

Synthesis and Structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{BePBUt}_2$: the First Diorganophosphide Derivative of Beryllium

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The first structurally characterized diorganophosphide derivative of beryllium, $(\eta^5\text{-C}_5\text{Me}_5)\text{BePBUt}_2$, is monomeric in the solid state and the PBUt_2 ligand acts as a one-electron donor.

Alkali metal derivatives of diorganophosphides are commonly used as PR_2^- transfer reagents in the synthesis of transition metal and main group phosphido complexes.^{1,2} In contrast little is known about group 2 phosphido compounds.^{3,4} We report here the synthesis and structure of $(\eta^5\text{-C}_5\text{Me}_5)\text{BePBUt}_2$ (**1**) which is the first reported diorganophosphide derivative of beryllium. An earlier report by Bell, Coates, and Fishwick describes the reaction of Me_2Be and Me_2PH in a sealed tube at elevated temperature.⁵ Although gas evolution was observed along with the formation of an insoluble white solid no data to support Be–P bond formation were obtained.

Reaction of $(\eta^5\text{-C}_5\text{Me}_5)\text{BeCl}$ ⁶ with LiPBUt_2 in diethyl ether at -78°C gave a fine white precipitate and a clear colourless solution after several hours. Removal of volatile materials under vacuum, extraction of the residue with hexane followed by concentration and cooling (-30°C) of the resulting

solution afforded colourless crystals of (**1**) in *ca.* 80% yield [equation (1)]. Spectroscopic data[†] for (**1**) are in accord with the solid-state structure as determined by X-ray crystallography. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 at ambient temperature consists of a 1:1:1:1 quartet at δ 0.07 with a large $^1J_{\text{Be-P}}$ coupling constant of 50.0 Hz (^9Be , 100% abundant, $S = 3/2$). This may be compared with much smaller

[†] (**1**), m.p. $84\text{--}86^\circ\text{C}$; NMR: ^1H (300 MHz; C_6D_6), δ 1.76 (s, C_5Me_5) and 1.32 (d, $^3J_{\text{P-H}}$ 11.4 Hz, PBUt_2); $^{31}\text{P}\{^1\text{H}\}$ (121.5 MHz; C_6D_6 ; rel. aq. H_3PO_4), δ 0.07 (1:1:1:1 q, $^1J_{\text{Be-P}}$ 50.0 Hz); $^9\text{Be}\{^1\text{H}\}$ [42.18 MHz; rel. $\text{Be}(\text{NO}_3)_2$ in D_2O], δ -20.55 (d, $^1J_{\text{Be-P}}$ 50.0 Hz). (**2**), m.p. $102\text{--}105^\circ\text{C}$; NMR: ^1H (300 MHz), δ 1.67 (s, C_5Me_5), 1.12 (d, $J_{\text{P-H}}$ 7.3 Hz, PBUt_2), and -0.19 (d, $J_{\text{P-H}}$ 3 Hz, AlMe_3); $^{31}\text{P}\{^1\text{H}\}$ δ -18.72 (1:1:1:1 q, $^1J_{\text{Be-P}}$ 67 Hz); $^9\text{Be}\{^1\text{H}\}$ δ -21.68 (d, J 67 Hz).

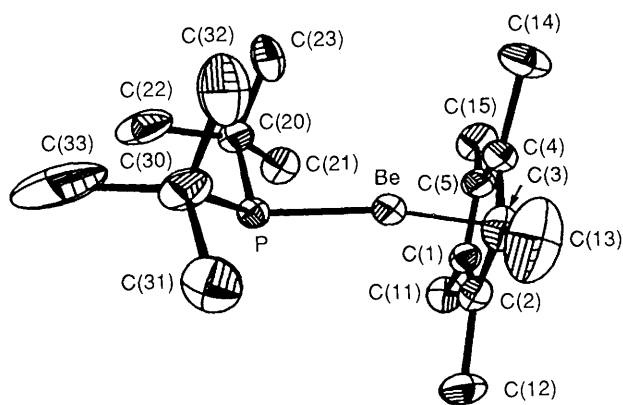
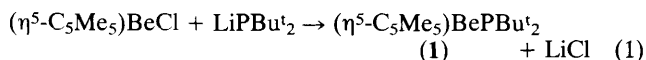


Figure 1. ORTEP view of (1) showing the atom numbering scheme.

values, typically from 4 to 6.2 Hz, for $^1J_{\text{Be-P}}$ coupling in Be-phosphine adducts.⁷

An X-ray crystallographic analysis was undertaken in order to determine the solid state structure of (1).[‡] An ORTEP view of one molecule of (1) is shown in Figure 1. The compound is monomeric in the solid state, no doubt owing to the steric demands of the bulky C_5Me_5 and PBUt_2 ligands. The C_5Me_5 ligand is bound in the familiar η^5 fashion. The phosphorus atom has a trigonal pyramidal geometry with an average Be-P-C angle of 105.1° and behaves as a one-electron donor giving the beryllium atom an electron count of 8.



The Be-P bond length of $2.083(6) \text{ \AA}$ has no precedent. The Be-P distance is shorter than the Mg-P distances of $2.592(5)$

[‡] Crystal data for (1), $\text{C}_{18}\text{H}_{33}\text{BeP}$, monoclinic, space group $P2_1/n$, $a = 8.658(1)$, $b = 15.710(1)$, $c = 14.462(1) \text{ \AA}$, $\beta = 91.88(2)^\circ$, $V = 1966(1) \text{ \AA}^3$, $Z = 4$, $D_c = 0.98 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 11.26 \text{ cm}^{-1}$, $\lambda(\text{Cu-K}\alpha) = 1.5418 \text{ \AA}$. A total of 1835 unique observed reflections [$F > 6\sigma(F)$] (2572 measured) were collected on an Enraf-Nonius CAD-4 diffractometer at $23 \pm 1^\circ \text{C}$. Data were collected over the range $3^\circ \leq 2\theta \leq 110^\circ$ using the $\omega/2\theta$ scan mode. The data were corrected for Lorentz, polarization, decay, and absorption. The structure was solved by direct methods (SHELX). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were either located or placed in idealized positions and refined isotropically. Final $R = 0.0546$, $R_w = 0.0546$. Highest peak in the final difference Fourier was 0.21 e \AA^{-3} and located near P. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

and $2.587(5) \text{ \AA}$ found in $[\text{Mg}(\text{PPh})_2(\text{tmeda})]$ (tmeda = tetramethylethylenediamine) recently reported by Raston and co-workers.⁴ The P-Be- $\text{C}_{\text{centroid}}$ angle of $168.3(7)^\circ$ in (1) reflects some steric strain between the Bu^t groups of the phosphorus atom and the methyl substituents of the C_5Me_5 ligand. The Be- C_5Me_5 (centroid) distance is $1.48(1) \text{ \AA}$ which is notably shorter than that found in $(\text{C}_5\text{H}_5)\text{BeMe}$ [$1.907(5) \text{ \AA}$].⁸

Preliminary reactivity studies indicate that the phosphorus atom of (1) still behaves as a Lewis base. Thus (1) reacts with Al_2Me_6 in toluene at room temperature to give a white crystalline solid formulated as $(\eta^5\text{-C}_5\text{Me}_5)\text{BePBUt}_2 \cdot \text{AlMe}_3$ (2) on the basis of spectroscopic data. The ^1H NMR spectrum of (2) contains resonances assigned to the protons of the C_5Me_5 and PBUt_2 groups as well as a doublet at $\delta -0.19$, $^3J_{\text{P-H}} 3 \text{ Hz}$, assigned to the AlMe_3 moiety. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum again shows a strong ^9Be - ^{31}P coupling ($^1J_{\text{Be-P}} 67 \text{ Hz}$) and the $^9\text{Be}\{^1\text{H}\}$ spectrum is again a doublet ($\delta -21.68$). Heating (2) in C_6D_6 in a sealed tube at 125°C for 2 h results in a disproportionation into $(\eta^5\text{-C}_5\text{Me}_5)\text{BeMe}$ and $[\text{Me}_2\text{Al}(\mu\text{-PBUt}_2)]_2$ ⁹ while reaction with EtOH produces $(\eta^5\text{-C}_5\text{Me}_5)\text{BeOEt}$ and HPBUt_2 .

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