Organomagnesium Phosphanide "Grignard" Analogues − Synthesis, Structural Characterisation and Solution Behaviour of $[BuMg\{P(CH[SiMe_3]_2)(C_6H_3\text{-}2\text{-}OMe\text{-}3R)\}]_2$ [R = H, Me]

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In memory of Ron Snaith

Keywords: Magnesium / P ligands / Grignard reaction / Rearrangement

The reaction between either one or two equivalents of the secondary phosphane $\{(Me_3Si)_2CH\}PH(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')$ [R′ = H (**1a**), Me (**1b**)] and Bu_2Mg yields the heteroleptic complexes $[BuMg\{P[CH(SiMe_3)_2](C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')\}]_2$ [R′ = H (**2a**), Me (**2b**)], irrespective of the ratio of **1** to Bu_2Mg. X-ray crystallography shows that **2a** and **2b** crystallise as dimers containing a central Mg_2P_2 core. Dissolution of either **2a** or **2b** in THF results in complex degradation and formation of the tertiary phosphanes $\{(Me_3Si)_2CH\}P(Me)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')$ and unidentified magnesium-containing products.

Introduction

Although the synthesis of the parent calcium phosphanide $Ca(PH_2)_2$, by metallation of PH_3 with calcium in liquid ammonia, was reported as early as 1942,[1] little progress was made in the synthesis of other alkaline earth metal phosphanides until 1987, when Raston and co-workers reported that the reaction between *n*Bu*s*BuMg and $PhPH_2$ in the presence of tmeda gave the adduct [(tmeda)$Mg(PHPh)_2$] in good yield (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[2] However, the last two decades have seen growing interest in such species, with Westerhausen and co-workers making a particularly important contribution to this area.[3,4] With few exceptions, crystallographically characterised alkaline-earth metal phosphanides are limited to complexes containing phosphanide ligands in which the donor phosphorus atom is directly bonded to a silyl substituent. Such species typically crystallise as solvated monomers, symmetrical or unsymmetrical dimers, or linear trimers. We recently reported the synthesis, structural characterisation and dynamic behaviour of a homologous series of mononuclear alkaline-earth metal phosphanides without a direct Si−P bond.[5] We now describe the synthesis and structural characterisation of two related, heteroleptic organomagnesium phosphanide "Grignard analogues" and their behaviour in solution.

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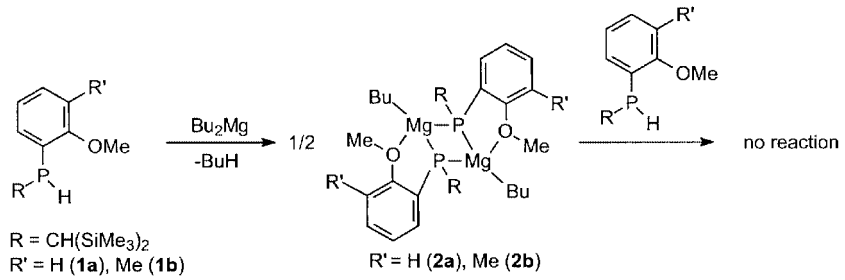
Results and Discussion

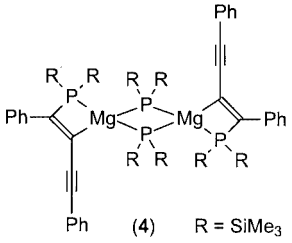
The reaction between Bu_2Mg and one equivalent of the secondary phosphanes $\{(Me_3Si)_2CH\}PH(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')$ [R′ = H (**1a**), Me (**1b**)][6] gives the heteroleptic dimeric organomagnesium phosphanides $[BuMg\{P[CH(SiMe_3)_2](C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')\}]_2$ [R′ = H (**2a**), Me (**2b**)] in good yields (Scheme 1).

Unexpectedly, when Bu_2Mg was reacted with *two* equivalents of **1** under the same conditions only **2** and one equivalent of unchanged **1** were recovered. This is in marked contrast to the reaction between Bu_2Mg and two equivalents of the related secondary phosphane $\{(Me_3Si)_2CH\}PH(C_6H_4\text{-}2\text{-}CH_2NMe_2)$, which proceeds cleanly to give the bis(phosphanide) $[Mg\{P[CH(SiMe_3)_2](C_6H_4\text{-}2\text{-}CH_2NMe_2)\}_2]$ (**3**) in essentially quantitative yield.[5] The reason for this mono-substitution is, as yet, unclear, although it is possible that the five-membered chelate ring in **2** engenders greater steric hindrance at the metal centre than the six-membered chelate ring present in **3**, disfavouring substitution of the second Bu group.

Compounds **2a** and **2b** are unusual examples of "Grignard analogues", RMgX, in which the halide X has been replaced by a phosphanide ligand. Although there are several examples of amide analogues of these species, $RMg(NR_2)$,[7] to the best of our knowledge there has been only one previous report of an organomagnesium phosphanide $RMg(PR_2)$: Westerhausen and co-workers found that the reaction between $Mg\{P(SiMe_3)_2\}_2$ and diphenylbutadiyne in toluene gave an unusual organomagnesium phosphanide addition product (**4**).[8]



Scheme 1



Compounds **2a** and **2b** are initially precipitated as colourless solids from reactions conducted in light petroleum and freshly prepared samples of either compound may be recrystallised from cold (6 °C) diethyl ether as colourless blocks suitable for X-ray crystallography. Compounds **2a** and **2b** are insoluble in hydrocarbon solvents such as light petroleum, benzene or toluene, but dissolve readily in THF to give deep yellow solutions. However, dissolution in donor solvents is accompanied by decomposition (see below), preventing satisfactory characterisation of these compounds by NMR spectroscopy.

The crystals of compounds **2a** and **2b** studied by X-ray diffraction differ both in the substitution of the aromatic ring and in the nature of the butyl group. This latter effect is a consequence of the mixture of isomers present in the commercially sourced Bu_2Mg used in their synthesis. Compounds **2a** and **2b** have very similar molecular structures but they do not form isomorphous crystals; the molecule of **2a** has crystallographic inversion symmetry, but **2b** occupies a general position in its crystal structure. The molecular structures of **2a** and **2b** are shown in Figure 1 and details of bond lengths and angles are given in Table 1. Both compounds crystallise as dimers in which each Mg centre is bound by the P and O atoms of a chelating phosphanide ligand, forming five-membered chelate rings with bite angles of 80.76(4)° (**2a**) and 81.13(9) and 81.23(9)° (**2b**). The P atoms of the ligands further bridge the two Mg centres, forming a planar, parallelogram-shaped Mg_2P_2 core with Mg−P−Mg angles of 97.16(2)° (**2a**) and 95.83(5)° (two crystallographically independent but equal values in **2b**). The two, essentially planar, chelate rings adopt a *transoid* conformation, generating a pseudo-ladder arrangement; the dihedral angles between the Mg_2P_2 core and the chelate rings in the two compounds are 80.8° (**2a**) and 81.8 and 82.9° (**2b**).

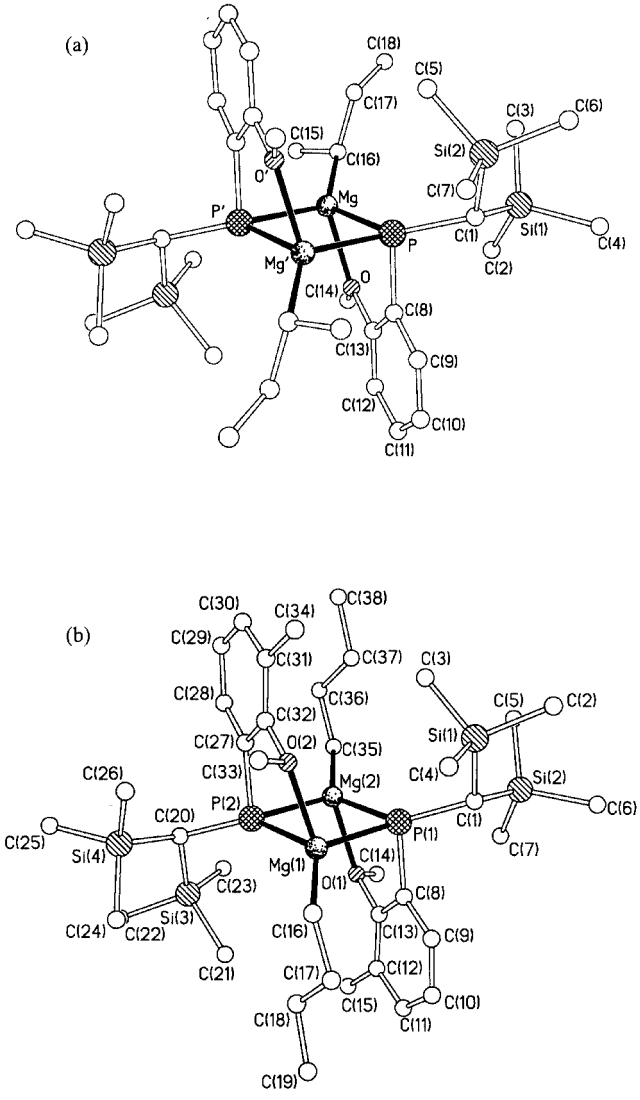


Figure 1. Molecular structures of (a) **2a** and (b) **2b**; H atoms omitted for clarity

In both **2a** and **2b** the phosphorus atoms bridge the two Mg centres in a slightly unsymmetrical fashion; the Mg−P distances in **2a** are 2.5760(8) and 2.5978(8) Å, whilst in **2b** they are 2.5765(17)/2.5730(16) Å [Mg(1)−P(2)/

Table 1. Selected bond lengths (Å) and angles (deg.) for **2a** and **2b**[a]

2a					
Mg−O	2.1088(15)	Mg−C(16)	2.127(2)	Mg−P	2.5760(8)
Mg−P′	2.5978(8)	P−C(8)	1.847(2)	P−C(1)	1.8745(19)
O−C(14)	1.444(2)	Si(1)−C(1)	1.884(2)	Si(1)−C(2)	1.868(2)
Si(1)−C(3)	1.865(2)	Si(1)−C(4)	1.873(2)	Si(2)−C(1)	1.890(2)
Si(2)−C(5)	1.860(3)	Si(2)−C(6)	1.870(3)	Si(2)−C(7)	1.867(3)
O−Mg−C(16)	109.54(9)	O−Mg−P	80.76(4)		
C(16)−Mg−P	133.81(8)	O−Mg−P′	104.21(5)		
C(16)−Mg−P′	132.83(8)	P−Mg−P′	82.84(2)		
C(8)−P−C(1)	102.68(9)	C(8)−P−Mg	92.88(6)		
C(1)−P−Mg	131.99(6)	C(8)−P−Mg′	92.49(6)		
C(1)−P−Mg′	126.62(6)	Mg−P−Mg′	97.16(2)		
C(13)−O−C(14)	117.54(16)	C(13)−O−Mg	123.01(12)		
2b					
Mg(1)−P(1)	2.6138(16)	Mg(1)−P(2)	2.5765(17)	Mg(1)−O(2)	2.113(3)
Mg(1)−C(16)	2.141(5)	Mg(2)−P(1)	2.5730(16)	Mg(2)−P(2)	2.6105(17)
Mg(2)−O(1)	2.121(3)	Mg(2)−C(35)	2.136(5)	P(1)−C(1)	1.869(4)
P(1)−C(8)	1.850(4)	P(2)−C(20)	1.878(4)	P(2)−C(27)	1.846(4)
Si(1)−C(1)	1.881(4)	Si(1)−C(2)	1.863(5)	Si(1)−C(3)	1.868(5)
Si(1)−C(4)	1.878(5)	Si(2)−C(1)	1.901(4)	Si(2)−C(5)	1.865(5)
Si(2)−C(6)	1.879(5)	Si(2)−C(7)	1.856(5)	Si(3)−C(20)	1.887(4)
Si(3)−C(21)	1.865(5)	Si(3)−C(22)	1.880(5)	Si(3)−C(23)	1.868(5)
Si(4)−C(20)	1.880(4)	Si(4)−C(24)	1.859(5)	Si(4)−C(25)	1.887(5)
Si(4)−C(26)	1.875(5)				
P(1)−Mg(1)−P(2)	84.09(5)	P(1)−Mg(1)−O(2)	103.64(9)		
P(1)−Mg(1)−C(16)	131.37(15)	P(2)−Mg(1)−O(2)	81.13(9)		
P(2)−Mg(1)−C(16)	136.88(16)	O(2)−Mg(1)−C(16)	107.15(16)		
P(1)−Mg(2)−P(2)	84.22(5)	P(1)−Mg(2)−O(1)	81.23(9)		
P(1)−Mg(2)−C(35)	137.76(16)	P(2)−Mg(2)−O(1)	102.93(9)		
P(2)−Mg(2)−C(35)	130.34(16)	O(1)−Mg(2)−C(35)	107.89(16)		
Mg(1)−P(1)−Mg(2)	95.83(5)	Mg(1)−P(1)−C(1)	123.25(14)		
Mg(1)−P(1)−C(8)	91.51(13)	Mg(2)−P(1)−C(1)	135.42(14)		
Mg(2)−P(1)−C(8)	93.69(13)	C(1)−P(1)−C(8)	104.72(18)		
Mg(1)−P(2)−Mg(2)	95.83(5)	Mg(1)−P(2)−C(20)	136.44(15)		
Mg(1)−P(2)−C(27)	93.15(13)	Mg(2)−P(2)−C(20)	122.36(14)		
Mg(2)−P(2)−C(27)	92.84(14)	C(20)−P(2)−C(27)	104.01(19)		

[a] The prime denotes an atom generated by inversion symmetry.

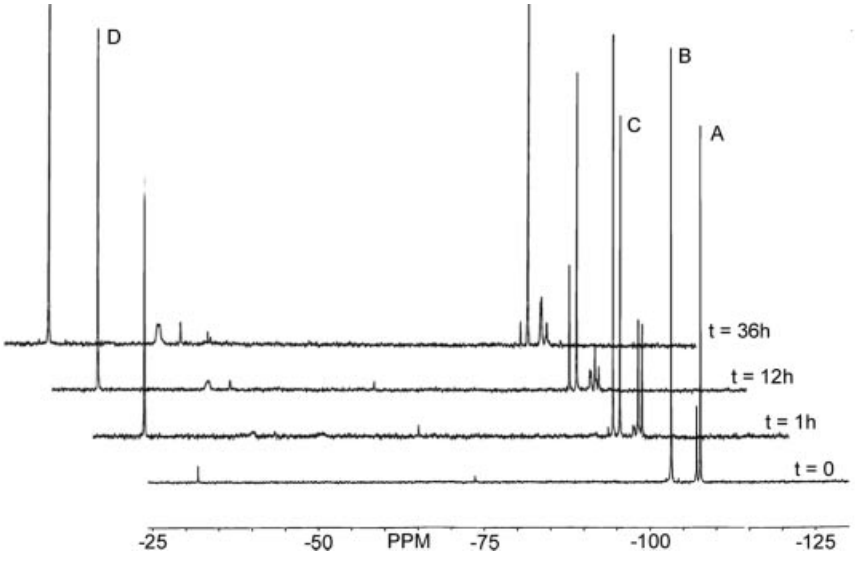
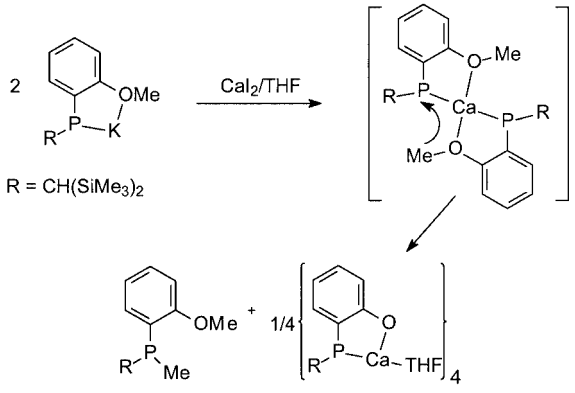


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra of **2a** in [D_8]THF recorded over 36 h

Mg(2)−P(1)] and 2.6138(16)/2.6105(17) Å [Mg(1)−P(1)/Mg(2)−P(2)]. These distances compare with Mg−P distances of 2.592(5) and 2.587(5) Å in [(tmeda)Mg(PHPh)$_2$],[2] 2.5031(6) Å in [(THF)$_2$Mg{P(SiMe$_3$)$_2$}$_2$],[4b] and 2.5555(11) and 2.5557(11) Å in **3**.[5] The Mg−C distances of 2.127(2) Å (**2a**) and 2.141(5) and 2.136(5) Å (**2b**) are similar to Mg−C distances in typical diorganomagnesium or Grignard-type compounds; for example, the Mg−C distance in {(1,4-dioxane)MgEt$_2$}$_n$ is 2.142(2) Å.[9]

The ^{31}P{^{1}H} NMR spectra of **2a** and **2b** in [D$_8$]THF recorded shortly after sample preparation show rapid decomposition at room temperature, preventing precise characterisation of these compounds by NMR spectroscopy. A ^{31}P{^{1}H} NMR spectrum of a solution of **2a** in [D$_8$]THF obtained immediately after sample preparation (Figure 2) exhibits two main peaks at δ = −107.0 (**A**) and −103.1 ppm (**B**), both signals arising from magnesium phosphanide species. After one hour peak **A** has decreased markedly in intensity and new signals have appeared at δ = −104.4 and −31.8 ppm (**C** and **D**, respectively). Peak **C** is likely to be due to a magnesium phosphanide species, whereas peak **D** is consistent with the presence of a tertiary phosphane. After a period of 36 hours peaks **A** and **B** have almost disappeared, leaving only peaks **C** and **D** with significant intensity (Figure 2). The ^{1}H NMR spectra of **2a** in [D$_8$]THF solution recorded at several intervals over a period of 24 hours are very complicated, with numerous peaks due to SiMe$_3$, aromatic and OMe protons; however, a clear doublet at δ = 1.43 ppm (J_{PH} = 6.4 Hz) is visible in the later spectra, consistent with the presence of a PMe group.

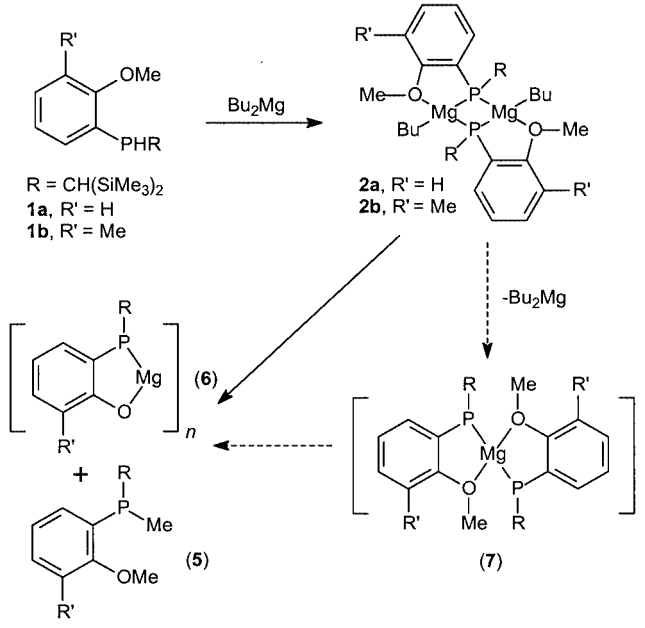
We recently reported that the metathesis reaction between [{(Me$_3$Si)$_2$CH}(C$_6$H$_4$-2-OMe)P]K and CaI$_2$ in THF yields the novel alkoxophosphanide cluster complex [{([Me$_3$Si]$_2$CH)(C$_6$H$_4$-2-O)P}Ca(THF)]$_4$·4THF via an unusual ligand degradation reaction, involving rapid migration of a methyl group from the oxygen atom of one phosphanide ligand to the phosphorus atom of another (Scheme 2).[10] This process yields the tertiary phosphane {(Me$_3$Si)$_2$CH}P(Me)(C$_6$H$_4$-2-OMe) (**5a**) as the sole phosphorus-containing side product [this phosphane has a ^{31}P chemical shift of δ = −31.8 ppm and a ^{1}H chemical shift of δ = 1.41 ppm (d, J_{PH} = 6.1 Hz) due to the PMe group].



Scheme 2

Thus, the ^{31}P and ^{1}H NMR spectra of **2a** are consistent with rapid complex degradation upon dissolution in [D$_8$]THF and formation of a new magnesium phosphanide species and the tertiary phosphane **5a** (peak **D**). Unfortunately, in spite of repeated attempts, it was not possible to separate the new magnesium phosphanide species from the tertiary phosphane **5a** for further characterisation; in contrast to **2a**, this new species appears to be highly soluble, even in the extremely poor solvent hexamethyldisiloxane. Compound **2b** displays similar behaviour to **2a** in THF solution. NMR spectra recorded shortly after sample preparation suggest the presence of two magnesium phosphanide species and the corresponding tertiary phosphane {(Me$_3$Si)$_2$CH}P(Me)(C$_6$H$_3$-2-OMe-3-Me) (**5b**). After several hours compound **2b** appears to have completely degraded to a new magnesium phosphanide and **5b**.

We therefore propose that in THF solution compounds **2a** and **2b** undergo a ligand degradation reaction, possibly forming a magnesium alkoxophosphanide complex of the form [{[(Me$_3$Si)$_2$CH](C$_6$H$_3$-2-O-3-R′)P}Mg(THF)$_n$]$_m$ (**6**; R′ = H, Me) and the corresponding tertiary phosphane **5**. This process may occur via the Grignard-type compounds **2**, or else these compounds may be subject to a Schlenk-type equilibrium in solution, generating the homoleptic phosphanides [{[(Me$_3$Si)$_2$CH](C$_6$H$_3$-2-OMe-3-R′)P}$_2$Mg] (**7**) and one equivalent of Bu$_2$Mg (Scheme 3). The homoleptic compound **7** may then undergo a methyl migration reaction analogous to that observed in the formation of [{[(Me$_3$Si)$_2$CH](C$_6$H$_4$-2-O)P}Ca(THF)]$_4$·4THF to give the alkoxophosphanide complex **6**.



Scheme 3

At present the available evidence does not allow these two reaction pathways to be distinguished. However, if such a Schlenk-type equilibrium were slow on the NMR time scale, this may account for the two magnesium phosphanide

species present in initially prepared samples of **2a**, peaks **A** and **B** perhaps arising from the Grignard analogue **2a** and the homoleptic bis(phosphanide) **7a**.

Experimental Section

General Comments: All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether and light petroleum (b.p. 40−60 °C) were distilled from sodium/potassium alloy under an atmosphere of dry nitrogen and were stored over a potassium film. Bu_2Mg was obtained from Aldrich as a 1.0 M solution of a mixture of isomers in heptanes. The compounds $\{(Me_3Si)_2CH\}PH(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R')$ (R′ = H, Me) were prepared by a previously published procedure.[6] All other compounds were obtained from commercial sources and were used as supplied.

Due to the poor solubility of **2a** and **2b** in non-donor solvents and their rapid degradation in THF, satisfactory NMR spectroscopic data could not be obtained. The constitutions of compounds **2a** and **2b** were confirmed by elemental analyses and X-ray crystallography. Elemental analyses for **2a** and **2b** were obtained by the Elemental Analysis Service of London Metropolitan University, UK.

Preparation of $[BuMg\{P[CH(SiMe_3)_2](C_6H_4\text{-}2\text{-}OMe)\}]_2$ (2a): Bu_2Mg (4.33 mL, 4.33 mmol) was added to a solution of $\{(Me_3Si)_2CH\}PH\{C_6H_4\text{-}2\text{-}OMe\}$ (1.29 g, 4.33 mmol) in light petroleum (10 mL) and the solution was stirred for 16 h. The colourless precipitate was isolated by filtration and dissolved in diethyl ether (10 mL). The resulting solution was concentrated and cooled to −30 °C for 48 h, yielding colourless blocks of **2a**. Yield 0.94 g, 57%. $C_{36}H_{70}Mg_2O_2P_2Si_4$ (757.84): calcd. C 57.05, H 9.31; found C 56.93, H 9.20.

Preparation of $[BuMg\{P[CH(SiMe_3)_2](C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)\}]_2$ (2b): Bu_2Mg (1.70 mL, 1.70 mmol) was added to a solution of $\{(Me_3Si)_2CH\}PH\{C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me\}$ (0.53 g, 1.70 mmol) in light petroleum (10 mL). The solution was stirred for 16 h and the resulting colourless precipitate was isolated by filtration. The solid was dissolved in diethyl ether, concentrated and cooled to −30 °C for 60 h, to yield **2b** as colourless blocks. Yield 0.41 g, 61%. $C_{38}H_{74}Mg_2O_2P_2Si_4$ (785.89): calcd. C 58.07, H 9.49; found C 57.94, H 9.43.

Crystal Structure Determination of 2a and 2b: All measurements were made at 150 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and narrow (0.3° in ω) frame exposures. Cell parameters were refined from the observed positions of all strong reflections in each data set. The structures were solved by direct methods and refined on F^2 values for all unique data. Table 2 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[11] CCDC-207042 (**2a**) and -207043 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystallographic data for **2a** and **2b**

	2a	**2b**
Molecular formula	$C_{36}H_{70}Mg_2O_2P_2Si_4$	$C_{38}H_{74}Mg_2O_2P_2Si_4$
Formula mass	757.8	785.9
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbc2_1$
a (Å)	10.9511(6)	10.8569(5)
b (Å)	10.6790(5)	18.8044(9)
c (Å)	19.4682(10)	23.9371(11)
β (deg.)	98.563(2)	
Volume (Å^3)	2251.4(2)	4886.9(4)
Z	2	4
Density (calculated) (g cm^{-3})	1.118	1.068
μ (mm^{-1})	0.259	0.240
Crystal size (mm)	0.36 × 0.26 × 0.14	0.36 × 0.34 × 0.30
Reflections collected	18668	33963
Independent reflections	5314 [R_{int} = 0.0315]	8554 [R_{int} = 0.0542]
Parameters	217	451
R (F, $F^2>2\sigma$)	0.0421	0.0448
R_w (F^2, all data)	0.1095	0.1174
Goodness-of-fit	1.082	1.085
Largest diff. peak and hole (e/Å^3)	0.60 and −0.32	0.40 and −0.27
Absolute structure parameter		−0.15(12)

Acknowledgments

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