

Synthesis, Characterization, and N.M.R. Spectra of Tetra-*n*-butylammonium Tris(diphenylthiophosphinoyl)methanide

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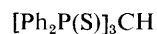
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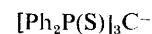
Tetra-*n*-butylammonium tris(diphenylthiophosphinoyl)methanide has been isolated as a stable solid which is useful synthetically in the formation of cage complexes by co-ordination with metal cations; its phosphorus-31 and carbon-13 n.m.r. spectra are reported.

Tris(diphenylthiophosphinoyl)methane (1), $\{[\text{Ph}_2\text{P}(\text{S})]_n\text{-}[\text{Ph}_2\text{P}]_{3-n}\text{CH}$, $n = 3$, and its analogues when $n = 0, 1$, or 2 , are of interest to co-ordination chemists as examples of versatile ligands which can act in a uni-, bi-, tri-, or ambi-dentate manner toward a wide range of neutral metal carbonyls and other substances.¹⁻⁴ Compound (1) can also yield cage complexes of cationic species with, for example, mercury(II) or cadmium(II) halides in the presence of base.¹ The formation

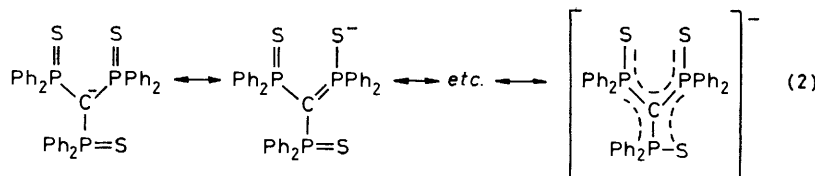
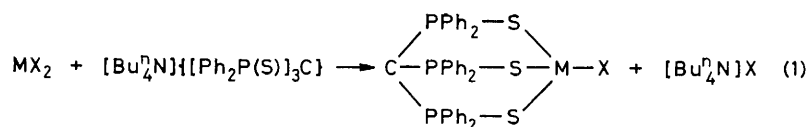
of these complexes involves loss of the hydrogen atom attached to the central carbon, and they are derivatives of the hitherto unknown tris(diphenylthiophosphinoyl)methanide anion $[\text{Ph}_2\text{P}(\text{S})]_3\text{C}^-$, (2).



(1)



(2)



We now report the isolation of this anion as its tetra-n-butylammonium salt from the reaction between (1) and methoxide in alcohol followed by metathesis with $[\text{Bu}_4^{\text{N}}\text{I}]$. This salt is a free-flowing, crystalline, high-melting, fairly air-stable substance for which satisfactory elemental analyses have been obtained, and is soluble in dichloromethane, acetone, and acetonitrile, but is not very soluble in methanol, tetrahydrofuran, or chloroform. Hydrolysis of the salt by treatment with wet acetone or with hydrogen bromide in dichloromethane produces the neutral parent compound (1) which may be readily identified² by its methine proton n.m.r. signal [δ 6.04, quart, $^2J(\text{PH})$ 16.5 Hz]. The isolation of this stable anion is important because reactions such as (1) [$\text{M} = \text{Hg}, \text{Cd}$] can provide a valuable clean synthetic route to a wide variety of cage co-ordination compounds in which the ligand behaves as a uninegative tridentate donor. The stability of this anion can be attributed to a large degree of mesomeric stabilization⁵ according to equation (2), which will tend to lead to a planar configuration at the central carbon atom.

The proton-decoupled ^{31}P n.m.r. spectrum of (2) is a single line which broadens only slightly on cooling to 178 K, thus indicating a low barrier to rotation about the phosphorus to central-carbon bonds. This behaviour may be contrasted with that observed⁶ for (1) whose ^{31}P spectrum is an AX_2 pattern at temperatures below 220 K because the barrier to internal rotation about these bonds is 49 kJ mol^{-1} , the preferred conformation having one P-S bond pointing along the central C-H direction, and the other two opposed to it. In the anion (2) the tendency to planarity at the central carbon atom will enlarge the PCP interbond angles and thus reduce the steric interference between the phenyl groups so that the barrier to internal rotation is lowered substantially. It is important to realize that the partial double bond character between the phosphorus atoms and the central sp^2 carbon will not hinder rotation since the π -overlap involves two degenerate phosphorus 3d-orbitals for each bond (*cf.* phosphine oxides and phosphorus ylides) thus creating an approach to cylindrical symmetry about the P-C bonds.

Selected ^{31}P and ^{13}C n.m.r. data (JEOL FX60 at 24.2 and 15.0 MHz, respectively) for (1) and (2) are compared in Table 1, and serve to confirm the identity of (2). In particular, the absence of any proton attached to the central carbon atom was demonstrated unequivocally by a $^{13}\text{C}\{^1\text{H}\}$ off-resonance decoupling experiment in which the appearance of the 1:3:3:1 quartet arising from coupling to three equivalent phosphorus nuclei remained unchanged. The substantial (19 p.p.m.) increase in the shielding of the central carbon on formation of the anion is consistent with increased electron density at this site, although the change from sp^3 to sp^2 hybridization would be expected to have the opposite effect.⁷ This hybridization change should also increase the s-character of the hybrid orbitals used to form the C-P bonds and hence increase the magnitude of $^1J(\text{PC}^{\text{central}})$. Such a change is indeed observed, but it is much too great to be attributed solely to this factor, and it is clearly incorrect to use the mean excitation energy approximation for the Fermi contact interaction⁸ in this type of system. The differences in the values of $^2J(\text{PP})$ are to be expected, since this coupling constant is known⁹ to be very sensitive to the hybridization of the intermediary atom.

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Table 1. Selected n.m.r. parameters^a of $[\text{Ph}_2\text{P}(\text{S})]_3\text{CH}$ and $\{[\text{Ph}_2\text{P}(\text{S})]_3\text{C}\}^-$.

Parameter ^b	$[\text{Ph}_2\text{P}(\text{S})]_3\text{CH}$	$\{[\text{Ph}_2\text{P}(\text{S})]_3\text{C}\}^-$
$^2J(\text{PP})^c$	<2	24.5
$^1J(\text{PC}^{\text{central}})$	22.3	75.7
$^1J(\text{PC}^{\text{arom}})$	84.2	86.7
$^3J(\text{PC}^{\text{arom}})$	1.5	2.8
$\delta(\text{P})$	46.9	44.0
$\delta(\text{C}^{\text{central}})$	52.1	33.1
$\delta(\text{C}^{\text{arom}})$	130.5	138.3

^a CH_2Cl_2 solution at 23 °C. ^b Coupling constants are in Hz; chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C). C^{arom} refers to the aromatic carbon atom attached to phosphorus. ^c The $^2J(\text{PP})$ values result from the analysis of the ^{13}C resonances (which are AA'AX spectra) in the phenyl region.

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