

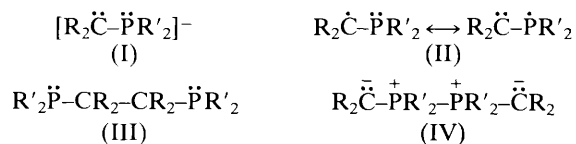
Oxidative Coupling of Phosphinomethanides at a Metal Centre: P-P vs. C-C Bond Formation and the Molecular Structure of the Novel Bis-ylide $(\text{Me}_3\text{Si})_2\text{C}=\text{PMe}_2-\text{PMe}_2=\text{C}(\text{SiMe}_3)_2$

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Metal induced coupling of $[\text{CH}_2\text{PMe}_2]^-$ leads to $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, whereas coupling of $[\text{C}(\text{X})(\text{SiMe}_3)(\text{PMe}_2)]^-$ ($\text{X} = \text{SiMe}_3$ or PMe_2) results in P-P bond formation affording $[(\text{X})(\text{SiMe}_3)\text{C}=\text{PMe}_2]_2$, with a central P-P bond of length 2.278(1) Å.

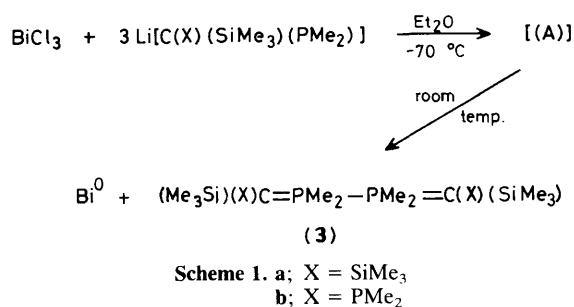
Parallels in structure and reactivity between phosphorus and carbon compounds have become increasingly evident in recent years. The chemistry of organophosphorus and carbon compounds is indeed comparable, provided both elements exist in an isoelectronic state, as is realized, *e.g.*, in phosphinomethanides (I).¹ This should also hold for the related radicals (II), and, consequently, both diphosphinomethanides (III) and P-P bonded bis-ylides (IV) might be expected from coupling reactions. In this study, metal centred redox reactions of the parent phosphinomethanides (I) have been investigated; these surprisingly lead to the coupling products (III) and (IV).



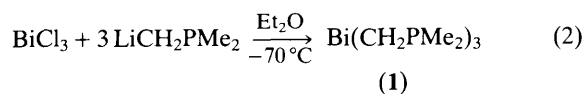
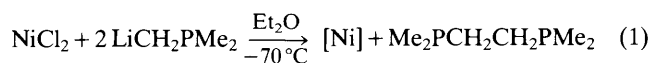
C-C coupling reactions at a nickel(II) centre have been well known for many years.² Consequently, it is not surprising that $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ is obtained as the main product in equation (1).[†] In contrast, with BiCl_3 , $\text{LiCH}_2\text{PMe}_2$ forms an isolable compound (I), which is obtained as a yellow oil [equation (2)].[‡] Compound (I) is thermally unstable; at room temperature Bi metal slowly precipitates, but the coupling product could not be identified.

[†] $[(\text{Me}_3\text{P})_4\text{Ni}]$, $[(\text{Me}_3\text{P})_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Ni}]$, and PMe_3 were also detected as by-products.

[‡] *N.m.r. data* (C_6D_6): (I), ¹H: δ 0.97 (d, J 0.6 Hz, CH_3) and 1.94 (d, J 0.3 Hz, CH_2); ¹³C- $\{^1\text{H}\}$: δ 19.40 (symmetrical m, N 18.1 Hz, PCH_3) and 20.59 (br. d, J 29.84 Hz, PCH_2); ³¹P- $\{^1\text{H}\}$ (rel. 85% H_3PO_4): -48.04 (s) p.p.m. (3a), ³¹P- $\{^1\text{H}\}$ δ + 4.86 (s) p.p.m.; (3b), AA'BB', $\delta(\text{P}^{\text{V}}) + 11.43$ and $\delta(\text{P}^{\text{III}}) - 43.22$ p.p.m.; $J(\text{P}^{\text{V}}\text{P}^{\text{V}}) 85.5$, $J(\text{P}^{\text{V}}\text{P}^{\text{III}}) 162.7$, $J(\text{P}^{\text{V}}\text{P}^{\text{III}}) 7.1$, $J(\text{P}^{\text{III}}\text{P}^{\text{III}}) 0$ Hz.



If Li[C(X)(SiMe₃)(PMe₂)] (2) is used instead of LiCH₂PMe₂, a yellow oil (A) is again obtained, from which elemental bismuth precipitates slowly at room temperature. No Bi-containing compound could be identified with certainty by ³¹P n.m.r. spectroscopy, but after prolonged periods (3a) (2 months) and (3b) (6 months) could be isolated and identified by ³¹P n.m.r. spectroscopy (Scheme 1).[‡]



Compounds (3a and b) are the first cases of bis-ylide compounds containing a P^V-P^V bond. Because of the positive charge at both phosphorus atoms and the steric bulk of the carbanionic substituents, a relatively long P-P bond would be expected. Compound (3a) gave colourless crystals from pentane, and its structure was determined by X-ray crystallography.[§] In the solid state the molecule possesses crystallographic C₂ symmetry (Figure 1) with an ethane-like, staggered conformation. It is slightly twisted around the central P-P bond, however, as shown by the torsion angle C(1)-P-P'-C(1') of 167.9°. The P-P bond [2.278(1) Å] is longer than in the dication [MeP{MeNC(O)NMe}₂PNEt₂]²⁺ (2.189 Å)³ and in Me₂P(S)P(S)Me₂ [2.245(6)/2.161(4) Å].⁴ Remarkably, it is even longer than the P-P bond between the five-co-ordinate P

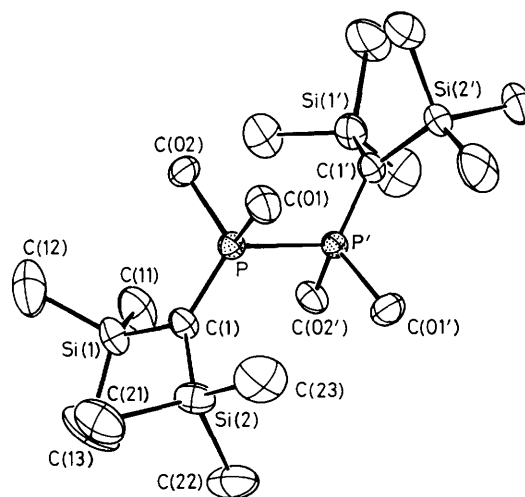


Figure 1. Molecular structure of (3a) (ORTEP plot, displacement ellipsoids at the 50% probability level, without H atoms). Selected bond lengths (Å) and angles (°) are: P-P' 2.278(1), P-C(1) 1.686(3), P-C(01) 1.823(3), P-C(02) 1.806(3), C(1)-Si(1) 1.848(3), C(1)-Si(2) 1.836(3); C(1)-P-P' 118.7(2), C(1)-P-C(01) 117.8(2), C(1)-P-C(02) 115.4(2), P'-P-C(01) 99.1(2), P'-P-C(02) 102.6(2), C(01)-P-C(02) 100.1(2), P-C(1)-Si(1) 119.0(2), P-C(1)-Si(2) 123.9(2), Si(1)-C(1)-Si(2) 117.0(2).

atoms in a bis-phosphorane [2.264(2) Å].⁵ The P-C(1) bonds [1.686(3) Å] are typical for ylidic phosphorus-carbon bonds. The geometry at the ylidic C(1) atoms is exactly planar (sum of the angles 359.9°), with the Si(1), C(1), Si(2) plane being roughly perpendicular to the P', P, C(1) plane (dihedral angle 86.2°). Interestingly, the bond angles at phosphorus not involving C(1) are much smaller than the tetrahedral value and are also smaller than the values in Me₂P(S)P(S)Me₂,⁴ which might be attributed to a higher degree of repulsion between the carbanion lone pair at C(1) and the phosphorus substituents.

In conclusion, metal centred oxidative coupling of phosphinomethanides proceeds by either carbon-carbon or phosphorus-phosphorus bond formation, which apparently depends on the steric and electronic influences of the phosphorus and carbon substituents. The latter route offers access for the first time to the novel class of P^V-P^V bonded bis-ylides.

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§ Crystal data for (3a): C₁₈H₄₈P₂Si₄, M = 438.88, tetragonal, space group I4₁cd (No. 110), a = b = 13.239(2), c = 31.531(2) Å, U = 5526.5 Å³, D_c = 1.055 g cm⁻³, Z = 8, μ(Mo-Kα) = 3.3 cm⁻¹. The intensities of 4569 reflexions were collected on a Syntex P2₁ diffractometer using graphite-monochromatized Mo-Kα radiation [λ = 0.71069 Å, ω-scan, Δω = 0.8°, +h, +k, ±l, (sinθ/λ)_{max} = 0.572, T = -35°C]. After Lorentz-polarisation corrections and merging of equivalent data 2160 unique structure factors remained, which were used for all further calculations. Solution was by direct methods (SHELXS-86). Refinement with anisotropic displacement parameters (Me as rigid groups) converged at R(R_w) = 0.039 (0.036), (SHELX-76). Δρ_{min} (max/min) = +0.60/-0.36 e/Å³. 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.