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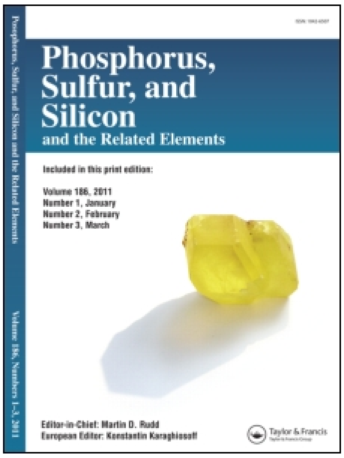

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Structures in solution of organophosphorus-lithium compounds

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STRUCTURES IN SOLUTION OF ORGANOPHOSPHORUS-LITHIUM COMPOUNDS

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Abstract Low temperature ^{31}P and ^{7}Li nmr spectra of Et_2O solutions of lithiated organophosphorus compounds have resolved coupling constants $^{1}J(^{31}P-^{7}Li)$ in the range 30-50 Hz. These spectra demonstrate the covalent nature of the species and also provide information regarding the state of molecular association. $[Ph_2PLi]$ is found to be a symmetrical dimer whilst [PhMePLi] gives a mixture of dimer and trimer. [PhHPLi] exists in only one form, detailed consideration of the ^{31}P and ^{7}Li results suggesting a trimeric structure. $(Ph_2P)_2CHLi$ and $[Ph_2P][Ph_2P(S)]CHLi$ are found to be covalent monomers. it is proposed that in the dimers and trimers phosphorus retains an electron lone pair and that the bonding is of the multi-centre electron deficient type as found in the organolithuims themselves.

INTRODUCTION

Lithiated organophosphorus species are important synthetic intermediates but hitherto little detailed information has been available regarding the structure of these compounds in solution. We now report the results of ^{7}Li (I = 3/2, abundance 92.6%) and ^{31}P nmr experiments which show well resolved $^{31}P-^{7}Li$ spin coupling[1] and demonstrate the presence of a variety of structural types. The compounds were prepared from R_2PH, RPH_2 or $(Ph_2P)_2CH_2$ and BuLi and were examined as diethyl ether solutions. ^{31}P(36.2 MHz) and ^{7}Li(34.8 MHz) spectra were recorded at temperatures below 230 K. At higher temperatures there is a loss of $^{31}P-^{7}Li$ coupling information as a result of intermolecular exchange.

RESULTS

(a) Ph$_2$PLi (1) The ^{7}Li spectrum is a 1:2:1 triplet showing that lithium is coupled equally to two phosphorus nuclei. The ^{31}P spectrum, a 1:2:3:4:3:2:1 septet, indicates that each phosphorus is associated symmetrically with two lithium atoms. These results, together with earlier molecular weight measurements[2], show that the species present is a covalent dimer in which two Ph$_2$P groups are bridged by a pair of lithium atoms. $^1J(^{31}P-^7Li)$ is 45 Hz, $\delta(^{31}P)$ -36.2 ppm.

(b) PhPHLi (2) was prepared from PhPH$_2$ and 1 equivalent of BuLi. (PhPLi$_2$ was found to be insoluble in Et$_2$O.) ^{7}Li and ^{31}P spectra of (2) are shown in Fig. 1. The ^{31}P spectrum, $\delta(^{31}P)$ -113.4, is apparently a decet indicating coupling of ^{31}P to three lithium nuclei but close inspection shows that successive line spacings are not all equal and that two pairs of lines are sharper than the rest. Furthermore the ^{7}Li spectrum is clearly indicative of some second order character. A detailed analysis of these nmr spectra as well as the proton coupled, ^{7}Li decoupled spectrum of (2) shows that the species present is a cyclic trimer (PhPHLi)$_3$ with ^{1}J(PLi) 39 Hz, ^{1}J(PH) 180 Hz and J(PP) 70 Hz.

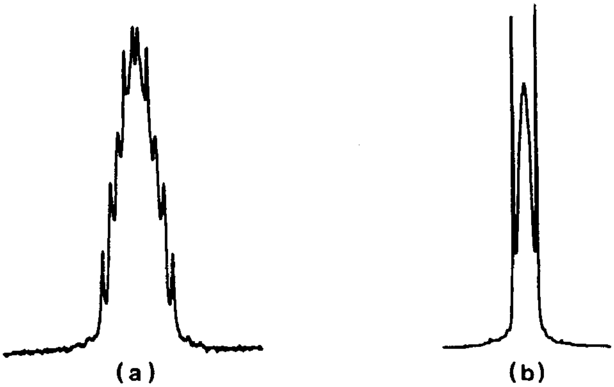

FIGURE 1 Nmr spectra of [PhPHLi] in Et$_2$O at 200 K
(a) ^{31}P (b) ^{7}Li

(c) MePhPLi (3) and mixed species The ^{31}P spectrum of (3) at 200 K consists of a well-resolved 1:2:3:4:3:2:1 septet (δ(^{31}P) -91 ppm, $^{1}J(^{31}P-^{7}Li)$ 48 Hz) superimposed on a broad resonance (δ(^{31}P) -95 ppm) with some sharp features just resolved (cf PhHPLi). We conclude that this solution contains a mixture of covalent dimer and trimer. The two components were present in approximately equal proportions.

Mixed species containing different phosphino groups have also been studied in order to investigate inter-aggregate exchange and ($^{31}P-^{31}P$) homonuclear coupling. For a mixture of Ph_2PLi and PhHPLi there was no evidence in the ^{31}P spectrum that any "scrambling" had occurred, but a mixture of Ph_2PLi and MePhPLi gave a very complex spectrum, mainly because of the presence of a mixed dimeric species which exhibited homonuclear ($^{31}P-^{31}P$) coupling as well as ($^{31}P-^{7}Li$) splittings. A ^{31}P two-dimensional J resolved (spin-echo) experiment[3] greatly simplified interpretation of the spectrum and allowed easy measurement of $J(^{31}P-^{31}P)$ in the mixed dimer (240 Hz).

(d) $(Ph_2P)_2CHLi$ (5) The ^{7}Li spectrum is a 1:2:1 triplet whilst the ^{31}P spectrum (δ(^{31}P) -3.7 ppm) is a 1:1:1:1 quartet ($J(^{31}P-^{7}Li)$ 46 Hz). The species present is therefore a covalent monomer in which the lithium is symmetrically related to the two phosphorus atoms.

$[Ph_2P(S)][Ph_2P]CHLi$ (6) The ^{7}Li spectrum shows that lithium is coupled to only one phosphorus ($J(^{31}P-^{7}Li)$ 54 Hz) and the ^{31}P spectrum indicates the presence of only one Li (1:1:1:1 quartet), coupling being to the trivalent phosphorus. [Ph_2P δ(^{31}P) -17.4 ppm; $Ph_2P(S)$ δ(^{31}P) +45.6 ppm; $^{2}J(^{31}P-^{31}P)$ 166 Hz.] Structures may be envisaged in which lithium is bonded to either the bridging carbon or to phosphorus but the nmr data does not allow us to discriminate between these two possibilities.

DISCUSSION/CONCLUSIONS

Two alternative bonding schemes may be invoked to account for the association of phosphorus/lithium species. In the first of these a phosphido-bridge is formed which involves donation of the phosphorus lone-pair to the metal. The other hypothesis is that multi-centre bonds are responsible for aggregate formation with the phosphorus atom retaining its electron lone-pair.

We favour the second alternative since rather small changes in $\delta(^{31}P)$ occur when $R_2PH(RPH_2)$ is converted to $R_2PLi(RPHLi)$ and the value of $^1J(PH)$ in $(PhPHLi)_3$ is typical for a P(III) compound. Also large values of the geminal coupling constant $^2J(PP)$ most commonly occur in situations where at least one of the phosphorus atoms possesses a lone-pair. In associated organolithium species four-centre (CLi_3) bonding units are common whereas the present work indicates that for phosphorus the three-centre (PLi_2) unit may be more favourable. The increasing prevalence of trimer over dimer in the sequence $[Ph_2PLi]$, [PhMePLi], [PhHPLi] suggests that substituent size is a major factor in determining the degree of association.

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