structure, we were unable to support this assignment with the observation of Se−Li *J* coupling. We therefore examined PhSeLi in ether in the expectation that exchange processes would be slower. Indeed, PhSeLi had a singlet at δ 1.50 in the ^{7}Li NMR spectrum which shows selenium satellites ($^1J_{Se-Li}$ = 18.0 Hz; Figure 2A). This is the first reported observation of lithium−selenium coupling. An analysis of the ^{77}Se NMR spectrum (Figure 2A) revealed a 1:2:3:4:3:2:1 septet at δ 35.1 indicating a selenium coupled to two lithiums. A cyclic oligomer is thus present, probably a dimer. The addition of only 1 equiv of THF to an ether solution of PhSeLi resulted in the loss of coupling in the ^{77}Se NMR, and addition of 16 equiv of THF (≈15:85 THF/ether) caused extreme broadening of the ^{77}Se NMR signal such that it was unobservable.

The addition of HMPA to ether solutions of PhSeLi is troublesome due to the formation of a colorless precipitate which was insoluble even above −78 °C. The precipitate did dissolve with 14 equiv of HMPA to give the characteristic quintet of the separated ion pair PhSe⁻//Li(HMPA)$_4$$^+$. In 3:2 toluene−ether a homogeneous solution could be maintained during part of the HMPA titration (Figure 3). In the early part of the titration a ^{31}P NMR signal at δ 26.5 appears which could indicate a mono HMPA dimer or trimer structure; however, adequate coupling information could not be obtained in the ^{7}Li and ^{77}Se NMR spectra. A second species which appears in the early part of the titration could be more securely identified. This species has a quartet (δ 1.17, $^2J_{Li-P}$ = 4.1 Hz) in the ^{7}Li NMR, characteristic of triply HMPA-bridged dimers (**1a**). The coupling could not be fully resolved in the ^{31}P NMR spectrum, but the chemical shift at δ 30.0 (well downfield of "normal" HMPA adducts of dimers and monomers) and narrow peak shape are similar to that found for the triply HMPA-bridged dimer (Bu$_3$SnLi)$_2$(HMPA)$_3$ (**1b**) formed under similar conditions.[1e] An X-ray structure and NMR observation of a related LiBr complex (**1c**) has been reported.[27a]



1a X = SePh
1b X = SnBu$_3$
1c X = Br

Lithium Diphenylphosphide in THF. Solutions of Ph$_2$PLi were prepared by metalation of diphenylphosphine with *n*-BuLi in 3:2 THF−ether. The ^{31}P NMR spectrum of the phosphide at −120 °C showed a singlet (δ_P −20.0). The absence of the phosphorus−lithium coupling expected for a tight contact ion pair could indicate the presence of a SIP species. However, the ^{7}Li NMR signal (singlet, δ 0.22) is well downfield (Figure 4; see Table 1 for additional data) of the chemical shift range of a typical SIP and suggests the presence of a contact species (Ph$_2$P−Li). The lack of one bond coupling to lithium in the ^{31}P NMR is analogous to the ^{119}Sn NMR spectrum of Bu$_3$SnLi or Me$_3$SnLi in THF[1e] and is likely due to rapid exchange of the Ph$_2$P ligand between lithium cations. The HMPA titration supported the assignment of a monomeric structure. The concentration of contact and separated ion pairs observed at 1.0 equiv of HMPA for Ph$_2$PLi is similar to that seen for Bu$_3$SnLi. Almost equimolar amounts of Ph$_2$P−Lih$_0$, "Ph$_2$PLih$_1$", and Ph$_2$P⁻//Lih$_2$$^+$ are present, where "Ph$_2$PLih$_1$" (doublet, δ −0.20) may be a mixture of Ph$_2$P−Lih$_1$ and Ph$_2$P⁻//Lih$_1$$^+$ in rapid exchange. As

Table 1. Chemical Shifts (ppm) and Coupling Constants (Hz) in Parentheses for Lithium Benzeneselenolate

species	conditions	$\delta(i\text{-C})$	$\delta(o\text{-C})$	$\delta(m\text{-C})$	$\delta(p\text{-C})$	δ_{Se} ($^1J_{Se-Li}$)	δ_{Li}	δ_P(HMPA) ($^2J_{P-Li}$)
PhSeH	*a*	124.4	132.8	129.2	126.4			
PhSeBu	*b*	131.2	131.1	129.9	126.5	290		
$PhSeLih_0$	*b*	144.1	137.0	127.2	120.1	89	1.12	
$PhSeLih_1$	*b*	146.2	137.1	126.9	119.3	110	0.85	27.9 (8.5)
$PhSe^-//Lih_4^+$	*b*	152.5	137.8	126.1	117.0	221	−0.35	27.3 (7.2)
$(PhSeLi)_2h_0$	*c*	140.0	137.4	127.9	122.2	36 (18)	1.40	
$PhSeLi-h_3-LiSePh$	*c*	144.5	137.5	127.4	120.4	100	1.17	30.0
$PhSe^-//Lih_4^+$	*c*	153.0	138.4	126.6	117.4	222	−0.25	27.2 (7.7)
$(PhSeLi)(LiPPh_2)$	*c*	139.7	137.0	127.6	121.8	38 (18)	1.21	

[a] $CDCl_3$ at room temperature. [b] 4:1 Me_2O−THF at −120 °C. [c] 4:1 toluene−ether at −100 °C.

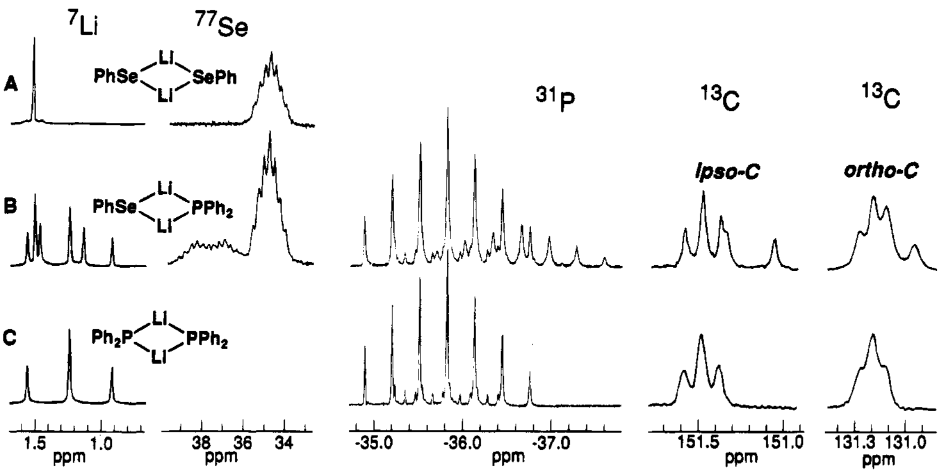


Figure 2. Selected signals in the ^{7}Li, ^{77}Se, ^{31}P, and ^{13}C NMR spectra in ether at −110 °C of PhSeLi (A), a mixture of PhSeLi and Ph_2PLi (mixed dimer) (B), and Ph_2PLi (C).

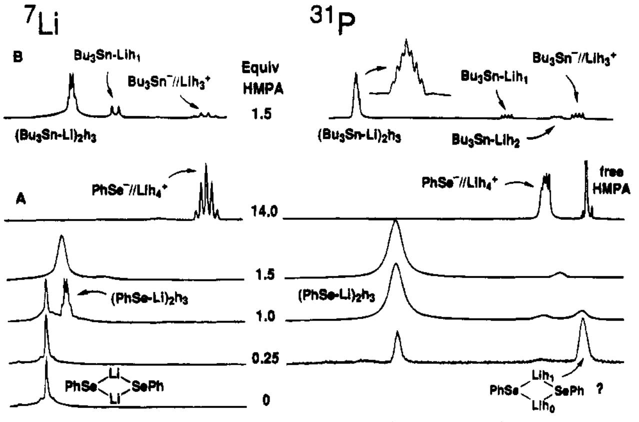


Figure 3. (A) ^{7}Li and ^{31}P NMR spectra of an HMPA titration of 0.18 M PhSeLi in 3:2 toluene−ether at −110 °C (h = HMPA). (B) Spectra of $(Bu_3SnLi)_2(HMPA)_3$ in ether at 1.5 equiv of HMPA.[1e]

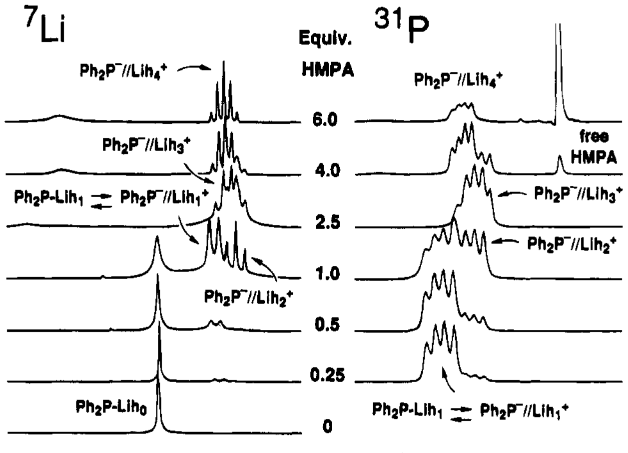


Figure 4. ^{7}Li and ^{31}P NMR spectra of an HMPA titration of Ph_2PLi in 3:2 THF−ether at −125 °C.

observed also for Bu_3SnLi,[1e] the chemical shift of the mono HMPA species was strongly temperature dependent, as expected for a CIP−SIP equilibrium. It should be noted that at 1.0 equiv of HMPA the ^{31}P NMR signal of the phosphide became broader and moved downfield almost 13 ppm (to δ −7.2). The ^{31}P chemical shift of the SIP (in ether or THF with 6.0 equiv of HMPA) was ≈+3.0 ppm. It is interesting that Ph_2PLi undergoes ion separation more easily than does PhSeLi, even though it is considerably more basic.

Lithium Diphenylphosphide in Ether. The HMPA titration of Ph_2PLi in ether (Figures 5 and 6) produced more informative spectra than those obtained for PhSeLi in ether because of better solubility and the high natural abundance of ^{31}P. The phosphide solution shows a well-resolved triplet (δ_{Li} 1.54, $^1J_{Li-P}$ = 45.1 Hz) in the ^{7}Li NMR and a 1:2:3:4:3:2:1 septet (δ_P −32.4, $^1J_{Li-P}$ = 45.1 Hz) in the ^{31}P NMR spectrum, as already reported by McFarlane.[11,21] This indicates that each phosphorus atom is coupled to two neighboring ^{7}Li nuclei, and vice versa, and defines a cyclic oligomer (most likely a dimer; more on this below). Interestingly, between the peaks of the septet in the ^{31}P NMR, a quartet of triplets (J = 45.1, 17.1 Hz) can be observed due to the 14% of dimer containing one ^{7}Li and one ^{6}Li (natural abundance 7.4%) nucleus (Figure 2C).

With the addition of up to 1.0 equiv of HMPA two new sets of signals are seen in the ^{7}Li and ^{31}P NMR.

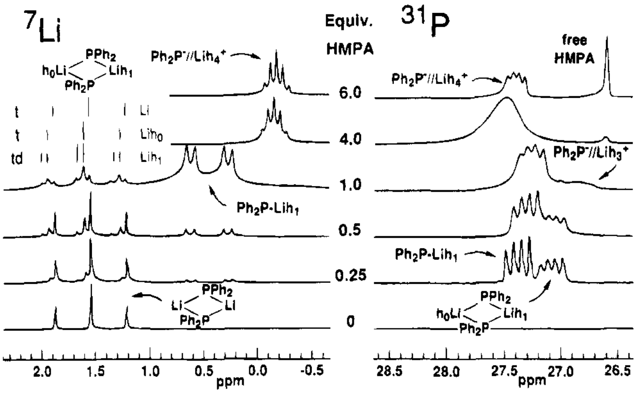


Figure 5. ^{7}Li and ^{31}P NMR (HMPA region) spectra of an HMPA titration of 0.18 M Ph_2PLi in ether at −126 °C.

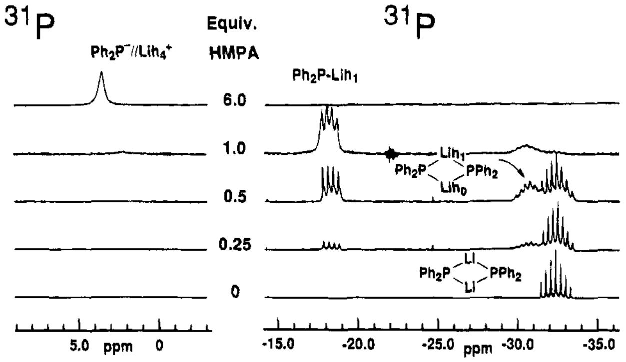


Figure 6. ^{31}P NMR spectra (phosphide region) of an HMPA titration of 0.18 M Ph_2PLi in ether at −126 °C.

The first is the mono HMPA-solvated dimer characterized by a 1:2:3:4:3:2:1 septet (δ_P −30.7, $^1J_{P-Li}$ = 44.2 Hz) and a 1:1:1:1 quartet (δ_P, 27.1, $^2J_{P-Li}$ = 9 Hz) in the ^{31}P NMR and a triplet (δ_{Li} 1.6, $^1J_{Li-P}$ = 44.7 Hz) and triplet of doublets (td, δ_{Li} 1.64, $^1J_{Li-P}$ = 43.6, $^2J_{Li-P}$ = 9 Hz) in the ^{7}Li NMR. The second set of signals (δ_P −18.1, 1:1:1:1 quartet, $^1J_{P-Li}$ = 47.6 Hz; δ_P +27.3, 1:1:1:1 quartet, $^2J_{P-Li}$ = 10.7 Hz; δ_{Li} 0.45, dd, J = 47.6, 10.7 Hz) is due to a mono HMPA-complexed monomer. A temperature dependent ^{31}P NMR chemical shift and a broad ^{7}Li NMR signal suggest that the mono HMPA monomer in ether, like in THF, is a mixture of Ph_3P—Lih_1 and $Ph_3P^-//Lih_1^+$ in rapid exchange. With a greater concentration of HMPA (4−6 equiv) one bond lithium−phosphorus coupling was lost in both spectra (a broad singlet was seen at δ +3.0 in the ^{31}P NMR) and the usual ^{7}Li and ^{31}P NMR signals for the tetra HMPA SIP were present. Thus HMPA transforms dimeric Ph_2PLi in ether through a series of intermediate structures to eventually form a separated ion pair. This can be contrasted with the behavior of dimeric lithium diisopropylamide in THF, which coordinates up to one HMPA per lithium but does not subsequently undergo deaggregation or ion separation even when excess HMPA is present.[1d]

Between 1.0 and 4.0 equiv of HMPA no spectra were obtained due to the formation of an unidentified white precipitate. The precipitate did not dissolve in the presence of toluene, furan, or triethylamine. In the presence of 4.0 equiv of HMPA, however, the solution again became homogeneous.

The ^{13}C NMR spectra show distinct signals for each of the species discussed (Table 2). The ipso carbon signals show a downfield shift from δ 135.1 for Ph_2PH ($^1J_{C-P}$ = 9.4 Hz) to δ 151.5 and 152.4 (no HMPA and mono HMPA dimers, respectively), to δ 156.7 (mono HMPA monomer), and finally to δ 161.1 for the tetra HMPA SIP ($^1J_{C-P}$ = 60.3 Hz). The corresponding para carbon signals move upfield from δ 129.2 for Ph_2PH, to δ 121.4 for the dimer, and finally to δ 115.8 for the SIP. Such chemical shift patterns, downfield for ipso and upfield for para, have been reported for a number of phenyl compounds where negative charge is present at atoms adjacent to the aromatic ring: e.g., PhSeM (Table 1), PhOM,[8c] and PhLi.[1h]

Distinguishing Cyclic Dimers and Trimers: ^{13}C NMR Spectrum of Lithium Phosphide Dimer. The dimer of Ph_2PLi in ether shows an unusual and unexpected spectroscopic feature: the ipso and ortho carbon signals are apparent triplets (Figure 2C), instead of the doublet expected for coupling to a single phosphorus. Since it is unlikely that these carbons are coupled equally to the directly bonded and remote P nuclei of the dimer, there must be a substantial coupling between the two phosphorus nuclei. This is thus a case of virtual coupling, such as is frequently seen for phosphine signals in symmetrical P—O—P compounds and in bis(triphenylphosphine) transition metal complexes of the close-coupled ABX type.[29] In principle this is a system of the AA′X type, but we expect a ^{13}C isotope shift between the two P nuclei, making the system ABX. We could not determine the one-bond ^{13}C isotope shift in Ph_2PLi dimer, so we measured it for Ph_3P and found a value of 2.8 Hz at 145.8 MHz (19.2 ppb).

To aid in the analysis of this spectrum we performed a variable-temperature experiment and observed the transformation of the apparent triplet at −98 °C to a normal doublet at 0 °C ($^1J_{C-P}$ = 28 Hz), consistent with the loss of $^2J_{PLiP}$ coupling due to interaggregate exchange of the dimer. We have not fully analyzed the curious variable-temperature behavior of this system, in which the low-temperature apparent triplet first transforms to an apparent singlet as temperature is raised and then transforms to a doublet. A similar doublet is found for the separated ion $Ph_2P^-//Li(HMPA)_4^+$ ($^1J_{CP}$ = 60 Hz, −126 °C). A change in aggregation at higher temperature is not likely since no noticeable temperature dependance was observed for the ^{7}Li or ^{31}P (<1.5 ppm downfield shift) NMR signals.

The separation between the outer lines of the apparent triplet in THF (19.7 Hz) corresponds to $^1J_{CP}$ + $^3J_{CPLiP}$ (J_{AX} + J_{BX} of the ABX system). Since this is smaller than the 28 Hz determined for the true value of $^1J_{C-P}$ in the high-temperature spectrum, we tentatively conclude that the ipso phenyl carbon is coupled to both P nuclei of the dimer, with $^3J_{CPLiP}$ = −8 Hz. Of course, it is possible that unknown structural changes in the Ph_2PLi aggregate at the higher temperature caused the change in the one bond coupling. The ortho carbon behaves similarly, except that the long range C—P coupling (J_{CCPLiP}) is apparently zero, since the separation between the outer lines of the low-temperature triplet and the two lines of the doublet are identical (14.6 Hz); hence, the ortho carbon is coupling only to the near phosphorus.

---

(29) Harris, R. K.; McVicker, E. M.; Hägele, G. *J. Chem. Soc., Dalton Trans.* **1978**, 9. Beckmann, H.; Grossmann, G.; Ohms, G. *Magn. Reson. Chem.* **1992**, *30*, 860.

(30) NMR simulations were done with the IBM-PC computer program RACCOON.

Table 2. Chemical Shifts (ppm) and Coupling Constants (Hz) in Parentheses for Lithium Diphenylphosphide

species	conditions	δ(*i*-C) ($^1J_{C-P}$)	δ(*o*-C) ($^2J_{C-P}$)	δ(*m*-C) ($^3J_{C-P}$)	δ(*p*-C)	δ_P ($^1J_{P-Li}$)	δ_{Li} ($^1J_{Li-P}$)	δ_P(HMPA) ($^2J_{P-Li}$)
Ph_2PH	*a*	135.1 (9.4)	134.5 (16.7)	129.3 (6.1)	129.2	−38.7		
Ph_2PLih_0	*a*	156.8 (46.5)	129.0 (17.8)	127.2	118.7	−16.8	0.09	
$Ph_2P^-//Lih_4^+$	*a*	161	127	126	116	2.6	−0.35	27.5 (7.6)
$(Ph_2PLi)_2h_0$	*b*	151.5	130.9	127.7	121.4	−32.4 (45.1)	1.54 (45.1)	
$(Ph_2PLi)_2h_1$	*b*	152.4	130.8	127.4	120.7	−30.7 (44.2)	1.61, 1.64 (44.7, 43.6)	27.1 (9)
Ph_2PLih_1	*b*	156.7 (43.5)	129.6 (18.6)	127.1	118.9	−18.1 (47.6)	0.21 (47.6)	27.3 (10.7)
$Ph_2P^-//Lih_4^+$	*b*	161.1 (60.3)	127.9	126.6	115.8	2.9	−0.18	27.4 (7.8)
(PhSeLi) ($LiPPh_2$)	*b*	151.3	130.8	127.7	121.4	−36.6	1.31	

[a] 6:4:1 THF−Et_2O−hexane at −125 °C. [b] 100% ether at −125 °C.

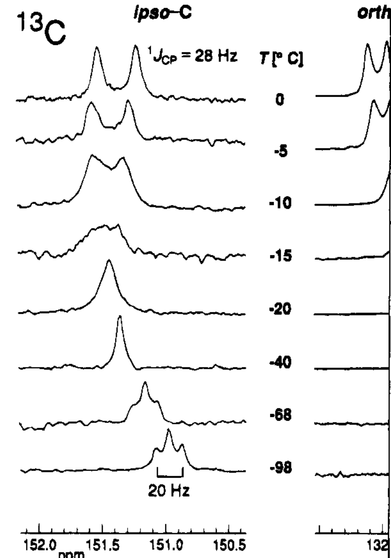


Figure 7. Variable-temperature ^{13}C NMR spectra (ipso and ortho phenyl carbons of aryl region) of Ph_2PLi dimer in ether from −98 to 0 °C.

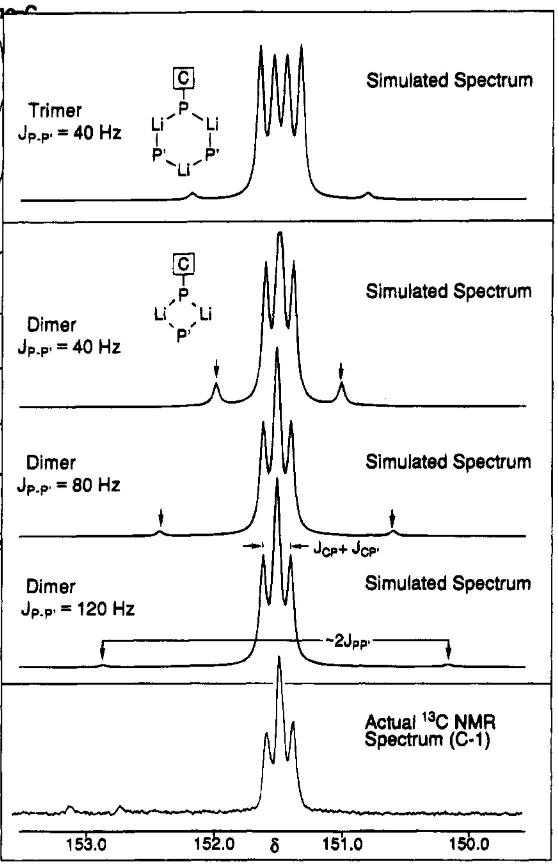


Figure 8. Experimental (lower trace) and simulated ^{13}C NMR spectra of the ipso-carbon signal of the Ph_2PLi dimer.[30] The simulations use $\Delta\delta_{PP'} = 2.8$ Hz, $^1J_{CP} = 28$ Hz, $^3J_{CPLiP'} = -8.3$ Hz, and $^2J_{PLiP'}$ = variable, as shown on the spectra.

We have attempted to estimate a lower limit for the size of $^2J_{PLiP}$ by performing a series of simulations. We used $^1J_{CP} = 28$ Hz and $^3J_{CPLiP} = -8.3$ Hz. From the absence of outer small lines (lines 14 and 15 of the ABX pattern[31]) in the experimental spectrum and the absence of detectable splitting of the central line of the triplet, we estimate that $^2J_{PLiP}$ must be at least 80 Hz (Figure 8). One caveat to this estimate is the small but unknown amount of dynamic broadening in the lowest temperature spectrum. Since such processes would broaden the small outer satellites more than the inner lines, it is possible that satellites of this size in the $J_{PP'} = 80$ Hz simulation could escape detection. The lower limit of 80 Hz is quite compatible with the directly detected coupling across lithium of 90.7 Hz in the mixed dimer reported below and with the coupling of 240 Hz reported for mixed dimer of $(Ph_2PLi)(PhMePLi)$.[11b]

Distinguishing between Cyclic Dimer and Trimer. The above analysis has another important implication for the structure of the Ph_2PLi aggregation. The Li−P couplings alone indicate that P is coupled to two Li, and Li is coupled to two P. As previously recognized for lithium amides and other aggregated structures,[7c] such information is consistent with but does not require a dimeric structure. Any cyclic oligomer would give such coupling (e.g., a cyclic trimer, as found for (2,6-bis(dimethylamino)phenyl)lithium[32]). In the present case, the observation of an apparent triplet for the ^{13}C of P-bonded carbon requires the cyclic dimer structure; otherwise the ^{13}C NMR signal would show a higher multiplicity; i.e., the carbon would be virtually coupled to more than two P nuclei. For a trimer, the spin system would be AB_2X (where X represents carbon, A represents the ^{31}P bonded to ^{13}C, and B represents the other two ^{31}P nuclei), and an apparent quartet would be observed (see top spectrum in Figure 8). A cyclic trimer structure has been found for PhHPLi on the basis of an analysis of the ^{31}P and ^7Li NMR spectrum.[11b]

Analysis of the ^7Li NMR spectrum of Ph_2PLi in ether also leads to the conclusion that only a cyclic dimer would give the observed triplet. For higher oligomers, with $J_{PP} > 0$, "virtual coupling" effects would result in more complex multiplets (see the simulations in Figure 9).

Mixed Dimer of PhSeLi and Ph_2PLi. The symmetric structure of the phosphide dimer prevents full

---

(31) Bovey, S. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: New York, 1969; p 107.

(32) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 1696.

analysis of the coupling pattern and direct measurement of J_{PLiP}. We therefore examined mixtures of Ph_2PLi and PhSeLi to test for the formation of mixed dimers and to explore the generality of such couplings.

Figure 2B shows ^{7}Li, ^{77}Se, ^{31}P, and partial ^{13}C NMR spectra of a ≈1:1 mixture of PhSeLi and Ph_2PLi in ether. In addition to the two homodimers, there are peaks in the spectra of all four nuclei for the mixed dimer $(Ph_2PLi)(LiSePh)$. In the ^{7}Li NMR there is a new doublet, $^1J_{LiP} = 45.8$ Hz, in the ^{31}P NMR there is a new 1:2:3:4:3:2:1 septet for coupling to two lithiums, and the ^{77}Se NMR spectrum shows a doublet of septets, the septet splitting ($^1J \approx 18$ Hz) from Se coupling to the two lithiums and the doublet due to $^2J_{SeLiP}$ coupling of 90.7 Hz. The ^{13}C NMR spectrum is informative; the ipso-carbon region at δ 151.5 shows, in addition to the apparent triplet at δ 151.5 for $(Ph_2PLi)_2$, a doublet with $J_{C-P} = 25.4$ Hz at δ 151.2 for the mixed dimer. The ortho-carbon at δ 131.0 is also a doublet ($^2J_{C-P} = 14$ Hz). These observations nicely confirm the conclusion reached above for the Ph_2PLi homodimer; there are indeed large couplings between nuclei bridged by lithium in dimeric structures, and analysis of these can give structural information.

Conclusions. The current study has shown that both PhSeLi and Ph_2PLi form dimers in ether and monomers in THF. In each case addition of excess HMPA produces separated ion pairs. The two species also form a mixed dimer in ether with nearly statistical distribution. For the lithium phosphide dimer and the mixed dimer the NMR analysis unambiguously ruled out higher oligomeric structures.

Experimental Section

General Methods. Tetrahydrofuran (THF) and ether were freshly distilled from sodium benzophenone ketyl before use. Hexamethylphosphoric triamide (HMPA) was obtained from Aldrich, distilled from CaH_2 at reduced pressure, and stored under N_2 over molecular sieves. Transfers of HMPA were done by syringe techniques in a fume hood. Glassware was dried overnight in an 110 °C oven or flame dried to remove moisture. Common lithium reagents were titrated with *n*-PrOH (or *i*-PrOH) in THF using 1,10-phenanthroline as indicator.

Diphenylphosphine and *n*-BuLi were obtained from Aldrich. Diphenyl diselenide was prepared by literature procedure.[33] Reported reaction temperatures are those of the cooling bath with −78 °C being maintained by a dry ice/ethanol bath.

NMR Spectroscopy. ^{1}H nuclear magnetic resonance (NMR) spectra were obtained on Bruker WP-200 or WP-270 spectrometers. All ^{1}H NMR spectra were measured in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard (δ 0.00).

All multinuclear low-temperature NMR experiments were run on a wide-bore AM-360 spectrometer at 139.962 MHz (^{7}Li), 145.784 MHz (^{31}P), or 68.683 MHz (^{77}Se) with the spectrometer unlocked. Digital resolution was 0.5−1.0 Hz for ^{7}Li and ^{31}P and 1.5 Hz for ^{77}Se. For a 0.15 M solution, 40 transients for the ^{7}Li spectrum and 80−120 scans for the ^{31}P spectrum afforded an excellent signal to noise ratio. For ^{77}Se NMR, 1000−5000 scans were required to obtain adequate resolution. (Note: Although the spectrometer was unlocked during acquisition, the field was generally very stable and only occasionally did an experiment have to be abandoned due to a field shift.)

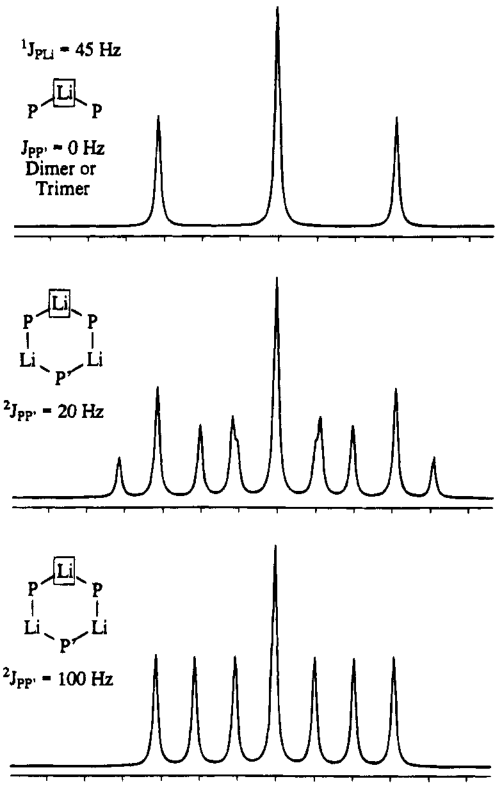


Figure 9. Simulated ^{7}Li NMR spectra of cyclic trimer (or higher oligomers with various values of J_{PP}.[30]

The NMR shift standards used were as follows: for ^{77}Se, *n*-BuSePh at δ 290 as a secondary internal standard; for ^{7}Li, 0.3 M LiCl in methanol as an external standard; for ^{31}P, PPh_3 in THF at −6 ppm as a secondary external standard.

General Procedure for HMPA Titration of Lithium Reagents. Samples of the lithium reagent (0.66 mmol) in THF or other solvent (3.5 mL) were prepared in 10-mm thin-walled NMR tubes which were oven-dried, N_2-flushed, and fitted with a septum (9-mm inner diameter). The outside top portion of the tube was lightly greased to make a better seal for the septa which were held securely by parafilm. Silicon grease was placed on the septa tops to seal punctures, and the tubes were stored at −78 °C until the experiment was performed. After adjustment of the field homogeneity values for the $CDCl_3$ lock sample, the AM-360 spectrometer was unlocked, the probe was cooled (−120 to −130 °C), and the temperature was measured before and after the experiment using a calibrated RTD (resistance temperature device) accurate to 0.03 °C. The reading was taken 10 to 15 min after the RTD element had been lowered into the probe. (The reading fluctuated within ~0.1 °C at this point.) The sample was inserted, and the spectrometer was tuned. Since deuterated solvents were not used, the field was tuned on the ^{13}C FID of C-3 of THF, and NMR spectra of ^{7}Li, ^{31}P, and other nuclei were measured. The sample was ejected, placed in a −78 °C bath, and, for example, 0.25 equiv of HMPA (28.0 μL, 0.161 mmol, 28.8 mg) was added. In order to get the HMPA to dissolve the tube had to be repeatedly warmed slightly and shaken. The sample was placed in the probe, and after about 10 min the NMR spectra were taken with various amounts of HMPA.

^{7}Li, ^{31}P, ^{77}Se, and ^{13}C NMR Spectroscopy of an HMPA Titration of 0.18 M Lithium Benzeneselenolate. To a 10-mm NMR tube containing 218 mg (0.70 mmol) of diphenyl diselenide dissolved in 2.4 mL of THF and 1.6 mL of ether was added *n*-BuLi (350 μL, 0.70 mmol, 2.00 M in hexane). The solution became colorless upon mixing, and an NMR experiment (^{7}Li and ^{31}P NMR taken during an HMPA titration) was performed with a probe temperature of −133 °C. Proton NMR analysis (using pentachloroethane as an internal reference)

---

[33] Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. Renga, J. M. Ph.D. Dissertation, University of Wisconsin—Madison, 1977; p 28.

of the MeI-quenched lithium reagent gave a 90% yield of PhSeCH$_3$. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 2.23 (s, 3H), 7.1–7.5 (m, 5H). The ^{77}Se and ^{13}C NMR spectra were obtained in 4:1 Me$_2$O–THF at −120 °C. The NMR data for the lithium benzeneselenolate ion pair species are presented in Table 1.

^{7}Li, ^{31}P, ^{77}Se, and ^{13}C NMR Spectroscopy of an HMPA Titration of 0.18 M Lithium Benzeneselenolate in Ether or 3:2 Toluene–Ether. To a 10-mm NMR tube containing 218 mg (0.70 mmol) of diphenyl diselenide dissolved in 3.6 mL of ether at −78 °C was added *n*-BuLi (259 μL, 0.70 mmol, 2.70 M in hexane). The solution became colorless upon mixing, and an NMR experiment was performed with a probe temperature of −110 °C. Upon addition of 0.5 equiv of HMPA a yellow suspension formed which made the acquisition of spectra difficult. With a mixture of 3:2 toluene–ether the solution remained homogeneous at −100 °C with up to 2.0 equiv of HMPA. The NMR data for the lithium benzeneselenolate ion pair species are presented in Table 1.

^{7}Li and ^{31}P NMR Spectroscopy of an HMPA Titration of Lithium Diphenylphosphide in THF/Ether at −125 °C. A 10-mm NMR tube was rinsed with MeLi solution to remove adventitious moisture. Diphenylphosphine (122 μL, 0.70 mmol), 2.1 mL of THF, and 1.4 mL of ether were added, the solution was cooled to −78 °C under an N$_2$ atmosphere, and *n*-BuLi (350 μL, 0.70 mmol, 2.0 M in hexane) was added. The solvent composition was 6:4:1 THF–ether–hexane. The solution turned yellow-orange upon shaking and was stored at −20 °C for 1 h. An HMPA titration was performed with a probe temperature of −125 °C. The NMR data for the lithium diphenylphosphide ion pair species are presented in Table 2.

^{7}Li and ^{31}P NMR Spectroscopy of an HMPA Titration of Lithium Diphenylphosphide in Ether at −125 °C. To a MeLi-flushed 10-mm NMR tube containing diphenylphosphine (122 μL, 0.70 mmol) and 1.5 mL of ether cooled to −78 °C under N$_2$ atmosphere were added MeLi (464 μL, 0.70 mmol, 1.51 M in ether) and 2.0 mL of additional ether. The solution turned yellow upon shaking and was allowed to stand at room temperature (or −20 °C) for 30 min (only starting material was present after 1 h at −78 °C). An HMPA titration was performed with a probe temperature of −125 °C. An orange solution resulted from the addition of up to 1.0 equiv of HMPA with the solution becoming red with 4.0 equiv of HMPA. With 1 or 2 equiv of HMPA present the solution was heterogeneous, even at temperatures warmer than −78 °C. The NMR data for the lithium diphenylphosphide ion pair species are presented in Table 2.

^{7}Li, ^{31}P, ^{13}C, and ^{77}Se NMR Spectroscopy of a Solution of Lithium Diphenylphosphide and Lithium Benzeneselenolate in Ether at 110 °C. The contents of two 10-mm NMR tubes containing ether solutions of lithium diphenylphosphide and lithium benzeneselenolate (prepared as described above) were combined at −78 °C by cannula. The volume of the solution was adjusted to 4.0 mL, and NMR data were acquired with a probe temperature of −105 °C. ^{13}C NMR (90.556 MHz, ether, −105 °C) of mixed dimer: δ 121.38 (P *p*-), 121.82 (Se *p*-), 127.58 (Se *m*-), 127.72 (P *m*-), 130.80 (P *o*-, doublet J_{C-P} = 14.6 Hz), 136.96 (Se *o*-), 139.70 (Se *i*-), 151.30 (P *i*-, doublet, J_{C-P} = 25.4 Hz). ^{77}Se NMR (68.683 MHz, ether): δ 37.9 (doublet of septets, J_{Se-P} = 90.7 Hz, $J_{Se-Li} \approx 18$ Hz).

Acknowledgment. We thank the National Science Foundation for support of this work.

OM940548C