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^{7}Li PGSE Diffusion Measurements on LiPPh$_2$: A Solvent Dependence of the Structure

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The first application of ^{7}Li pulsed-gradient spin–echo (PGSE) diffusion methods to structural lithium chemistry is reported. The data, which provide quantitative diffusion constants at 155 K, lead to a new method of estimating solvent viscosity at this temperature and clearly show a solvent dependence for the structure of LiPPh$_2$. In THF, LiPPh$_2$ exists as a mononuclear solvated species, whereas in Et$_2$O, a dinuclear structure is found. *D* values for the model compound PHPh$_2$ in THF have been measured.

Although chemical shifts and coupling constants from one- and two-dimensional NMR methods remain the most useful NMR tools, diffusion methods[1–3] are slowly beginning to be recognized by inorganic/organometallic chemists as a worthwhile structural complement. For complex salts, diffusion measurements on the anion and cation provide insight into how these charged species interact while simultaneously affording an estimate of molecular volumes via their various diffusion constants.[2a,c,d,3] We have recently shown that ^{31}P,[4] and to a lesser extent, even ^{35}Cl,[4] can serve as diffusion probes, thereby increasing the flexibility of this methodology.

There is much interest in lithium chemistry;[5] unfortunately, it is often the case that differing degrees of solvation and/or aggregation complicate the structural picture. Specifically, lithium phosphides are widely used as organophosphide transfer reagents.[5a,6] Their structures have been investigated in solution[7] and in the solid state,[8] and it is recognized that these materials can be ionic, e.g., [Li-(12-crown-4)$_2$][PPh$_2$];[9] dimeric, e.g., [{LiP(CH(SiMe$_3$)$_2$)$_2$}$_2$];[10] or tetrameric, [{Li$_2$-(μ_3-*t*-Bu$_2$P)(μ-*t*-Bu$_2$P)(THF)}$_2$].[11] In more polar solvents, these reagents are thought to form ion pairs with different degrees of solvation.[7a,b] For LiPPh$_2$, it has been suggested that, in THF and Et$_2$O, polymeric chainlike structures exist in solution.[8b]

We communicate here our room- and low-temperature[12] ^{7}Li pulsed-gradient spin–echo (PGSE) diffusion data on LiPPh$_2$ in THF and Et$_2$O, which provide a clearer view of

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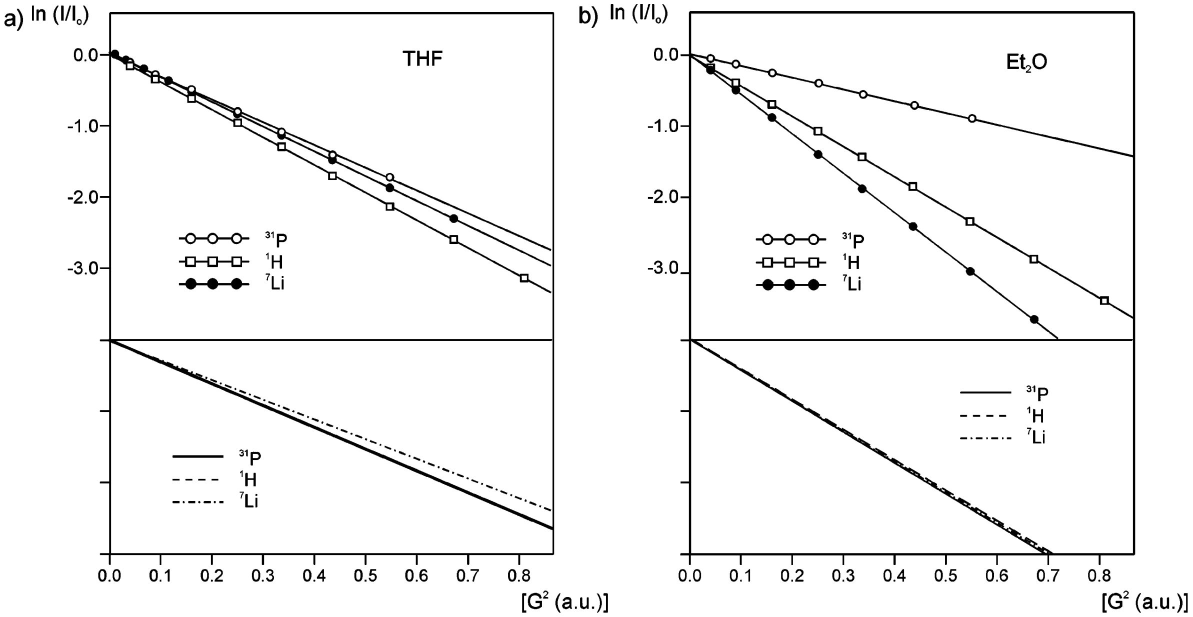

Figure 1. Plot of $\ln(I/I_o)$ vs arbitrary units proportional to the square of the gradient amplitude for ^{1}H (□), ^{7}Li (●), and ^{31}P (○) PGSE diffusion measurements on 60 mM Ph_2PLi samples at room temperature in (a) THF (^{1}H $\delta = 1.75$ ms, $\Delta = 59.3$ ms; ^{7}Li $\delta = 4$ ms, $\Delta = 70$ ms; ^{31}P $\delta = 8$ ms, $\Delta = 16$ ms) and (b) Et_2O (^{1}H $\delta = 1.75$ ms, $\Delta = 43$ ms; ^{7}Li $\delta = 4$ ms, $\Delta = 70$ ms; ^{31}P $\delta = 3$ ms, $\Delta = 33$ ms). The observed intensity attenuation depends on the D values, the gyromagnetic ratio (γ) of the observed nucleus, and the diffusion parameters δ and Δ (see Supporting Information). The lower sections of the figures show the calculated lines adjusted to a hypothetical unified set of parameters ($\Delta = 84$ ms, $\delta = 1.75$ ms, and γ of ^{1}H), and in Et_2O, the slopes are equal for the three measurements.

Table 1. D ($\times 10^{10}$ m^2 s^{-1}) and r_H (Å) Values[a] in THF and Et_2O at Room Temperature

	nucleus	D^b	$r_H{}^c$	$(r_H)^d$
$LiPPh_2$ (THF)	^{7}Li	10.1	4.7	(5.6)
	^{1}H	11.0	4.3	(5.2)
	^{31}P	11.0	4.3	(5.2)
$LiPPh_2$ (Et_2O)	^{7}Li	16.1	6.2	(6.7)
	^{1}H	16.0	6.2	(6.7)
	^{31}P	16.2	6.1	(6.7)
Ph_2PH (THF)	^{31}P	15.8	3.0	(4.5)
	^{1}H	15.8	3.0	(4.5)

[a] All at 60 mM. [b] Experimental error is ca. ±2%. [c] Standard deviation is ca. ±0.1 Å. η (THF, 299 K) = 0.461×10^{-3} kg s^{-1} m^{-1}. η (Et_2O, 299 K) = 0.221×10^{-3} kg s^{-1} m^{-1}. [d] These eight r_H values were calculated using the constants 5.0, 5.5, and 4.0 (instead of 6) for $LiPPh_2$ (THF), $LiPPh_2$ (Et_2O), and $HPPh_2$, respectively.[18]

the solution structure of this salt in these two solvents. These represent the first ^{7}Li diffusion measurements on organophosphorus salts.[13] We know of only one application of ^{7}Li as a diffusion probe in organometallic chemistry,[14] and this involves *n*-BuLi compounds and uses the DOSY (diffusion-ordered spectroscopy) and not the PGSE methodology. Although this report proved to be both elegant in conception and quite useful, the low-temperature diffusion measurements on relatively concentrated 0.2 M solutions resulted in large errors (up to 12% in the D values).

Figure 1 and Table 1 show the PGSE results for 60 mM solutions of $LiPPh_2$ in THF and Et_2O at ambient temperature. The table contains ^{7}Li, as well as ^{1}H and ^{31}P, results for the anion and the D values for 60 mM $HPPh_2$ in THF as a model. The equivalence of the ^{1}H and ^{31}P D values in each solvent provides a check on the reproducibility of the measurements in that these nuclei reside in the same fragment.

In the following discussion, we use the hydrodynamic radius, r_H, as defined by the Stokes–Einstein relation.[15] This allows us to use measured D values to estimate r_H and thus eliminate the viscosity difference between THF and Et_2O.

From the data in Table 1, several points are obvious: (a) The r_H values indicate a much smaller volume of $LiPPh_2$ in THF than in Et_2O (but larger than the volume for $HPPh_2$, because of the phosphide–lithium interaction). (b) In Et_2O, all three nuclei (^{7}Li, ^{1}H, and ^{31}P) afford the same r_H value, suggesting that they are translating at the same rate. The larger D value in Et_2O relative to THF is due to the different viscosities. (c) In THF, the ^{7}Li diffusion constant is significantly smaller (and the r_H value larger) than those from the ^{1}H and ^{31}P measurements.

In a fundamental paper, Power and co-workers[8a] reported the solid-state structures of the dinuclear salt $[\{Li(Et_2O)(P(mesityl)_2)\}_2]$ and mononuclear $[Li(THF)_3(PH(mesityl))]$. From their X-ray data, one can estimate the rotational radius[16]

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(15) $D = kT/6\pi\eta r_H$, where k is the Boltzman constant, T is the temperature, η is the viscosity of the solvent, and r_H is the hydrodynamic radius of the diffusing particle. It has been suggested that the factor of 6 in this equation is not valid for small species whose van der Waals radii are <5 Å (Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261). To be consistent and to facilitate comparisons, we have used the Stokes–Einstein equation as shown. Viscosities at room temperature (of nondeuterated solvents) were taken from: Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999 (online at http//www-.knovel.com). The difference in viscosity between pure THF and a 60 mM solution of $LiPPh_2$ in THF can be estimated using the experimental D values for the pure solvent (D = 27.8) and for THF in the phosphide solution (D =27.5). Clearly, the viscosity difference is small.

(assuming phenyl instead of mesityl) to be ca. 6.4 Å for the dimer and ca. 5.0 Å for the mononuclear derivative (see Supporting Information). The X-ray structure for the $Li(THF)_4^+$ cation is known[17] and affords a rotational radius of ca. 4.9 Å, i.e., replacing one THF by a PHPh has only a modest effect on *r*. We have shown that there is a reasonable correlation between a crystallographically determined rotational radius and the hydrodynamic radius, r_H, measured via PGSE methods.[3c] Our calculated r_H values of 4.3 and 4.7 Å in THF are somewhat small,[18] but they clearly indicate a mono- rather than a dinuclear species in this solvent. These different r_H values suggest equilibria that involve: (a) some separation of the Li^+ and PPh_2^- moieties and (b) a Li cation with less than four THF molecules.[19] The 6.2 Å r_H value in Et_2O is consistent with the expected dinuclear structure.[20]

Several groups have suggested this type of structural solvent dependence, on the basis of the presence or absence of $^{1}J(^{7}Li,^{31}P)$ values.[20] We find a septet in the ^{31}P NMR spectrum and a triplet in the ^{7}Li spectrum, both with $^{1}J(^{7}Li,^{31}P) = 44$ Hz at 202 K in Et_2O, but we observe no coupling in THF, in agreement with the literature.[7a−c, 20c]

To suppress possible dynamics, we measured our $LiPPh_2$ THF solution at 155 K, and we report these data in Table 2. There are no literature viscosity data for THF at 155 K, which is slightly below its freezing point. To circumvent this problem, we measured a 60 mM THF solution of $PHPh_2$ and a reference material, TMSS ($Si(SiMe_3)_4$),[2d] at room temperature and 155 K. Because the r_H values for $PHPh_2$ and TMSS at ambient temperature can be determined,[15] the measured *D* values at 155 K, together with the Stokes−Einstein equation,[15] afford a realistic estimate of the THF viscosity, η (10.4×10^{-3} Kg s^{-1} m^{-1}) at 155 K. With this η value, the observed *D* values for our $LiPPh_2$ solution can be used to evaluate the r_H values, which are now 4.5 and 4.9 Å for the phosphide anion and lithium cation, respectively. Clearly, even at this very low temperature, the cation and anion reveal different *D* values. We note that the 4.9 Å r_H value is consistent with $Li(THF)_4^+$. Moreover, the ^{7}Li line width at 155 K is only ca. 8.5 Hz. This might well have been larger if the local symmetry at the lithium atom had been reduced. Consequently, we favor a low-temperature structure in which the lithium is solvated by four molecules.

Table 2. *D* ($\times 10^{10}$ m^2 s^{-1}) and r_H (Å) Values[a] for Ph_2PLi in THF (155 K) and Et_2O (202 K)[b]

	nucleus	*D*[c]	r_H[d]
$LiPPh_2$ (THF)	^{7}Li	0.221	4.9
	^{31}P	0.242	4.5
	^{1}H	0.239	4.5
Ph_2PH (THF)	^{31}P	0.380	2.9
	^{1}H	0.386	2.9
TMSS (THF)	^{1}H	0.233[e]	4.3
$LiPPh_2$ (Et_2O)	^{7}Li	*f*	–
	^{1}H	2.78[g]	6.6
TMSS (Et_2O)	^{1}H	4.47[h]	4.1

[a] All at 60 mM. [b] At 155 K, the $LiPPh_2$ precipitates from Et_2O solution. [c] Experimental error is ca. ±2%. [d] Standard deviation is ca. ±0.1 Å. [e] Room-temperature values: $D = 10.9 \times 10^{-10}$ m^2 s^{-1}, $r_\mathrm{H} = 4.3$ Å. [f] Not measurable. [g] A coaxial NMR tube (i.d. = 1.96 mm, o.d. = 2.97 mm) separated by a spacer was used. See ref 12. [h] Room-temperature values: $D = 24.2 \times 10^{-10}$ m^2 s^{-1}, $r_\mathrm{H} = 4.1$ Å. Estimated viscosities: η (THF, 155 K) = 10.4×10^{-3} kg s^{-1} m^{-1}, η (Et_2O, 202 K) = 0.807×10^{-3} kg s^{-1} m^{-1}.

The low-temperature results are still consistent with a mononuclear species in THF. Further, although $LiPPh_2$ is not soluble in Et_2O at 155 K, at 202 K, we find an r_H value of 6.6 Å, again indicating a dinuclear species. The viscosity of Et_2O at 202 K was estimated in an analogous way to that explained for THF. The result, $\eta = 0.807 \times 10^{-3}$ kg s^{-1} m^{-1}, is similar to the value obtained by interpolation of published data.[21] Although we cannot define the exact solvation shell in Et_2O, clearly, the PGSE diffusion approach allows one to readily recognize the solvent-dependent change of structure.

Summarizing, our novel ^{7}Li diffusion studies readily reveal the solvent-dependent structure of $LiPPh_2$. Further, the low-temperature measurements confirm this difference and provide a novel way to estimate solvent viscosity at relatively low temperature.

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Supporting Information Available: Experimental conditions for the PGSE measurements. Three figures showing PGSE results, and details of the Chem3D Ultra 8.0 studies with one figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) From ^{13}C T_1 relaxation times, it had been suggested that $LiPPh_2$ in THF forms a tetrameric structure (see ref 7a). This supposition was already considered erroneous by ref 7c, where a contact monomeric species $Ph_2P{-}Li$, without separation of ions, was suggested [the absence of $^{1}J(^{7}Li,^{31}P)$ coupling was explained in ref 7c as being due to rapid exchange of the Ph_2P ligand between Li cations]. Our PGSE results clearly show that there is partial separation of ions in $LiPPh_2$ in THF.

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(21) The range of viscosity data for Et_2O in ref 15 does not reach 202 K. In *Pure Organic Liquids, Landort-Börnstein-Group IV, Physical Chemistry* (Springer-Verlag: Heidelberg, Germany, 2002; Vol. 18B, pp 191), the following viscosity values for Et_2O are given: η (−65.4 °C) = 0.693×10^{-3} kg s^{-1} m^{-1} and η (−75.4 °C) = 0.866×10^{-3} kg s^{-1} m^{-1}. By interpolation, a value of η (202 K) = 0.785×10^{-3} kg s^{-1} m^{-1} is found.