

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

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The first application of  $^7\text{Li}$  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  $\text{LiPPh}_2$ . In THF,  $\text{LiPPh}_2$  exists as a mononuclear solvated species, whereas in  $\text{Et}_2\text{O}$ , a dinuclear structure is found.  $D$  values for the model compound  $\text{PHPPh}_2$  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<sup>1–3</sup> 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.<sup>2a,c,d,3</sup> We have recently shown that  $^{31}\text{P}$ ,<sup>4</sup>

and to a lesser extent, even  $^{35}\text{Cl}$ ,<sup>4</sup> can serve as diffusion probes, thereby increasing the flexibility of this methodology.

There is much interest in lithium chemistry;<sup>5</sup> 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.<sup>5a,6</sup> Their structures have been investigated in solution<sup>7</sup> and in the solid state,<sup>8</sup> and it is recognized that these materials can be ionic, e.g.,  $[\text{Li}-(12\text{-crown-4})_2][\text{PPh}_2]$ ,<sup>9</sup> dimeric, e.g.,  $[\{\text{LiP}(\text{CH}(\text{SiMe}_3)_2)_2\}_2]$ ,<sup>10</sup> or tetrameric,  $[\{\text{Li}_2-(\mu_3\text{-}t\text{-Bu}_2\text{P})(\mu\text{-}t\text{-Bu}_2\text{P})(\text{THF})_2\}_2]$ .<sup>11</sup> In more polar solvents, these reagents are thought to form ion pairs with different degrees of solvation.<sup>7a,b</sup> For  $\text{LiPPh}_2$ , it has been suggested that, in THF and  $\text{Et}_2\text{O}$ , polymeric chainlike structures exist in solution.<sup>8b</sup>

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

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