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Article

Arylphosphanide Complexes of the Alkaline-Earth Metals Magnesium, Calcium, Strontium, and Barium of the Formula (THF)$_n$M[P(H)Ph]$_2$ and Formation of Potassium Diphenylphosphinomagnesiates

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The reaction of diethylmagnesium with diphenylphosphane yields [(THF)Mg(Et)PPh$_2$]$_\infty$ (**1**; THF = tetrahydrofuran) with bridging PPh$_2$ ligands and average Mg−P bond lengths of 262.2 pm. The metalation reaction of MgEt$_2$ with HPPh$_2$ and H$_2$PPh with a 1:2 stoichiometry gives [(THF)$_4$Mg(PPh$_2$)$_2$] (**2**) and [(THF)$_6$Mg$_4${P(H)Ph}$_8$] (**3**), respectively. Tetranuclear **3** contains three chemically different phenylphosphanide groups with characteristic P−H stretching frequencies at 2261, 2286, and 2310 cm^{-1}. The metathesis reaction of potassium phenylphosphanide with CaI$_2$ yields oligomeric (THF)$_3$Ca[P(H)Ph]$_2$ (**4**). A similar reaction with SrI$_2$ and BaI$_2$ gives polymeric [(THF)$_2$Sr{P(H)Ph}$_2$]$_\infty$ (**5**) and [(THF)Ba{P(H)Ph}$_2$]$_\infty$ (**6**), respectively, showing one stretching frequency at 2285 cm^{-1}. These compounds crystallize polymeric with bridging phenylphosphanide substituents. The addition of Et$_2$O to a mixture of KPPh$_2$ and Mg(PPh$_2$)$_2$ in THF initiates the crystallization of (Et$_2$O)K[(THF)Mg(PPh$_2$)$_3$] (**7**) with a strand structure and (Et$_2$O)$_x$(THF)$_y$K$_2$[Mg(PPh$_2$)$_4$] (**8**) with a layer structure depending on the stoichiometry. The crystals of **8** easily lose THF and Et$_2$O and, therefore, the content of these ethers varies. Recrystallization of **8** from hot 1,4-dioxane (diox) yields (diox)$_2$K$_2$[Mg(PPh$_2$)$_4$] (**9**) with a layer structure comparable to that of **8**. The central structural units are eight-membered K$_2$Mg$_2$P$_4$ rings that are interconnected by P−K−P bridges. In a THF solution, the magnesiates **7**−**9** dissociate into the homometallic derivatives KPPh$_2$ and Mg(PPh$_2$)$_2$, as can be seen from NMR experiments.
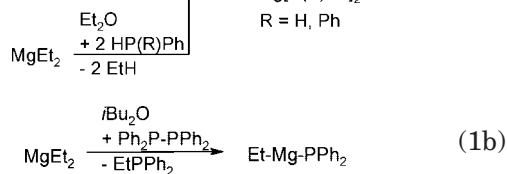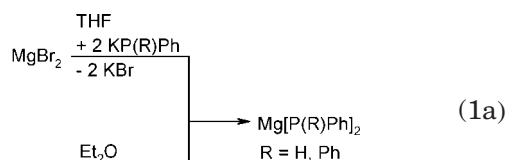
Introduction

During recent years, the interest in alkaline-earth metal complexes (especially of calcium) has been increasing not least because of catalytic activity in, e.g., hydrophosphination,[1] hydroamination,[2] and hydrosilylation processes.[3] However, the lack of a rich variety of easily accessible and soluble derivatives hinders the broad repercussion on catalysis. Nevertheless, trialkylsilyl-substituted amides and phosphanides have been well-known for many years.[4,5]

Recently, arylphosphanides have gained in interest. Phenyl-substituted magnesium phosphanides represent a compound class that was already investigated more than 40 years ago. Several preparative procedures were developed as shown in eqs 1a and 1b. Issleib and Deylig[6] prepared magnesium bis(diphenylphosphanide) via the metathesis reaction of KPPh$_2$ with MgBr$_2$ in tetrahydrofuran (THF) or via metalation of diphenylphosphane with diethylmagnesium in diethyl ether (eq 1a). The P−P bond of tetraphenyldiphosphane was cleaved with MgEt$_2$ in refluxing dibutyl ether, yielding EtPPh$_2$ and EtMgPPh$_2$ (eq 1b).[7] The metalation of phenylphosphane with MgEt$_2$[6] or MgBu$_2$[8] gave polymeric magnesium bis(phenylphosphanide). The addition of 1,2-bis(dimethylamino)ethane (TMEDA) yielded soluble (TMEDA)Mg[P(H)Ph]$_2$ with Mg−P bond lengths of 259.2(5) and 258.7(5) pm.[8]

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$$\underset{\text{MgBr}_2}{} \xrightarrow[\text{- 2 KBr}]{\substack{\text{THF}\\ \text{+ 2 KP(R)Ph}}}$$

$$\underset{\text{MgEt}_2}{} \xrightarrow[\text{- 2 EtH}]{\substack{\text{Et}_2\text{O}\\ \text{+ 2 HP(R)Ph}}} \quad \substack{\text{Mg[P(R)Ph]}_2\\ \text{R = H, Ph}} \qquad (1a)$$

$$\underset{\text{MgEt}_2}{} \xrightarrow[\text{- EtPPh}_2]{\substack{i\text{Bu}_2\text{O}\\ \text{+ Ph}_2\text{P-PPh}_2}} \quad \text{Et-Mg-PPh}_2 \qquad (1b)$$

The metalation of diphenylphosphane with Ph_3-CCa(THF)$_2$Cl led to the formation of yellow (diphenylphosphino)calcium chloride and triphenylmethane.[9] The metathesis reaction of KP(R)C$_6$H$_4$-2-OMe with CaI$_2$ in THF was accompanied by an ether cleavage reaction and gave pale-yellow needles of the tetramer [(THF)CaP(R)C$_6$H$_4$O]$_4$ with R as CH(SiMe$_3$)$_2$. The central structural fragment consisted of a distorted Ca$_4$O$_4$ heterocubane cage with bridging phosphanide moieties between the Ca atoms [Ca–P, 296.12(6) and 296.95(7) pm].[10] No cleavage reactions were observed during the synthesis of the strontium and barium derivatives; hexacoordination of these metal atoms was obtained by coordination of two additional THF molecules [Sr–P, 302.55(7) and 304.76(6) pm; Ba–P, 315.72(8) and 315.29(8) pm].[11] Metalation of the secondary phosphane HP(R)C$_6$H$_4$-2-CH$_2$NMe$_2$ with M[N(SiMe$_3$)$_2$]$_2$ or metathesis reaction of KP(R)C$_6$H$_4$-2-CH$_2$NMe$_2$ with MI$_2$ also gave the corresponding alkaline-earth metal bis(phosphanides); the magnesium [Mg–P, 255.6(1) pm] and calcium [Ca–P, 282.58(6) and 282.39(6) pm] derivatives crystallized solvent-free; the heavier congeners showed increased coordination numbers of five due to complexation of an additional THF molecule [Sr–P, 309.02(6) pm; Ba–P, 327.2(1) pm].[12] Only slightly elongated Ca–P bond lengths of 288.1(1) and 294.4(1) pm were observed for (THF)$_3$Ca[N(PPh$_2$)$_2$]$_2$.[13]

Diphenylphosphane reacted with strontium and barium in a THF solution, yielding (THF)$_4$Sr(PPh$_2$)$_2$ [Sr–P, 314.29(9) pm] and (THF)$_5$Ba(PPh$_2$)$_2$ [Ba–P, 332.8(2) and 334.5(2) pm], whereas calcium was not reactive enough for this deprotonation reaction.[14] Therefore, (THF)$_4$Ca(PPh$_2$)$_2$ [Ca–P, 298.65(6)[14] and 298.82(4)[1] pm] was prepared via the metathesis reaction of KPPh$_2$ with CaI$_2$ in THF. Enhanced bulkiness led to smaller coordination numbers such as, for example, in (THF)$_4$Ba(PMes$_2$)$_2$ with a Ba–P bond length of 318.72(9) pm. Surprisingly, substitution of one phenyl group by an ethyl group led to the formation of polymeric [(THF)$_2$Ba{P(Ph)Et}$_2$]$_\infty$ with bridging phosphanide ligands.[14] Thereafter, Crimmin et al.[15] prepared diphenylphosphanido

derivatives of the heavy alkaline-earth metals calcium, strontium, and barium via metalation of HPPh$_2$ with (THF)$_2$M[N(SiMe$_3$)$_2$]$_2$ (M = Ca, Sr, Ba).

In addition to the homoleptic phosphanides of the heavy alkaline-earth metals mentioned above, also a few heteroleptic phosphanides of calcium were isolated. In [(THF)-Ca(PPh$_2$)(CH{C(Me)NAryl}$_2$)] (Aryl = 2,6-diisopropylphenyl) and [(THF)$_4$Ca(Ph)PPh$_2$], Ca–P distances of 287.2(4)[1] and 301.0(2)[16] pm, respectively, were observed. Here we were interested in the physical properties and molecular structures of the sterically less crowded phenylphosphanides as well as in the molecular structures of heteroleptic EtMgPPh$_2$, which was prepared earlier by Issleib and co-workers.[6,7] Furthermore, the reactivity of Mg(PPh$_2$)$_2$ toward KPPh$_2$ and the possibility of producing potassium magnesiates were investigated. Organomagnesiates are well-known for many decades such as, e.g., in the reaction of KH with diphenylmagnesium.[17] However, special interest was given to the mixed alkali metal–magnesium amides[18–22] because of their enormous reactivity and their behavior as inverse crown ethers.[23–26] Far less investigations deal with mixed alkali metal–magnesium phosphanides.

Results and Discussion

Synthesis. The metathesis reaction of potassium phenylphosphanide with an equimolar amount of ethylmagnesium bromide in THF yielded [(THF)Mg(Et)PPh$_2$]$_\infty$ (1). No Schlenk equilibrium was observed in the THF solution. The synthesis of the diethyl ether adduct [(Et$_2$O)Mg(Et)PPh$_2$]$_\infty$ was already published by Issleib and Deylig.[6] A similar reaction with a 2:1 stoichiometry in THF gave [(THF)$_4$-Mg(PPh$_2$)$_2$] (2), which was also reported by Issleib and Deylig.[6] Magnesiation of H$_2$PPh led to the formation of polymeric [Mg{P(H)Ph}$_2$]$_\infty$,[6,8] which is insoluble in hydrocarbons and Et$_2$O. The reaction of diethylmagnesium with 2 equiv of phenylphosphane in THF allowed isolation of the tetranuclear cage compound [(THF)$_6$Mg$_4${P(H)Ph}$_8$] (3) according to eq 2. This cage contains three chemically different phosphanides, which was also seen in the IR spectrum with P–H stretching frequencies of 2261, 2286, and 2310 cm^{-1}. In the ^{31}P{^{1}H} NMR spectrum, only a singlet

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at δ -131.9 was observed at a THF-d_8 solution of **3** because of exchange and dissociation processes that were fast on the NMR time scale.

(2)
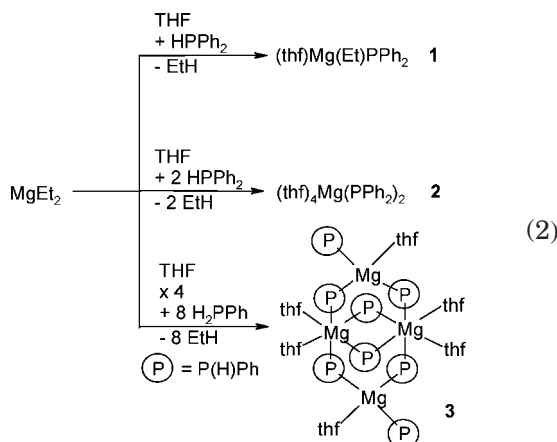
A comparison of the diphenylamides[27] with the anilides[28] (phenylamides) of calcium, strontium, and barium showed the tendency to aggregate with decreasing bulkiness of the substituents. THF coordination led to monomeric alkaline-earth metal diphenylamides. In contrast to this observation, the anilides showed a higher degree of aggregation. The calcium compound formed tetranuclear complexes, whereas the strontium and barium derivatives crystallized with a strand structure. The diphenylphosphanides also precipitated from a THF solution as monomeric molecules with hexa-coordinate calcium and strontium atoms as well as hepta-coordinate barium atoms.[14]

For the phenylphosphanides, we also expected a higher degree of aggregation, as was already found for the magnesium derivatives. Therefore, the phenylphosphanides of calcium (**4**), strontium (**5**), and barium (**6**) were prepared via the metathesis reaction of KP(H)Ph with MI$_2$ in THF according to eq 3. For the crystalline calcium derivative **4**, a formula of (THF)$_3$Ca[P(H)Ph]$_2$ was found that showed two P—H stretching frequencies at 2270 and 2283 cm^{-1}. This fact indicated two chemically different phosphanide substituents. Therefore, a dimeric structure (THF)$_3$Ca[μ-P(H)Ph]$_3$Ca(THF)$_2$P(H)Ph with hexacoordinate calcium atoms, as shown in eq 3, can be proposed with one THF molecule in the gaps between these molecules. However, the single crystals had the shape of extremely thin needles, which were not suitable for X-ray structure determination experiments. The structural motif of trigonal bipyramids Ca$_2$P$_3$ with the metal atoms in apical positions is rather common within the chemistry of alkaline-earth metal phosphanides.[4,5,29–32] In the ^{31}P{^{1}H} NMR spectrum, a singlet at δ -100.8 was observed, suggesting a fast exchange on

the NMR time scale of bridging and terminal phosphanide groups. The ^{1}H as well as ^{13}C NMR experiments also showed only one phosphanide ligand.

(3)
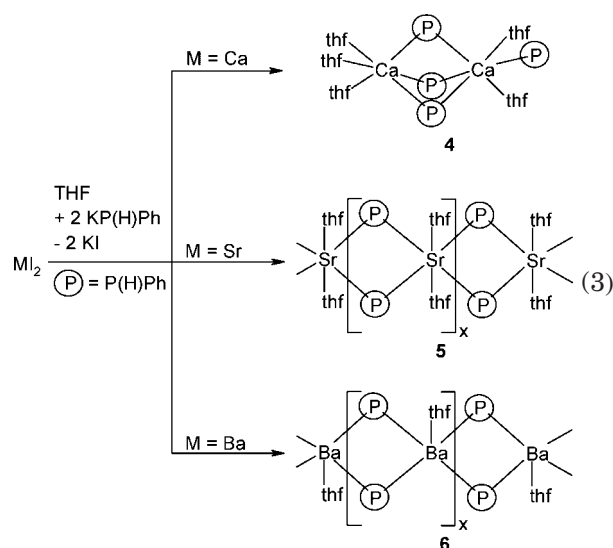
The strontium and barium bis(phenylphosphanides) show only one P—H stretching frequency in the IR spectrum at 2286 (**5**) and 2284 cm^{-1} (**6**), respectively, which suggests very similar solid-state structures. These compounds crystallized as [(THF)$_2$Sr{P(H)Ph}$_2$]$_\infty$ (**5**) and [(THF)Ba{P(H)Ph}$_2$]$_\infty$ (**6**). The X-ray structure of **5** revealed a strand structure with bridging phosphorus atoms and hexacoordinate metals. For **6**, a very similar structure can be assumed but the lower THF content suggests that η^6-coordination to the phenyl π systems competes with THF coordination, as observed for the anilides of barium.[28]

The reactivity of magnesium bis(diphenylphosphanide) toward potassium diphenylphosphanide is represented in eq 4. Depending on the stoichiometry, [(THF)Mg(PPh$_2$)$_3$] (**7**) and [Mg(PPh$_2$)$_4$] anions (**8** and **9**) were formed. The addition of Et$_2$O to a mixture of KPPh$_2$ and Mg(PPh$_2$)$_2$ in THF initiated the crystallization of (Et$_2$O)K[(THF)Mg(PPh$_2$)$_3$] (**7**) with a strand structure and (Et$_2$O)$_x$(THF)$_y$K$_2$[Mg(PPh$_2$)$_4$] (**8**) with a layer structure depending on the stoichiometry. The crystals of **8** easily lost THF and Et$_2$O and, therefore, the content of these ethers varied. A structure determination at single crystals of **8** allowed one to deduce a formula of (Et$_2$O)$_{1.5}$(THF)K$_2$[Mg(PPh$_2$)$_4$]. Recrystallization of **8** from hot 1,4-dioxane (diox) yielded (diox)$_2$K$_2$[Mg(PPh$_2$)$_4$] (**9**). In all of these magnesiates **7**–**9**, the alkaline-earth metal atoms are in distorted tetrahedral environments. Because of this fact, larger numbers than $n = 2$ (eq 4) do not lead to higher magnesiates but to mixtures of KPPh$_2$ and K$_2$[Mg(PPh$_2$)$_4$].

(4)
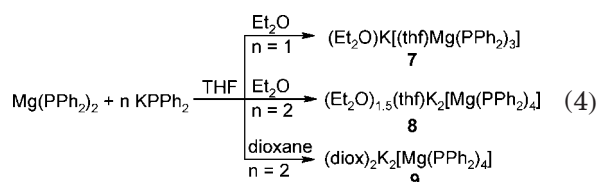
The potassium atoms interconnect these anions via coordination to the phosphorus atoms or to the π system of the

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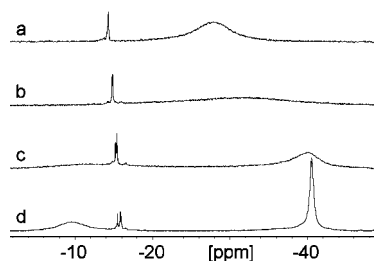(28) Gärtner, M.; Görls, H.; Westerhausen, M. *Inorg. Chem.* **2007**, *46*, 7678–7683.
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Figure 1. Dynamic $^{31}P\{^1H\}$ NMR experiments of **7** in THF-d_8 at 81 MHz. At 27 °C (spectrum a), a broad singulet at δ –28 is observed that broadens at 0 °C (spectrum b) and splits into two signals at –25 °C (spectrum c). Further cooling to –50 °C (spectrum d) leads to a narrowing of these signals at δ –10 (KPPh$_2$) and δ –41 [Mg(PPh$_2$)$_2$]. The resonance at δ –15 stems from impurities.

phenyl groups. These interactions lead to a strand structure for **7** and layer structures for **8** and **9**. The formation of polymeric structures explains the insolubility of these potassium magnesiates in hydrocarbons. A THF solution of **7** showed a broad singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ −28. In dynamic NMR experiments shown in Figure 1, two resonances at δ −10 and −41 appeared at low temperatures, which stem from the mononuclear compounds KPPh$_2$ (δ −10.0)[33] and Mg(PPh$_2$)$_2$ (δ −39.7). In solution, the potassium magnesiates dissociate; however, a fast phosphanide exchange process occurs. Similar observations are also valid for the other potassium magnesiates.

NMR Spectroscopy. Selected NMR data of the phenylphosphanides of magnesium (**3**), calcium (**4**), strontium (**5**), and barium (**6**) are listed in Table 1 together with the NMR parameters of phenylphosphane.[33] For comparison reasons, also the data of HPPh$_2$[33] and the alkaline-earth metal bis(diphenylphosphanides) are integrated.[14] In solution, only one set of signals was observed for **3** and **4** because of fast exchange processes of bridging and terminally bound phosphanide substituents.

The ^{31}P NMR chemical shift moves toward lower field with increasing size of the alkaline-earth metals, with the magnesium derivatives **2** and **3** being close to the phosphanes HPPh$_2$ and H$_2$PPh. These trends are in agreement with the corresponding alkali-metal phosphanides.[33] Increasing ionicity of the metal−phosphorus bonds leads to enhanced charge on the phosphorus atoms and to increased charge back-donation from phosphorus into the phenyl π system. This effect leads to a downfield shift of the *ipso*-carbon atoms of approximately 20 ppm and to strongly increased $^1J(C,P)$ coupling constants compared to the neutral phosphanes. The other carbon atoms show shifts and coupling constants similar to those of the phosphanes. The phosphorus-bound hydrogen atoms of H$_2$PPh and **3** show similar chemical shifts and $^1J(H,P)$ coupling constants. The phenylphosphanides of the heavier alkaline-earth metals display smaller $\delta(^1H)$ values and smaller $^1J(H,P)$ coupling constants.

Molecular Structures. Figure 2 shows the molecular structure and numbering scheme of **1**. The diphenylphosphanide ligand is in a bridging position between two magnesium atoms, giving a one-dimensional polymer with

Mg−P distances of 260.90(8) and 263.46(7) pm. These bonds are extremely large compared to known ether adducts such as (DME)Mg[P(SiMe$_3$)$_2$]$_2$ [Mg−P, 248.7(2) pm][34] and (THF)$_2$Mg[P(SiMe$_3$)$_2$]$_2$ [250.31(6) pm].[35] This observation can be explained by the bridging position of the phosphanide in **1** and by a reduction of the charge on the phosphorus atom due to mesomeric effects. The Mg−C bond length of 213.6(2) pm is rather short compared to [(TMEDA)MgEt$_2$][36] and [(Et$_2$O)$_2$Mg(Et)Br][37,38] but within the expected region for tetracoordinate magnesium.[39–41] The magnesium atoms are in distorted tetrahedral environments with Mg−P−Mg and P−Mg−P angles of 113.85(3)° and 116.17(3)°, respectively.

The molecular structure of [(THF)$_6$Mg$_4$\{P(H)Ph\}$_8$] (**3**) is represented in Figure 3. Symmetry-related atoms ($−x +$ 1, $−y + 2$, $−z − 1$) are marked with an "A". The two magnesium atoms of the asymmetric unit show different environments. Hexacoordinate Mg1 binds to four bridging phosphanide ligands and to two THF molecules with a cis arrangement. The tetracoordinate atom Mg2 is in a distorted tetrahedral environment of two bridging phosphanide groups, a terminally bound phosphanide, and one THF molecule. The smaller coordination number of Mg2 leads to shorter Mg2−O and Mg2−P bonds than are observed for Mg1. This effect is rather small for the Mg−O distances, whereas large differences exist between the Mg1−P and Mg2−P values. Surprisingly, the endocyclic (Mg2−P2 and Mg2−P4) and exocyclic (Mg2−P3) bond lengths are very similar and show an average value of 255.2 pm, whereas an average Mg1−P value of 273.6 pm was observed. The Mg2−P bonds are elongated compared to the ether complexes (DME)Mg[P(SiMe$_3$)$_2$]$_2$[34] and (THF)$_2$Mg[P(SiMe$_3$)$_2$]$_2$[35] but significantly shorter than was observed in **1**. This finding can be explained by inductive and mesomeric effects, which reduce the charge on phenyl-substituted phosphanides and enhance the charge on trialkylsilyl-substituted ones. A related cage structure was found for [(THF)$_6$Mg$_4$Et$_2$Cl$_6$], with the ethyl groups as terminal ligands and the chlorine atoms in bridging positions.[42]

The molecular structure and numbering scheme of **5** are represented in Figure 4. The phosphanide ligands are in bridging positions with an average Sr−P distance of 313.9 pm. Two THF molecules (av Sr−O 252.1 pm) in a cis arrangement complete the distorted octahedral coordination sphere of the alkaline-earth metal atoms. In (THF)$_4$Sr[P(SiMe$_3$)$_2$]$_2$ with terminally bound phosphanide groups, much shorter Sr−P bonds with an average value of

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Table 1. Selected NMR Data of M[P(H)Ph]$_2$ of Magnesium (**3**), Calcium (**4**), Strontium (**5**), and Barium (**6**) and M[PPh$_2$]$_2$ of Magnesium (**2**), Calcium (**A**), Strontium (**B**), and Barium (**C**) in a THF Solution at Room Temperature (Chemical Shifts [ppm] and Coupling Constants [Hz]) [a]

|	H$_2$PPh[33]	3	4	5	6	HPPh$_2$[33]	2	A	B	C
R	H	H	H	H	H	Ph	Ph	Ph	Ph	Ph
M		Mg	Ca	Sr	Ba		Mg	Ca	Sr	Ba
δ(^{31}P)	−125.7	−131.9	−100.8	−93.1	−70.9	−41.1	−39.7	−13.1	−9.8	+5.8
δ(*ipso*-C)	129.2	150.8	156.3	155.7	156.4	136.0	149.5	153.2	153.4	154.2
^1J(C,P)	10^b	34.0	34.8	36.4	11^b	33.8	37.3	43.0		
δ(*o*-C)	135.3	135.3	130.3	130.5	130.2	134.8	133.4	131.2	130.9	130.5
^2J(C,P)	15	15.4	14.8	14.3	13.6	17	15.6	16.5	17.1	17.2
δ(*m*-C)	129.2	129.1	127.1	127.3	127.8	129.3	127.8	127.7	127.7	128.0
^3J(C,P)	6	5.8	4.8	5.2	4.6	5	4.3	5.6	5.9	5.3
δ(p-C)	128.8	121.5	118.4	118.6	118.7	129.5	120.7	120.9	120.8	120.6
δ(H$_P$)	3.97	3.94	2.39	2.58	2.77	5.24				
^1J(H,P)	199	198.5	175.7	179.3	183.7	216				
δ(*o*-H)	7.51	7.12	7.11	7.19	7.24	7.51	7.35	7.35	7.35	7.38
δ(*m*-H)	7.28	6.74	6.67	6.69	6.72	7.31	6.82	6.82	6.80	6.84
δ(*p*-H)	7.28	6.67	6.41	6.43	6.43	7.31	6.68	6.58	6.55	6.58

^{a} The values of H$_2$PPh and HPPh$_2$ were taken from Yokoyama and Takahashi.[33] ^{b} Broad signal.
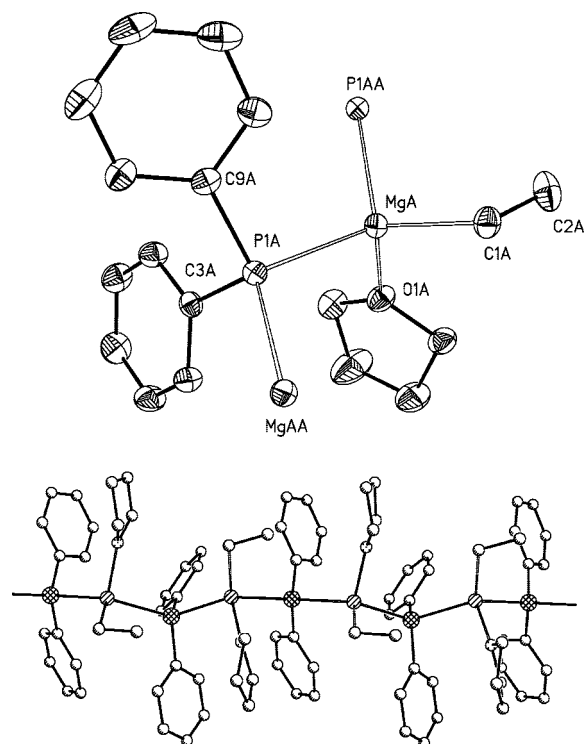
Figure 2. Molecular structure of **1** (top). Only the structure of one molecule is shown. The ellipsoids represent a probability of 40%. Hydrogen atoms are neglected for clarity reasons. The formation of the strand structure is shown at the bottom. Selected bond lengths (pm): MgA−O1A 204.6(1), MgA−C1A 213.6(2), MgA−P1A 260.90(8), MgA−P1AA 263.46(7), P1A−C3A 183.5(2), P1A−C9A 183.5(2), C1A−C2A 152.2(3).

302.1 pm were found.[31] However, in (THF)$_3$Sr[μ-P(SiMe$_3$)$_2$]$_3$Sr[P(SiMe$_3$)$_2$], the hexacoordinate strontium atom shows elongated Sr−P distances (av Sr−P 317.8 pm), whereas tetracoordinate strontium atoms display Sr−P values between 304 and 308 pm.[31]

The potassium magnesiates **7**−**9** dissociate in a THF solution and, therefore, a characterization was performed via X-ray structure determinations. In all of these heterobimetallic compounds, the magnesium atoms show coordination numbers of four. In Figure 5, the molecular structure of **7** is shown. The tetracoordinate magnesium atom is bound to three phosphanide ligands and one THF molecule. Two of these phosphanides bind also to potassium cations. The crystal structure consists of one-dimensional polymers
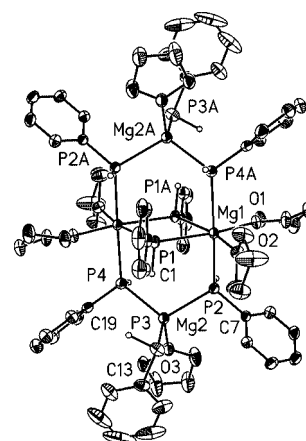

Figure 3. Molecular structure of **3**. Atoms generated by a crystallographic inversion center (−x + 1, −y + 2, −z − 1) are marked with "A". The ellipsoids represent a probability of 40%. Hydrogen atoms are neglected for clarity reasons. Selected bond lengths (pm): Mg1−O1 208.7(3), Mg1−O2 213.2(3), Mg1−P1 270.0(2), Mg1−P2 273.4(2), Mg1−P1A 275.7(2), Mg1−P4A 275.2(2), Mg2−O3 204.2(3), Mg2−P2 254.7(2), Mg2−P3 255.0(2), Mg2−P4 255.9(2), P1−C1 181.9(4), P2−C7 183.0(4), P3−C13 182.2(4), P4−C19 183.2(4).
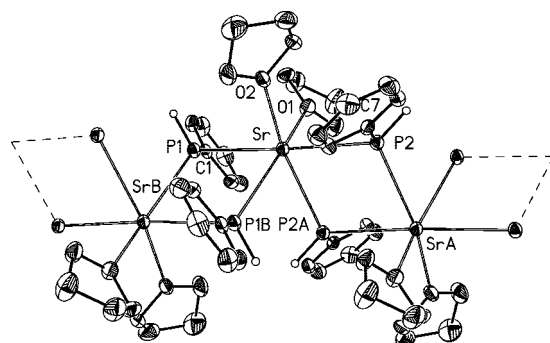
Figure 4. Part of the strand structure of polymeric **5**. The ellipsoids represent a probability of 40%. Carbon-bound hydrogen atoms are neglected for clarity reasons. Symmetry-related atoms are marked with "A" (−x, −y + 1, −z + 1) and "B" (−x + 1, −y + 1, −z + 1). Selected bond lengths (pm): Sr−O1 250.9(2), Sr−O2 253.3(2), Sr−P1 313.26(8), Sr−P2 314.76(9), Sr−P2A 312.78(8), Sr−P1B 314.67(7), P1−C1 181.9(3), P1−H1 133(4), P2−C7 182.3(3), P2−H2 132(4). Angles (deg): P1−Sr−P2 177.02(2), O1−Sr−P1B 161.53(6), O2−Sr−P2A 165.99(6), O1−Sr−O2 91.39(7), P1−Sr−P1B 79.33(2), P2−Sr−P2A 80.46(2).

[−K−P1−Mg−P3−]$_\infty$. The potassium atom binds to two phosphanide substituents and a diethyl ether molecule and shows an additional η^2 contact to a phenyl group, yielding
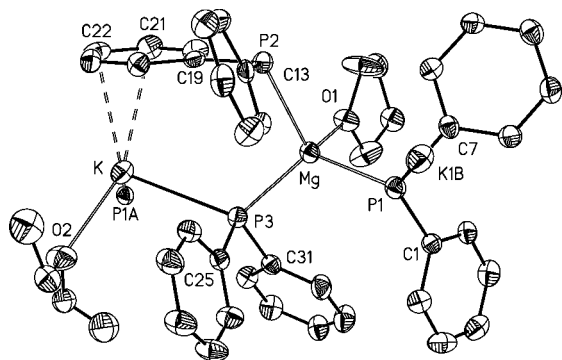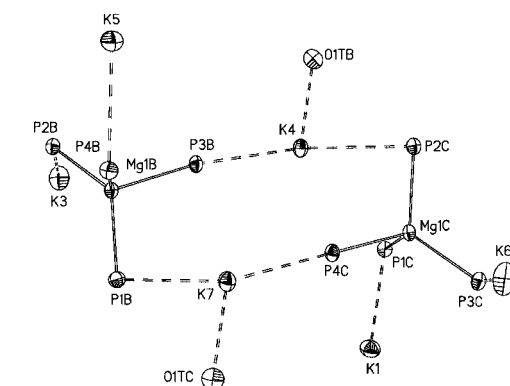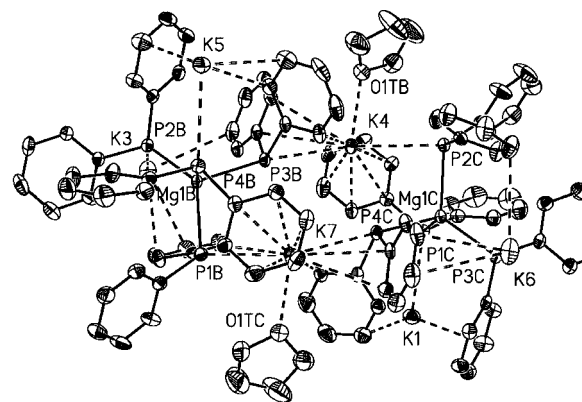
Figure 5. Molecular structure of **7**, which represents part of a one-dimensional polymer. Symmetry-related atoms are marked with "A" ($x - 1$, y, z) and "B" ($x + 1$, y, z). The ellipsoids represent a probability of 40%. All hydrogen atoms are omitted for clarity reasons. Selected bond lengths (pm): Mg−O1 203.5(6), Mg−P1 259.5(3), Mg−P2 257.2(3), Mg−P3 255.8(3), K−O2 271.4(7), K−C21 319.8(9), K−C22 310.4(8), K−P3 326.4(3), K−P1A 334.0(3).

a strongly distorted tetrahedral environment. The high thermal motion of the diethyl ether ligand spoils the quality of the crystal structure. The average Mg−P bond length of 257.5 pm is slightly elongated compared to Mg2−P of **3**. The coordination environment of the soft potassium cations contains ether molecules and contacts to phenyl groups, which is quite common because the soft π system of the phenyl groups can compete with the anionic phosphorus atoms. In [KP(H)Mes*]$_2$ (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) with a polymeric ladder-type structure,[43] in tetrameric [KP(H)(2,6-MesC$_6$H$_3$]$_4$,[44] and in polymeric [(THF)$_2$K$_3${P(H)Mes}$_3$][45] (Mes = 2,4,6-Me$_3$C$_6$H$_2$), the potassium atoms show coordination to the phosphorus atoms as well as to the π systems of the aryl moieties.

Crystals of **8** were obtained by diffusion of diethyl ether into a saturated THF solution of K$_2$Mg[P(H)Ph]$_4$ at room temperature. The structure is displayed in Figure 6. The quality of the structure determination is very poor because of high thermal motion and disordering of unsolvated solvent molecules (THF and Et$_2$O). Nevertheless, the structural motif clearly shows a polymeric layer structure consisting of eight-membered K$_2$Mg$_2$P$_4$ rings with a chair conformation. These rings are interconnected by additional potassium cations to a two-dimensional framework. The magnesium binds to four phenylphosphanide groups, and the tetracoordinate phosphorus atoms are in bridging positions between potassium and magnesium atoms.

In order to obtain a structure of higher quality, **8** was recrystallized from a 1,4-dioxane solution, which was saturated at 50 °C. The structure of **9** is represented in Figure 7 and shows much similarity to the structure of **8**. The disordered Et$_2$O and THF molecules are substituted by monodentate 1,4-dioxane without destruction of the framework. The magnesium atom is surrounded by four diphenylphosphanide ligands, which also bind to potassium atoms.

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Figure 6. Molecular structure and numbering scheme of **8**. Disordered solvent molecules as well as all hydrogen atoms are neglected for clarity reasons. The ellipsoids represent a probability of 40%. The two-dimensional net is symbolized at the bottom. The eight-membered K$_2$Mg$_2$P$_4$ ring represents the main structural fragment in the solid-state structure.

Again, eight-membered K$_2$Mg$_2$P$_4$ rings with chair conformations are formed that are interconnected by additional potassium cations. The gaps of this rather open layer structure contain 1.5 intercalated 1,4-dioxane molecules that show no short contact to a metal atom.

The Mg−P bonds with an average bond length of 259.7 pm are elongated compared to magnesiate **7** by approximately 2 pm. This fact can be explained by additional electrostatic repulsion between the negatively charged phosphorus atoms. All phosphanide groups act as bridging ligands between magnesium and potassium atoms. Part of the potassium atoms bind to 1,4-dioxane molecules, which act as monodentate bases. The coordination spheres of the potassium atoms are completed by additional contacts to the π systems of the phenyl groups.

Conclusion and Perspective

The reduction of steric hindrance by going from the diphenylphosphanides to the phenylphosphanides leads to aggregation and formation of oligonuclear compounds (Mg, Ca) or polymeric structures (Sr, Ba). The soft phosphorus atoms favor the coordination of four and, hence, the bridging position between the alkaline-earth metals. The different coordination modes can clearly be distinguished by the P−H stretching frequencies in the IR spectra. Wavenumbers of approximately 2285 cm^{-1} indicate bridging phenylphosphanides in four-membered M$_2$P$_2$ rings irrespective of the
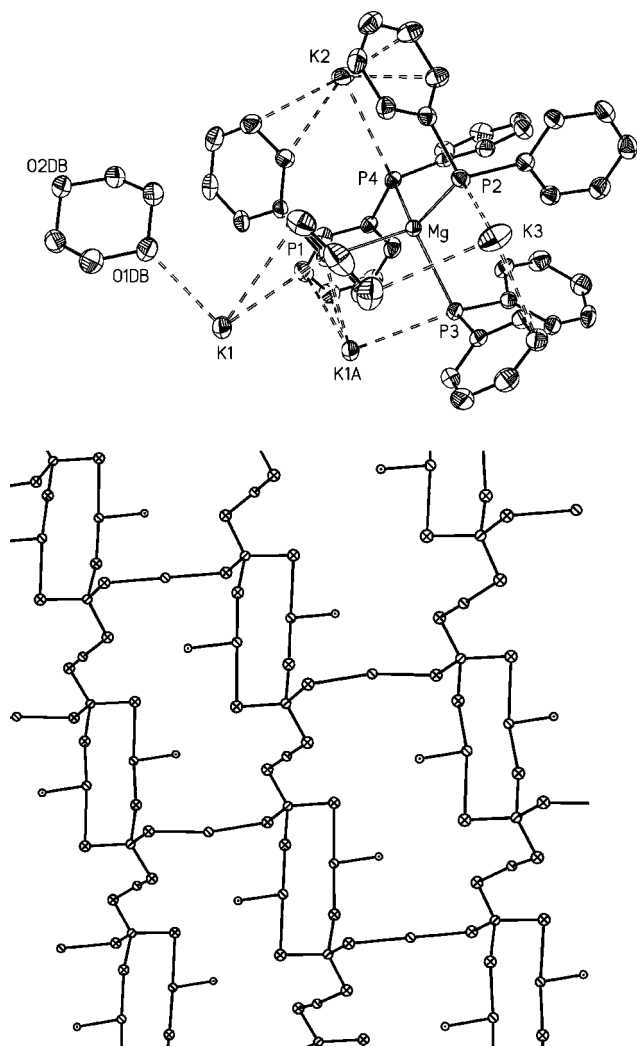
Figure 7. Molecular structure and numbering scheme of **9** (top). At the bottom, linking of the eight-membered $K_2Mg_2P_4$ rings is represented. The two-dimensional net shows large gaps that contain disordered solvent molecules (not shown). The symbols inside the circles clarify the atom type: (•) O, (×) P, (/) Mg, (\) K. Selected bond lengths (pm): Mg−P1 263.4(1), Mg−P2 257.75(9), Mg−P3 259.3(1), Mg−P4 258.50(9), K1−P1 349.13(9), K1A−P1 367.30(8), K1A−P3 334.51(8), K2−P4 333.26(6), K3−P2 327.65(6).

metal M (Mg, Ca, Sr, Ba). Larger energies of 2310 cm⁻¹ were found terminally at magnesium-bound phenylphosphanides. In the ³¹P{¹H} NMR spectra, a low-field shift of the resonance was observed with increasing size of the alkaline-earth metal atom. In a THF solution, dynamic exchange processes lead to a single resonance for the cage compounds on the NMR time scale.

The potassium magnesiates of the type K[(THF)Mg-$(PPh_2)_3$] and $K_2[Mg(PPh_2)_4]$ dissociate in a THF solution into the homoleptic compounds. At high temperature, all phosphanide substituents are equivalent on the NMR time scale, whereas at low temperature, broad resonances were observed, as was also found for the homoleptic compounds $KPPh_2$ and $Mg(PPh_2)_2$. The crystal structures show that the magnesium and phosphorus atoms favor distorted tetrahedral environments. The magnesiate anions [(THF)Mg(PPh_2)_3]⁻ and [Mg(PPh_2)_4]²⁻ are interconnected with potassium atoms that complete their coordination spheres by additional ether

ligands and contacts to the π systems of the phenyl rings. The bridging mode of the potassium atoms leads to the formation of coordination polymers in the solid state, although these compounds can also be regarded as salts.

Experimental Section

General Procedure. All manipulations were carried out in an argon atmosphere under anaerobic conditions. The compounds are extremely moisture-sensitive and lose coordinated THF once isolated. It was not possible to weigh out a definite amount because the weight of the substances changed permanently during handling and weighing. Therefore, the analysis is limited to NMR and IR spectroscopic investigations as well as X-ray structure determinations. ¹H, ¹³C, and ³¹P NMR spectra were recorded in THF-d_8 solutions at ambient temperature on a Bruker AC 200 or a Bruker AC 400 spectrometer. Deuterated electron impact (DEI) mass spectra were obtained on a Finnigan MAT SSQ 710 system (2,4-dimethoxybenzyl alcohol as the matrix), and IR measurements were carried out on a Perkin-Elmer system 2000 FT-IR. Decomposition points were measured with a Reichert−Jung apparatus type 302102 and are uncorrected. Prior to use, all solvents were thoroughly dried and distilled in an argon atmosphere. $PhPH_2$,[46] $KP(H)Ph$,[47] $(diox)MgEt_2$,[48] $(THF)_4MgBr_2$,[6] $(THF)_3Ca(Ph)N(SiMe_3)_2$,[49] $(THF)_5$-SrI_2,[50] and $(THF)_5BaI_2$[51] were prepared according to literature procedures. A THF solution of potassium diphenylphosphanide was purchased from Aldrich.

Synthesis of [(THF)Mg(Et)PPh_2]∞ (1). This substance was prepared in accordance with a known procedure.[6] A solution of phenylmagnesium bromide was freshly prepared from magnesium turnings and bromobenzene in THF. From this solution, 11.1 mL (0.9 M, 10.0 mmol) was added to 20.0 mL of a stirred solution of potassium diphenylphosphanide in THF (0.5 M, 10.0 mmol). After 1 h of stirring, precipitated potassium bromide was removed by filtration and the volume of the obtained orange-colored solution was reduced to one-third of its original volume. The addition of 10 mL of diethyl ether led to the crystallization of **1** at −40 °C within 2 days. These yellow crystals were collected on a cooled frit and dried in vacuo. The yield was 1.72 g (5.54 mmol, 55%). Decomposition was above 100 °C. ¹H NMR: δ −0.62 (2H, q, ³$J_{H,H}$ = 8.4 Hz, CH_2), 1.19 (3H, t, ³$J_{H,H}$ = 8.0 Hz, CH_3), 1.73 (THF), 3.59 (THF), 6.80 (2H, t, ³$J_{H,H}$ = 7.6 Hz, *p*-CH), 6.97 (4H, t, ³$J_{H,H}$ = 7.2 Hz, *m*-CH), 7.42 (4H, dt, ⁴$J_{H,H}$ = 1.0 Hz, ³$J_{H,H}$ = 6.8 Hz, *o*-CH). ¹³C{¹H} NMR: δ −2.1 (CH_2), 13.9 (CH_3), 25.4 (THF), 67.5 (THF), 123.0 (*p*-C), 128.0 (*m*-C, ³$J_{C,P}$ = 5.8 Hz), 132.8 (*o*-C, ²$J_{C,P}$ = 16.2 Hz), 148.8 (*ipso*-C, ¹$J_{C,P}$ = 31.5 Hz). ³¹P{¹H} NMR: δ −45.2 (s). MS (DEI, *m/z*): 29 ([Et⁺], 28%), 41 (78%), 42 (75%), 50 (39%), 71 (80%), 78 ([C_6H_6]⁺, 77%), 107 ([PhP − H]⁺, 100%), 185 ([Ph_2P]⁺, 75%), 187 ([Ph_2PH + H]⁺, 44%), 215 ([Ph_2P − H]⁺, 57%), 239 (35%), 262 ([Ph_3P]⁺, 38%), 293 ([Ph_2P−PPh]⁺, 5%), 370 ([Ph_2P−PPh_2]⁺, 80%). IR (Nujol, KBr, cm⁻¹): 3062 w, 1579 w, 1433 m, 1066 vw, 1026 s, 976 vw, 916 vw, 878 m, 746 m, 693 vs, 499 w, 468 m.

Synthesis of (THF)_4Mg(PPh_2)_2 (2). 2 was prepared according to a literature procedure with a yield of approximately 50%.[6] ¹H

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NMR (400 MHz): δ 1.73 (THF), 3.58 (THF), 6.68 (4H, t, $^3J_{H,H}$ = 7.2 Hz, p-CH), 6.82 (8H, t, $^3J_{H,H}$ = 7.2 Hz, m-CH), 7.35 (8H, t, $^3J_{H,H}$ = 7.2 Hz, o-CH). ^{13}C{^{1}H} NMR (100 MHz): δ 25.4 (THF), 67.1 (THF), 122.5 (p-C), 127.8 (m-C, $^3J_{C,P}$ = 4.3 Hz), 133.4 (o-C, $^2J_{C,P}$ = 15.6 Hz), 149.5 (ipso-C, br). ^{31}P{^{1}H} NMR (81 MHz): δ −39.7 (s). MS (DEI, m/z): 51 (28%), 77 ([Ph]$^+$, 30%), 152 (23%), 183 ([Ph$_2$P − 2H]$^+$, 70%), 185 ([Ph$_2$P]$^+$, 50%), 201 ([Ph$_2$PO]$^+$, 5%), 262 ([Ph$_3$P]$^+$, 17%), 293 (16%), 370 ([Ph$_2$P−PPh$_2$]$^+$, 100%), 371 ([Ph$_2$P−PPh$_2$ + H]$^+$, 52%). IR (Nujol, KBr, cm^{-1}): 3055 m, 1572 m, 1434 s, 1301 vw, 1183 vw, 1096 w, 1068 w, 1025 m, 888 w, 695 vs, 504 w, 473 vw.

Synthesis of [(THF)$_{1.5}$Mg(PHPh)$_2$]$_4$ (3). In a Schlenk flask, (diox)MgEt$_2$ (0.65 g, 3.81 mmol) was dissolved in 15 mL of THF and 0.84 g of phenylphosphane (7.62 mmol) was added dropwise at room temperature. Ethane evolved, and a clear, colorless solution was obtained. After 1 h of stirring, the volume of the solution was reduced in vacuo to 5 mL. Then 5 mL of diethyl ether was added. Thereafter, the solution was filtered and stored at −40 °C. Colorless crystals of **3**, suitable for X-ray structure measurements formed within 1 week. The solid (0.93 g, 0.66 mmol, 70%) was collected on a cooled frit and dried in vacuo. Decomposition was above 80 °C. ^{1}H NMR: δ 1.76 (THF), 3.61 (THF), 3.94 (8H, d, $^1J_{P,H}$ = 198.5 Hz, PH), 6.67 (8H, s, br, p-CH), 6.74 (16H, s, br, m-CH), 7.12 (16H, s, br, o-CH). ^{13}C{^{1}H} NMR: δ 25.4 (THF), 67.3 (THF), 121.5 (p-C), 129.1 (m-C, $^3J_{C,P}$ = 5.8 Hz), 135.3 (o-C, $^2J_{C,P}$ = 15.4 Hz), 150.8 (ipso-C, br). ^{31}P{^{1}H} NMR: δ − 31.9 (s). MS (DEI, m/z): 51 (22%), 77 ([Ph]$^+$, 77%), 107 ([PhP − H]$^+$, 99%), 108 ([PhP]$^+$, 100%), 110 ([PhPH$_2$]$^+$, 67%), 183 ([Ph$_2$P − 2H]$^+$, 50%), 185 ([Ph$_2$P]$^+$, 48%), 187 ([Ph$_2$PH + H]$^+$, 28%), 201 ([Ph$_2$PO]$^+$, 18%), 218 ([Ph$_2$P(O)OH]$^+$, 28%), 262 ([Ph$_3$P]$^+$, 44%), 278 ([Ph$_3$PO]$^+$, 3%), 324 ([Ph$_2$P(O)−P(O)Ph − H]$^+$, 30%). IR (Nujol, KBr, cm^{-1}): 3055 m, 2310 w, 2286 w, 2261 s, 1577 vs, 1430 m, 1296 vw, 1262 w, 1183 vw, 1093 w, 1067 vw, 1027 vs, 922 vw, 874 s, 740 vs, 698 s, 476 m.

Synthesis of (THF)$_3$Ca(PHPh)$_2$ (4). Phenylcalcium bis(trimethylsilyl)amide (4.68 g, 9.47 mmol) was dissolved in THF (30 mL), and phenylphosphane (1.04 g, 9.47 mmol) was added. The yellow reaction mixture was stirred for 1 h at ambient temperature. After filtration, the solution was reduced to 10 mL and stored at −25 °C. As a consequence of dismutation, colorless needles of **4** (1.84 g, 3.88 mmol, 82%) precipitated overnight, whereas Ca[N(SiMe$_3$)$_2$]$_2$ remained in solution. The crystals were collected on a cooled frit and dried in vacuo. They were too thin for X-ray structure studies. The THF content was determined by acidic titration of a defined amount of **4**. Decomposition was above 130 °C. ^{1}H NMR (400 MHz): δ 1.77 (THF), 2.39 (2H, d, $^1J_{P,H}$ = 175.7 Hz, PH), 3.61 (THF), 6.41 (2H, t, $^3J_{H,H}$ = 7.2 Hz, p-CH), 6.70 (4H, t, $^3J_{H,H}$ = 7.2 Hz, m-CH), 7.11 (4H, $^3J_{H,H}$ = 6.8 Hz, o-CH). ^{13}C{^{1}H} NMR (50 MHz): δ 25.2 (THF), 67.3 (THF), 118.4 (p-C), 127.1 (m-C, $^3J_{C,P}$ = 4.8 Hz), 130.3 (o-C, $^2J_{C,P}$ = 14.8 Hz), 156.3 (ipso-C, $^1J_{C,P}$ = 34.0 Hz). ^{31}P{^{1}H} NMR (81 MHz): δ −100.8 (s). MS (DEI, m/z): 77 ([Ph]$^+$, 50%), 78 ([C$_6$H$_6$]$^+$, 35%), 107 ([PhP − H]$^+$, 83%), 108 ([PhP]$^+$, 100%), 110 ([PhPH$_2$]$^+$, 48%), 124 ([PhPO]$^+$, 32%), 149 (29%), 183 ([Ph$_2$P − 2H]$^+$, 78%), 186 ([Ph$_2$PH]$^+$, 46%), 201 ([Ph$_2$PO]$^+$, 53%), 218 ([Ph$_2$P(O)OH]$^+$, 14%), 262 ([Ph$_3$P]$^+$, 60%), 278 ([Ph$_3$PO]$^+$, 12%), 324 ([Ph$_2$P(O)−(O)Ph − H]$^+$, 16%). IR (Nujol, KBr, cm^{-1}): 3070 m, 3057 m, 3044 m, 2283 m, 2270 m, 1579 s, 1306 w, 1263 w, 1135 w, 1074 vs, 1035 vs, 983 w, 917 w, 888 vw, 734 m, 694 m, 550 w.

General Method for the Synthesis of [(THF)$_2$Sr(PHPh)$_2$]$_∞$ (5) and (THF)Ba(PHPh)$_2$ (6). In a Schlenk flask, the alkaline-earth metal diiodide (THF)$_5$SrI$_2$ in the case of strontium and (THF)$_5$BaI$_2$ in the case of barium were dissolved in THF. A solution of potassium phenylphosphanide (0.269 M) in THF was added dropwise via a syringe. During this procedure, the solution turned red and a colorless precipitate of KI could be observed. After 1 h, KI was removed by filtration and the volume of the filtrate was reduced to one-third of its original volume and stored in a freezer. After 1 day, colorless crystals of the appropriate alkaline-earth metal bis(phenylphosphanide) were obtained, collected on a cooled frit, and dried under reduced pressure.

Synthesis of 5. 5 was prepared according to the general method from (THF)$_5$SrI$_2$ (2.25 g, 3.21 mmol) and a solution of potassium phenylphosphanide in THF (0.269 M, 6.41 mmol, 23.83 mL) in THF (20 mL). Colorless crystals of **5** (1.12 g, 2.49 mmol, 78%) were obtained at 5 °C. Decomposition was above 40 °C. ^{1}H NMR (400 MHz): δ 1.78 (THF), 2.58 (2H, d, $^1J_{P,H}$ = 179.3 Hz, PH), 3.61 (THF), 6.43 (2H, t, $^3J_{H,H}$ = 7.2 Hz, p-CH), 6.69 (4H, t, $^3J_{H,H}$ = 7.6 Hz, m-CH), 7.19 (4H, $^3J_{H,H}$ = 6.4 Hz, o-CH). ^{13}C{^{1}H} NMR (50 MHz): δ 25.2 (THF), 67.3 (THF), 118.6 (p-C), 127.3 (m-C, $^3J_{C,P}$ = 5.2 Hz), 130.5 (o-C, $^2J_{C,P}$ = 14.3 Hz), 155.7 (ipso-C, $^1J_{C,P}$ = 34.8 Hz). ^{31}P{^{1}H} NMR: δ −93.1 (s). MS (DEI, m/z): 77 ([Ph]$^+$, 39%), 78 ([C$_6$H$_6$]$^+$, 100%), 107 ([PhP − H]$^+$, 63%), 108 ([PhP]$^+$, 98%), 110 ([PhPH$_2$]$^+$, 48%), 124 ([PhPO]$^+$, 7%), 183 ([Ph$_2$P − 2H]$^+$, 30%), 186 ([Ph$_2$PH]$^+$, 59%), 201 ([Ph$_2$PO]$^+$, 10%), 218 ([Ph$_2$P(O)OH]$^+$, 5%), 262 ([Ph$_3$P]$^+$, 8%), 278 ([Ph$_3$PO]$^+$, 3%), 324 ([Ph$_2$P(O)−P(O)Ph − H]$^+$, 4%). IR (Nujol, KBr, cm^{-1}): 3054 m, 2286 s, 1575 s, 1261 vw, 1183 w, 1098 w, 1074 w, 1035 vs, 993 vw, 913 vw, 877 m, 843 w, 694 s, 474 m.

Synthesis of 6. 6 was prepared according to the general method from (THF)$_5$BaI$_2$ (1.05 g, 1.40 mmol) and a solution of potassium phenylphosphanide in THF (0.269 M, 2.79 mmol, 10.39 mL) in THF (20 mL). Colorless plates of **6** (0.52 g, 1.22 mmol, 87%) were obtained at −90 °C. They were too thin for X-ray structure studies. The THF content was determined by acidic titration of a defined amount. Decomposition was above 105 °C. ^{1}H NMR: δ 1.78 (THF), 2.77 (2H, d, $^1J_{P,H}$ = 183.7 Hz, PH), 3.62 (THF), 6.43 (2H, t, $^3J_{H,H}$ = 7.2 Hz, p-CH), 6.72 (4H, t, $^3J_{H,H}$ = 7.6 Hz, m-CH), 7.24 (4H, $^3J_{H,H}$ = 6.4 Hz, o-CH). ^{13}C{^{1}H} NMR: δ 25.6 (THF), 67.3 (THF), 118.7 (p-C), 127.8 (m-C, $^3J_{C,P}$ = 4.6 Hz), 130.2 (o-C, $^2J_{C,P}$ = 13.6 Hz), 156.4 (ipso-C, $^1J_{C,P}$ = 36.4 Hz). ^{31}P{^{1}H} NMR: δ −70.9 (s). MS (DEI, m/z): 78 ([C$_6$H$_6$]$^+$, 100%), 108 ([PhP]$^+$, 12%), 124 ([PhPO]$^+$, 12%), 183 ([Ph$_2$P − 2H]$^+$, 12%), 186 ([Ph$_2$PH]$^+$, 9%), 201 ([Ph$_2$PO]$^+$, 3%). IR (Nujol, KBr, cm^{-1}): 2285 w, 1572 vs, 1073 m, 990 vw, 732 vs, 697 m.

Synthesis of (Et$_2$O)K[(THF)Mg(PPh$_2$)$_3$] (7). A solution of potassium diphenylphosphanide (25.65 mL, 0.5 M, 12.28 mmol) was added to a vigorously stirred solution of (THF)$_4$MgBr$_2$ (2.02 g, 4.28 mmol) in 15 mL of THF. The red suspension was stirred at room temperature for an additional 2 h, and precipitated potassium bromide was removed by filtration. The clear solution was concentrated to a volume of 10 mL, and 20 mL of diethyl ether was allowed to diffuse into this solution overnight. Large pale-yellow crystals of **7** were obtained, collected on a frit, and dried shortly in vacuo. The yield was 2.42 g (3.16 mmol, 74%). Decomposition was above 75 °C. ^{1}H NMR: δ 1.12 (Et$_2$O), 1.77 (THF), 3.39 (Et$_2$O), 3.61 (THF), 6.67 (6H, t, $^3J_{H,H}$ = 6.4 Hz, p-CH), 6.83 (12H, t, $^3J_{H,H}$ = 7.0 Hz, m-CH), 7.39 (12H, dt, $^4J_{H,H}$ = 1.4 Hz, $^3J_{H,H}$ = 6.8 Hz o-CH). ^{13}C{^{1}H} NMR: δ 14.5 (Et$_2$O), 25.4 (THF), 63.5 (Et$_2$O), 67.3 (THF), 120.7 (p-C), 127.8 (m-C, $^3J_{C,P}$ = 5.5 Hz), 133.5 (o-C, $^2J_{C,P}$ = 18.5 Hz), 154.0 (ipso-C, br). ^{31}P{^{1}H} NMR: δ −30.1 (s, br). MS (DEI, m/z): 39 (67%), 51 (84%), 78 ([C$_6$H$_6$]$^+$, 100%), 109 ([PhPH]$^+$, 92%), 154 ([Ph−Ph]$^+$, 73%), 183 ([Ph$_2$P − 2H]$^+$, 93%), 201 ([Ph$_2$PO]$^+$, 42%), 262 ([Ph$_3$P]$^+$, 18%), 293 ([Ph$_2$P−PPh]$^+$, 28%), 370 ([Ph$_2$P−PPh$_2$]$^+$, 30%). IR (Nujol, KBr, cm^{-1}): 3056 w, 1573 s, 1434 s, 1182 vw, 1153 vw, 1068 w, 1024 w, 888 w, 803 vw, 696 vs, 564 vw, 503 w, 469 w.

Table 2. Crystal Data and Refinement Details for the X-ray Structure Determinations

Compound	1	3	5	7	8	9
formula	$C_{18}H_{23}MgOP$	$C_{72}H_{96}Mg_4O_6P_8$	$C_{20}H_{28}O_2P_2Sr$	$C_{44}H_{48}KMgO_2P_3$	$C_{58}H_{62}K_2MgO_{2.5}P_4$	$C_{58}H_{64}K_2MgO_5P_4$
fw/g·mol^{-1}	310.64	1402.49	449.98	765.14	1025.47	1067.48
T/°C	$-90(2)$	$-90(2)$	$-90(2)$	$-90(2)$	$-90(2)$	$-90(2)$
cryst syst	orthorhombic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	20.0202(5)	13.4719(8)	8.3679(4)	9.6598(18)	18.8759(4)	13.5941(3)
b/Å	8.7848(2)	13.6066(9)	10.2922(3)	10.660(2)	21.5826(5)	14.6614(3)
c/Å	39.2963(10)	13.6413(9)	13.4054(5)	20.077(4)	23.9692(6)	15.1541(3)
α/deg	90.00	60.518(3)	107.746(2)	93.212(11)	75.727(2)	68.139(1)
β/deg	90.00	85.434(3)	90.931(2)	97.418(11)	80.1670(10)	84.705(1)
γ/deg	90.00	63.506(3)	93.475(3)	90.266(13)	70.8860(10)	80.340(1)
V/Å^3	6911.2(3)	1916.5(2)	1096.84(7)	2046.8(7)	8898.4(4)	2761.9(1)
Z	16	1	2	2	6	2
ρ/g·cm^{-3}	1.194	1.215	1.362	1.242	1.148	1.284
μ/cm^{-1}	1.92	2.62	26.13	2.98	3.16	3.46
measd data	38 258	13 025	7553	11 127	64 550	20 447
data with $I > 2\sigma(I)$	5582	4484	3861	3938	22005	9195
unique data/R_{int}	7878/0.0642	8653/0.0596	4989/0.0330	7074/0.0758	36 483/0.1168	12 572/0.0283
wR2 (all data, on F^2)^a	0.1157	0.1743	0.0968	0.2599	0.3235	0.1504
R1 ($I > 2\sigma(I)$)^a	0.0454	0.0673	0.0408	0.1054	0.1083	0.0506
s^b	1.009	0.998	1.012	1.116	1.031	0.961
residual density/e·Å^{-3}	0.322/-0.337	0.401/-0.407	0.619/-0.770	0.688/-0.475	1.512/-0.582	0.642/-0.726
CCDC no.	664834	664835	664836	664837	664838	664839

^{a} Definition of the R indices: R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. ^{b} $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Synthesis of (THF)K₂[Mg(PPh₂)₄]·Diethyl Ether·¹/₃THF (8). To a solution of (THF)$_4$MgBr$_2$ (2.16 g, 4.57 mmol) in THF (20 mL) was added a solution of potassium diphenylphosphanide (36.57 mL, 0.5 M, 18.28 mmol). The obtained red suspension was stirred at room temperature for 2 h, and precipitated potassium bromide was removed by filtration. The clear solution was concentrated to a volume of 15 mL, and 30 mL of diethyl ether was allowed to diffuse into this solution within 1 day. Pale-yellow crystals of **8** were obtained, collected on a frit, and dried shortly in vacuo. The yield was 2.37 g (2.52 mmol, 55%).

Synthesis of (diox)K₂[Mg(PPh₂)₄]·1.5(1,4-Dioxane) (9). Compound **8** was dissolved in hot 1,4-dioxane, and the obtained solution was allowed to cool to room temperature overnight. The formation of a pale-yellow precipitate was observed within 2 weeks. Decomposition was above 110 °C. ^{1}H NMR: δ 3.56 (dx), 6.65 (8H, t, $^3J_{H,H}$ = 7.0 Hz, p-CH), 6.74 (16H, t, $^3J_{H,H}$ = 7.4 Hz, m-CH), 7.38 (16H, dt, $^4J_{H,H}$ = 1.2 Hz, $^3J_{H,H}$ = 6.6 Hz, o-CH). ^{13}C{^{1}H} NMR: δ 65.0 (dx), 121.6 (p-C), 127.7 (m-C, $^3J_{C,P}$ = 5.3 Hz), 132.4 (o-C, $^2J_{C,P}$ = 16.5 Hz), 151.3 (ipso-C, br). ^{31}P{^{1}H} NMR: δ -30.9 (s, br). MS (DEI, m/z): 39 (35%), 50 (44%), 52 (49%), 78 ([C$_6$H$_6$]$^+$, 50%), 106 ([PhP $-$ 2H]$^+$, 100%), 154 ([Ph$-$Ph]$^+$, 88%), 187 ([Ph$_2$PH + 2H]$^+$, 50%), 203 ([Ph$_2$PO + 2H]$^+$, 23%), 262 ([Ph$_3$P]$^+$, 22%), 294 ([Ph$_2$P$-$P(H)Ph]$^+$, 50%), 296 ([Ph$_2$P$-$P(H)$_2$Ph + H]$^+$, 70%), 371 ([Ph$_2$P$-$PPh$_2$ + H]$^+$, 55%). IR (Nujol, KBr, cm^{-1}): 3055 w, 1573 vs, 1434 s, 1254 w, 1120 m, 1078 w, 1023 w, 887 w, 874 m, 735 vs, 697 vs, 503 vw, 470 w.

Structure Determinations. The intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were corrected for Lorentz polarization and not for absorption effects.[52,53] The crystal data and refinement details are summarized in Table 2. The structures were solved by direct methods (*SHELXS*[54]) and refined by full-matrix least-squares techniques against F_o^2 (*SHELXL-97*[55]).

For the phenylphosphane groups of **3** and **5**, the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nondisordered non-hydrogen atoms were refined anisotropically.[55] XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

Supporting Information Available: A listing of data collection and refinement procedures as well as positional coordinates of all atoms (CIF file). This material is available free of charge via the Internet at http:/pubs.acs.org. In addition, the data deposited at the Cambridge Crystallographic Data Centre under CCDC-664834 for **1**, -664835 for **3**, -664836 for **5**, -664837 for **7**, -664838 for **8**, and -664838 and -664839 for **9** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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