# Phosphorus-31 to Lithium-7 Nuclear Spin Coupling in Lithiated Organophosphorus Compounds

**Ian J. Colquhoun, H. Christina E. McFarlane, and William McFarlane***

*Department of Chemistry, City of London Polytechnic, 31 Jewry Street, London EC3N 2EY, U.K.*

$^{31}$P and $^{7}$Li n.m.r. spectra with $J$ ($^{31}$P–$^{7}$Li) = *ca.* 50 Hz show LiCH($PPh_2$)$_2$ and LiCH[$PPh_2$][P(S)$PPh_2$] to be covalent monomeric, and Li$PPh_2$ to be covalent dimeric in $Et_2O$ solution at low temperatures.



The reaction between alkyl-lithiums and a range of organophosphorus compounds with an active hydrogen can yield synthetically important reagents whose structures in solution are not yet established, but which may in principle be ionic, or covalent with the lithium attached either to carbon or to phosphorus.[1–3] Furthermore, since most known alkyl-lithiums exist as polymers in solution,[4] this possibility must also be considered for the lithiated organophosphorus species. We now report $^{7}$Li ($I = \frac{3}{2}$, abundance 92.6%) and $^{31}$P n.m.r. spectra, together with $^{31}$P{$^{7}$Li, $^{1}$H} decoupling experiments from several of these species in ethereal solution at temperatures below 240 K, which show the first reported examples of well resolved $^{31}$P–$^{7}$Li spin coupling, and demonstrate the presence of covalent monomers and dimers.

The $^{7}$Li spectrum [JEOL FX90Q, Figure 1(a)] of a 0.5 M solution of $Ph_2PLi$ (from $Ph_2PH$ and BuLi) in $Et_2O$ at 200 K is a well resolved 1 : 2 : 1 triplet [δ ($^{7}$Li) 0.5 p.p.m. rel. to molar LiBr in $D_2O$] showing each lithium to be coupled to two phosphorus nuclei with $J$($^{31}$P–$^{7}$Li) 45 Hz; the proton-decoupled $^{31}$P spectrum [Figure 1(b)] is a 1 : 2 : 3 : 4 : 3 : 2 : 1 septet [δ($^{31}$P) −36 p.p.m., $J$($^{31}$P–$^{7}$Li) 45 Hz] indicating that each phosphorus is associated symmetrically with two lithium atoms. The major species present is thus covalent, and in view of earlier molecular weight measurements[5] can be assigned the dimeric structure (**1**) in which the two $Ph_2P$ units are joined by a pair of bridging lithium atoms. (On a statistical basis the abundance of dimers containing only one $^{7}$Li is <14%.) The $^{7}$Li (δ 0.3 p.p.m.) spectrum of ($Ph_2P$)$_2$CHLi [from ($Ph_2P$)$_2CH_2$ and BuLi] under the same conditions showed that each lithium is coupled to two phosphorus atoms, and the $^{31}$P spectrum was a 1 : 1 : 1 : 1 quartet [δ ($^{31}$P) −3.7 p.p.m.] with $J$($^{31}$P–$^{7}$Li) 46 Hz. This species is therefore a covalent monomer in $Et_2O$. Each lithium (δ 0.5 p.p.m.) in [$Ph_2P$(S)][$Ph_2P$]CHLi {from [$Ph_2P$(S)][$Ph_2P$]$CH_2$ and BuLi} was similarly found to be coupled to only one phosphorus, and the $^{31}$P spectrum of this species is shown in Figure 2(a). The $^{31}$P{$^{7}$Li, $^{1}$H} decoupling experiment [Figure 2(b)] confirms the assignments: $Ph_2P$(S), δ($^{31}$P) +45.6 p.p.m., $J$($^{31}$P–$^{7}$Li) <4 Hz; $Ph_2P$, δ($^{31}$P) −17.4 p.p.m., $J$($^{31}$P–$^{7}$Li) 54 Hz; $^{2}J$($^{31}$P–$^{31}$P) 166 Hz. This species is therefore also a covalent monomer in $Et_2O$.

These results do not establish unequivocally whether the lithium is attached to carbon or to phosphorus in the last two compounds, but for ($Ph_2P$)$_2$CHLi we *tentatively* favour the structure (**2a**) rather than (**2b**), and for [$Ph_2P$(S)][$Ph_2P$]-CHLi the structure (**3a**) rather than (**3b**) because (i) in each the magnitude of $J$($^{31}$P–$^{7}$Li) is very close to that in (**1**) in which P–Li bonds must be present; (ii) (**2b**) and (**3b**) are substituted alkyl-lithiums which can be expected to exist as

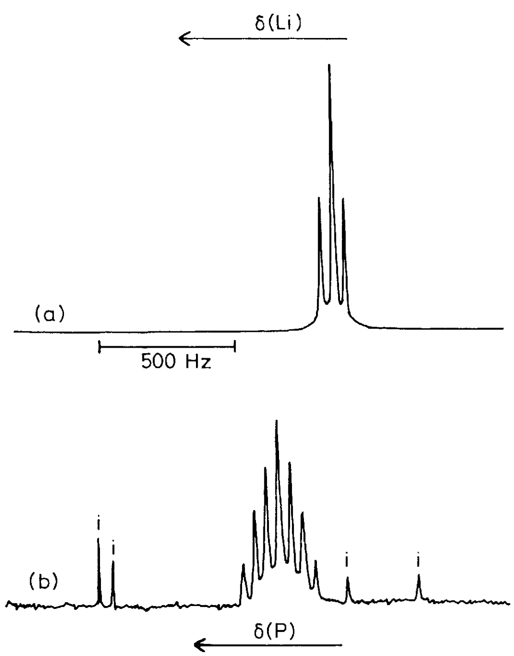
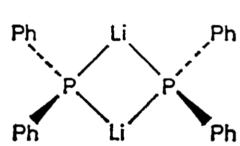



**Figure 1.** N.m.r. spectra of $Ph_2PLi$ in $Et_2O$ at 200 K. (a) $^{7}$Li at 34.8 MHz. (b) $^{31}$P at 36.2 MHz. Peaks marked i are impurities.




(**1**)

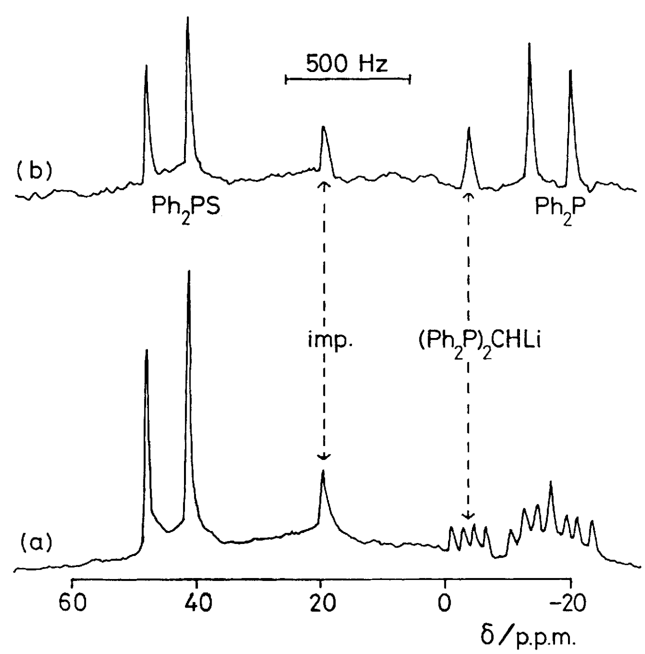
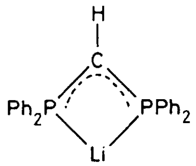
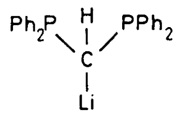


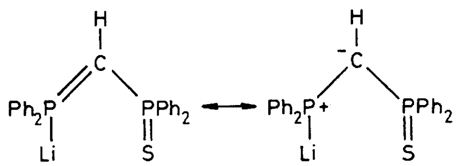

**Figure 2.** Proton-decoupled $^{31}$P n.m.r. spectra at 24.2 MHz of [$Ph_2P$(S)][$Ph_2P$]CHLi in $Et_2O$ at 200 K. (a) Normal spectrum showing $^{7}$Li coupling to the $Ph_2P$-resonance only. (b) With $^{7}$Li decoupled at 23.2 MHz to give an AB pattern. Time sharing of the receiver and the $^{7}$Li irradiating field was used to avoid frequency interference.



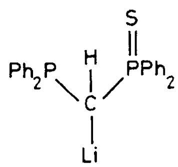

(2a)




(2b)




(3a)




(3b)

dimers or higher polymers; and (iii) it is unlikely that in **(3b)** $^{2}J$ [$^{31}P(S)$–$^{7}Li$] would be zero, although this possibility cannot be completely excluded in view of the wide variability of coupling constants involving phosphorus.

We have also used $^{7}Li$ and $^{31}P$ n.m.r. spectroscopy to examine several other solutions of lithiated organophosphorus compounds including $(Ph_2P)_3CLi$ which contained several different species showing $^{31}P$–$^{7}Li$ spin coupling, and $(Me_2P)_2$-CHLi, $(Me_2P)(Ph_2P)CHLi$, and $[Ph_2P(S)]_2CHLi$ which have not yet given satisfactory results. However, the spectra obtained depend upon the conditions, and indeed we have found $^{7}Li$ and $^{31}P$ n.m.r. spectroscopy a valuable guide to reagent quality in synthetic work.

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