This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Reactivity of Bis(organoamino)phosphanes with Magnesium(II) Compounds.

Jan Vrána, Roman Jambor, Aleš Růžička, Mercedes Alonso, Frank De Proft, Antonín Lyčka and Libor Dostál

Reactivity of three phosphanes \( \text{PhP(NHR)} \), \( \text{PhP(NEt)} \) and \( \text{PhP(NH)} \) (where Dip = 2,6-\( \text{i-Pr}_2\)C\( \text{H}_3 \)) with \( \text{n-Bu}_2\text{Mg} \) and MeMgBr is presented. In the case of \( \text{a} \), the reaction with \( \text{n-Bu}_2\text{Mg} \) gave \( \text{[PhP(NHt-Bu)(Nt-Bu)]Mg(n-Bu)} \) (4) and \( \text{[PhP(NHt-Bu)(Nt-Bu)]Mg} \) (5) depending on the stoichiometry. The treatment of \( \text{a} \) with MeMgBr led to the phosphinate \( \text{[Ph(H)P(Nt-Bu)_2]Mg} \) (7) as a result of both the NH→PH tautomeric transformation and elimination of MgBr, from non-isolable intermediate \( \text{[PhP(NHt-Bu)(Nt-Bu)]MgBr(THF)} \) (6). Phosphane \( \text{b} \) reacted with \( \text{n-Bu}_2\text{Mg} \) in 1:1 molar ratio under formation of \( \text{[PhP(NPh),_2]Mg(THF)} \), (8), but analogous reaction in 2:1 molar ratio yielded phosphinate \( \text{[Ph(H)P(NPh)_2]Mg(THF)} \) (9). Heteroleptic compound \( \text{[Ph(H)P(NPh)_2]MgBr(THF)} \) (10) was obtained by the reaction of \( \text{c} \) with MeMgBr. Finally, reaction of \( \text{d} \) with \( \text{n-Bu}_2\text{Mg} \) and MeMgBr produced compounds \( \text{[PhP(NEt)_2]Mg(THF)} \), (11) and \( \text{[PhP(NEt)_2]Mg(µ-Br)(THF)} \), (12), respectively. All products were characterized by the help of \( ^1\text{H} \), \( ^{13}\text{C}[\text{H}] \) and \( ^{31}\text{P} \) NMR spectroscopy and except for 4 and 6 molecular structures were determined using single-crystal X-ray diffraction analysis. In addition, a theoretical study on plausible isomers of 10 was performed to provide additional evidence for the presence of a syn- and anti- isomer in dynamic equilibrium in solution of 10.

Introduction

The chemistry of electron rich anionic amido- ligands, which are able to close strained four-membered chelating ring with a central atom, is very rich and miscellaneous (Figure 1). Their ligand backbones may be easily tuned from both sterically and electronic point of view by a simple selection of appropriate R and R’ groups (Figure 1). Prominent examples include amidinates (A), guanidinates (B) and boramidinates (C). Some attention has also been devoted to bulky sila-substituted amides (D). These ligands found widespread applications in coordination chemistry of both transition metals and main group elements. In contrast, the chemistry of phosphorus analogues i.e. amido(amino)phosphanes (E), bis(amido)phosphanes (F) or bis(imino)phosphinates (G) seems to be significantly less developed in spite of the fact that their backbones contain \(^{31}\text{P} \) NMR active nuclei perfectly suited for the monitoring of studied reactions. Furthermore, the presence of the phosphorus atom allows to switch between +II and +V oxidation state. In this regard, it has been demonstrated that bis(amino)phosphanes (and related deprotonated species) are under certain circumstances liable to NH→PH tautomeric transformation (Scheme 1) leading to amino(imino)phosphoranes (or bis(imino)phosphinates), thereby proving a high synthetic potential of such ligand-precurors.

![Figure 1 Structures of discussed ligands and a magnesium(ii) dimer](image_url)

Recently, we have successfully applied this synthetic strategy in the case of aluminum(III) complexes. We report herein on the reactivity of analogous phosphanes 1-3 (Figure 2) with magnesium(II) compounds. There exists a number of magnesium(II) amides containing a P-N linkage in the ligand backbone, but there is only a few structurally authenticated magnesium bis(imino)phosphinates.
As an important contribution, Stasch has very recently succeeded in preparation of a dimeric magnesium(I) compound \( \text{[Ph}_2\text{P(NDip)}_2\text{Mg]}\) stabilized the bis(imino)phosphinate \( \text{(H)} \).\(^{10}\)

The main aim of this work is to further develop the field of main group element complexes stabilized by ligands of the type E, F, G and to study a possible utilization NH→PH tautomerism (Scheme 1) for synthetic purposes.

### Results and Discussion

#### Syntheses and NMR studies

Starting phosphanes \( \text{PhP(NHR)}_2 [\text{R} = \text{t-Bu (1), Ph (2)}] \) were synthesized according to the literature procedures, while \( \text{PhP(NEt}_3\text{)(NHDip)} (3) \) was prepared by the reaction of \( \text{PhP(NHDip)(Cl)} \) with two molar equivalents of \( \text{Et}_2\text{NH} \). 3 was isolated as a white solid in good yield of 91% and characterized by the help of \( ^1\text{H}, ^{31}\text{P} \) NMR spectroscopy (see the Experimental section). The \( ^{31}\text{P} \) NMR spectrum of 3 revealed a singlet at 82.5 ppm. The reactivity of titled phosphanes 1-3 with \( \text{n-Bu}_2\text{Mg} \) and MeMgBr differs and thus is discussed separately for each phosphane.

The reaction of 1 with \( \text{n-Bu}_2\text{Mg} \) gave, depending on the stoichiometry (Scheme 2), compounds \( \text{[PhP(NH-t-Bu)(N-t-Bu)]Mg(n-Bu)} (4) \) and \( \text{[PhP(NH-t-Bu)(N-t-Bu)]}_2\text{Mg} (5) \) as the result of evolution of one or two equivalents of \( \text{n-Bu} \). Both compounds were isolated as colourless crystals in 35% and 52% yield, respectively, which are well soluble both in aliphatic and aromatic solvents. The \( ^1\text{H} \) spectra showed two signals for magnetically non-equivalent \( \text{t-Bu} \) groups at 0.88 and 1.71 ppm for 4 and 1.05 and 1.57 ppm for 5 and one signal for the NH moiety at 1.86 ppm (5) (in the case of 4 this resonance is overlapped by the signals of \( \text{n-Bu} \) fragment). Similarly, two sets of signals for \( \text{t-Bu} \) groups were observed in the corresponding \( ^{13}\text{C} \{^1\text{H} \} \) NMR spectra, thereby proving the structure of 4 and 5. The \( ^{31}\text{P} \) NMR spectra of 4 and 5 revealed signals at 88.3 and 92.5 ppm, respectively, both significantly shifted in comparison with the starting phosphane 1 \( \delta(^{31}\text{P}) = 41.6 \text{ ppm} \). Recently, we have demonstrated that related aluminum amide \( \text{[PhP(NH-t-Bu)(N-t-Bu)]AlMe}_2 \) smoothly underwent a tautomeric hydrogen shift upon heating with quantitative formation of the phosphinate \( \text{[Ph(H)P(N-t-Bu)]}_2\text{AlMe}_2} \).\(^7\)

Analogously, heating of a THF solution of 5 \((70^\circ\text{C}) \) led to magnesium phosphate \( \text{[Ph(H)P(N-t-Bu)]}_2\text{Mg} (7) \) (Scheme 1) as monitored and judged by the \( ^1\text{H} \) and \( ^{31}\text{P} \) NMR spectroscopy. However, this tautomeric shift is significantly slower than in the case of the aluminum derivative (less than 10% conversion after 5 days) and more importantly prolonged heating of 5 resulted in the formation of numerous side-products. Nevertheless, the phosphinate 7 is easily accessible by the treatment of 1 with MeMgBr (Scheme 2). In the first step of this reaction, compound \( \text{[PhP(NH-t-Bu)(N-t-Bu)]MgBr(THF)} (6) \) is formed as shown by the analysis of the evaporated reaction mixture by \( ^1\text{H}, ^{13}\text{C} \{^1\text{H} \} \) and \( ^{31}\text{P} \) NMR spectroscopy. Thus, \( ^1\text{H} \) and \( ^{13}\text{C} \{^1\text{H} \} \) NMR spectra proved the presence of two magnetically non-equivalent \( \text{t-Bu} \) groups \( \delta(^1\text{H}) = 1.34 \text{ and } 1.57 \text{ ppm} ; \delta(^{13}\text{C} , \text{C(CH}_3)) = 31.2 \text{ and } 35.9 \text{ ppm} \) and the \( \text{NH} \) group \( \delta(^1\text{H}) = 1.80 \text{ ppm} \). Furthermore, the signals due to the coordinated THF were detected as well \( \delta(^1\text{H}) = 1.14 \text{ and } 3.55 \text{ ppm} ; \delta(^{13}\text{C}) = 25.3 \text{ and } 69.7 \text{ ppm} \). The \( ^{31}\text{P} \) NMR spectrum of 6 revealed one singlet at 89.1 ppm close to the values observed for related 4 and 5. Interestingly, all attempts for recrystallization of 6 to obtain an analytically pure sample resulted in both elimination of magnesium bromide and tautomeric hydrogen shift giving phosphinate 7 (Scheme 2). This procedure is also applicable on a preparative-scale (yield of 7 after recrystallization is 64%). Compound 7 was isolated as colourless crystals well soluble in aromatic solvents. The \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra revealed expected set of signals. The
observation of doublets at 7.76 ppm in the $^1$H NMR spectrum and at 8.9 ppm ($J_{P,H} = 432$ Hz) in the $^{31}$P NMR spectrum proved formation of the PH functionality and thereby the tautomeric shift. These values are also well comparable to related aluminum phosphinates reported by us earlier.\textsuperscript{7}

The reaction of 2 with 1 molar equivalent of $n$-Bu$_2$Mg in THF gave compound ($[\text{PhH}(\text{NPh})_2]$Mg(THF)$_2$)$_2$ (8) as the result of deprotonation of both NH functionalities (Scheme 3). This finding is in contrast to the phosphane deprotonation of both NH functionalities (Scheme 3). This finding is in contrast to the phosphane, where the deprotonation of the second NH group was not possible (Scheme 2). Importantly, all attempts to obtain a heteroleptic compound (similar to 4) remained unsuccessful probably reflecting higher acidity of the NH group of 2 in comparison with 1. Compound 8 crystallized in the form of colourless single-crystals from benzene and is nearly insoluble in THF and aliphatic solvents. The $^1$H and $^{13}$C($^1$H) NMR spectra revealed one set of expected signals for the phenyl substituents and coordinated THF molecules [$\delta(^1$H) = 1.10 and 3.31 ppm; $\delta(^{13}$C) = 25.5 and 69.8 ppm]. The $^{31}$P NMR spectrum contained one singlet at 93.3 ppm [$\delta(^{31}$P) = 46.8 ppm for the parent phosphane 2]. Importantly, there was no evidence for the presence of the NH group thereby proving full deprotonation of the bis(amine)phosphane 2.

Scheme 3 Reactivity of 2 with $n$-Bu$_2$Mg and MeMgBr.

Importantly, crude reaction mixtures during preparation of 8 were always contaminated by a remarkable (10-15%) amount of a by-product, which was shown to be the phosphinate [Ph(H)(NPh)$_2$]Mg(THF) (9). This compound may be isolated from this mixture, but it is better prepared (in yield of 42%) by the reaction of 2 with 0.5 molar equivalent of $n$-Bu$_2$Mg (Scheme 3). Compound 9 was isolated as colourless crystals soluble in aromatic solvents and moderately in THF. The $^1$H and $^{31}$P NMR spectra revealed doublets [at $\delta(^1$H) = 8.31 ppm; $\delta(^{31}$P) = 11.6 ppm; $J_{P,H} = 442$ Hz] confirming the presence of the PH group and the tautomerization leading to the phosphinate backbone. The $^1$H and $^{13}$C($^1$H) NMR spectra contained one set of expected signals for the phenyl substituents and coordinated THF molecule [$\delta(^1$H) = 1.27 and 3.63 ppm; $\delta(^{13}$C) = 25.8 and 68.9 ppm]. The treatment of 2 with MeMgBr (Scheme 2) resulted in the formation of the phosphinate [Ph(H)(NPh)$_2$]MgBr(THF)$_2$ (10) and methane elimination. Compound 10 was obtained as colourless crystals well soluble in THF and aromatic solvents. It is also noteworthy that compound 10 is the PH tautomeric form. Similar reaction of the phosphane 1 with MeMgBr, gave compound 6, which represents the NH tautomer. This fact is reflected in different behaviour of both compounds. While compound 6 was seen only as an intermediate in the formation of the final product 7, the phosphinate 10 is fairly stable and showed no tendency for any elimination of magnesium bromide. This finding well coincides with our recent findings (including a theoretical approach), which showed that derivatives of the phosphane 2 are more liable to the NH$\rightarrow$PH tautomeric transformation in comparison with 1. This tautomerization and formation of the phosphinate backbone is also most probably responsible for higher stability of 10 compared to 6. The $^{31}$P NMR spectra of 10 (both of isolated single-crystals and bulk sample, in THF-d$_8$) surprisingly revealed two doublets [$\delta(^{31}$P) = 8.9 ppm; $J_{P,H} = 439.9$ Hz and $\delta(^{31}$P) = 9.3 ppm; $J_{P,H} = 444.3$ Hz] similarly two doublets were detected in corresponding $^1$H NMR spectrum indicating the presence of two species containing PH functionality [$\delta(^1$H) = 8.16 ppm; $J_{P,H} = 439.9$ Hz and $\delta(^1$P) = 8.27 ppm; $J_{P,H} = 444.3$ Hz]. The integral ratio between both species is 1:0.85.

Analogously, two sets of signals were observed for remaining atoms in $^1$H and $^{13}$C($^1$H) NMR spectra. The observation of these two species is most probably caused by the presence of different isomers of 10 in solution. To approve this hypothesis, the $^{31}$P,$^{31}$P EXSY NMR spectrum of 10 in THF-d$_8$ was acquired. Appropriate cross-peaks were observed for two isomers of compound 10 (mixing time being from 0.1 to 1.5 s, Figure 3) indicating that isomers are in a slow chemical exchange on the NMR time scale.
We added some an amount of the parent phosphane 2 to the solution of compound 10 and repeated $^{31}$P-$^{31}$P EXSY measurement (mixing time being again from 0.1 to 1.5 s, Figure 3). No additional cross-peaks were observed and, thus, no exchange exists for the free phosphane and any isomer of compound 10 under above mentioned experimental conditions. Isomers of 10 are probably formed by different orientations of the phosphorus bonded phenyl ring and the bromine atom attached to the central planar MgPN$_2$ core (Figure 4). Thus, two possible isomers came into mind. It is the syn-10 (also observed in the solid state vide infra) and anti-10. A third isomer with the bromine atom in the same plane as the MgN$_2$P core (isomer plane-10) is also considered (Figure 4). To shed more light to this phenomenon, a theoretical survey dealing with suggested isomers of 10 was performed.

**Figure 4** Schematic drawing of anticipated isomers of 10.

First, the performance of different DFT methods (BP86-D, M06 and B3LYP-D) in reproducing the molecular structure of the syn-10 isomer was assessed by the comparison with the X-ray diffraction data. Several statistical criteria were considered in our benchmark study: the root-mean-square deviation (RMSD) between the DFT/cc-pVDZ-optimized and X-ray set of Cartesian coordinates and the mean absolute error (MAE) from comparison of selected interatomic distances and dihedral angles. Table 1 contains the RMSD for the superimposed structures (Figure 5) considering the geometry of the MgPN$_2$ core alone (RMSD$_{a}$) and all atoms (RMSD$_{d}$) together with the MAE for the bond lengths and dihedral angles. The M06-optimized geometry is in better agreement with the X-ray structure when considering the overall structure. However, The lowest RMSD$_{a}$ and MAE$_{torsions}$ correspond to the B3LYP-D geometries. In any case, the optimized geometries obtained with B3LYP-D and M06 are very similar according to the RMSD and MAE values. On the other hand, BP86 gives the largest statistical errors. Moreover, extending the basis set to the aug-cc-pVDZ is seen to improve the optimized structures (Figure 5), as the RMSD and MAE values are significantly reduced. Therefore, the B3LYP-D/aug-cc-pVTZ level of theory was chosen to perform the optimization and frequency calculations of the syn- and anti- isomers of 10.

**Table 1.** Root mean square deviations (RMSD in Å) and mean absolute errors (MAE) of the DFT optimized geometries relative to the X-ray structures of the syn-10 isomer together with the relative energies of different isomers ($E$ in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>Method</th>
<th>RMSD$_d$</th>
<th>MAE$_{bonds}$</th>
<th>MAE$_{torsions}$</th>
<th>syn10</th>
<th>anti10</th>
<th>plane10</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP86-D$^b$</td>
<td>0.038</td>
<td>0.082</td>
<td>4.64</td>
<td>0.00</td>
<td>2.47</td>
<td>2.11</td>
</tr>
<tr>
<td>M06$^b$</td>
<td>0.034</td>
<td>0.073</td>
<td>4.21</td>
<td>0.00</td>
<td>2.04</td>
<td>3.89</td>
</tr>
<tr>
<td>B3LYP-D$^c$</td>
<td>0.029</td>
<td>0.074</td>
<td>4.01</td>
<td>0.00</td>
<td>1.27</td>
<td>3.24</td>
</tr>
<tr>
<td>B3LYP-D$^d$</td>
<td>0.029</td>
<td>0.073</td>
<td>3.45</td>
<td>0.00</td>
<td>1.70</td>
<td>3.34</td>
</tr>
</tbody>
</table>

$^a$ Zero-point corrected relative energies. $^b$ The cc-pVDZ basis set was used for the optimization and frequency calculations. $^c$ The aug-cc-pVDZ basis set was used.

The zero-point corrected relative energies of the syn-, anti- and plane- isomers of 10 computed with the different functionals are collected in Table 1. Importantly, all the methods predict that the syn- isomer is the most stable, followed by the anti-isomer. The small energy difference between the syn- and anti-isomers computed with all the methods suggests that both isomers coexist in a dynamic equilibrium in solution of 10. The plane- isomer is less stable, being more than 3 kcal mol$^{-1}$ higher in energy than the syn- conformer according to B3LYP-D and M06 energies. Moreover, the use of diffuse basis functions does not change significantly the relative energies of the different isomers of 10.

**Figure 5.** Comparison of BP86-D, B3LYP-D and M06-optimized geometries of syn-10 isomer, overlaid with the X-ray structure. The all-atom RMSDs (in Å) are also displayed.
Nevertheless, the energy difference between the pVDZ level of theory at 298.15 K and 1 atm.

plane-free energy of 3.13 kcal mol

Table 2. Relative energies (ΔE), enthalpies (ΔH) and Gibbs free energies (ΔG) for the different isomers of 10 (in kcal mol⁻¹) in gas phase and different solvents computed at the B3LYP-D/aug-cc-pVTZ level of theory.a

<table>
<thead>
<tr>
<th>Method</th>
<th>syn-10</th>
<th>anti-10</th>
<th>Plane-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Egas</td>
<td>0.00</td>
<td>1.21</td>
<td>3.49</td>
</tr>
<tr>
<td>ΔHgas</td>
<td>0.00</td>
<td>1.34</td>
<td>3.30</td>
</tr>
<tr>
<td>ΔGgas</td>
<td>0.00</td>
<td>1.72</td>
<td>2.70</td>
</tr>
<tr>
<td>Ecorr</td>
<td>0.00</td>
<td>2.06</td>
<td>2.38</td>
</tr>
<tr>
<td>ΔHcorr</td>
<td>0.00</td>
<td>2.04</td>
<td>2.52</td>
</tr>
<tr>
<td>ΔGcorr</td>
<td>0.00</td>
<td>2.20</td>
<td>2.56</td>
</tr>
</tbody>
</table>

a Thermochromial corrections computed at the B3LYP/aug-cc-pVDZ level of theory at 298.15 K and 1 atm.

Increasing to a triple ζ-basis set results in an electronic energy difference of 1.2 kcal mol⁻¹ between the syn- and the anti-conformations. Inclusion of the thermochromial corrections yields a relativeenthalpy of 1.35 kcal mol⁻¹ and a relative Gibbs free energy of 3.13 kcal mol⁻¹ for the syn-isomer. In addition, solvation energies in benzene and THF were calculated by using the SMD model (Table 2). In both solvents, the syn-isomer of 10 is predicted to be the most stable conformation. Nevertheless, the energy difference between the syn- and anti-isomers increases as the dielectric constant increases, whereas the plane-isomer becomes more stable. All these findings indicate that compound 10 exist in solution as a mixture of two isomers syn-10 and anti-10, while the presence of plane-10 seems to be less probable.

![Figure 6](image.png)

Figure 6. B3LYP-D/aug-cc-pVDZ optimized geometries of the syn-, anti- and plane-isomers of 10. The Mg-N and P-N distances (in Å), Br-Mg-P-C dihedral angle (in °) and relative enthalpies in benzene (in kcal mol⁻¹) are also displayed. The computed δ(31P) (in ppm) are shown in orange.

Finally, the 31P chemical shifts for the three isomers were computed using the GIAO/B3LYP/cc-pVTZ method. Interestingly, the computed δ(31P) of the syn- and anti-isomers are in excellent agreement with the experimental chemical shifts (9.3 and 8.9 ppm), providing an additional evidence for the presence of both isomers in solution of 10. On the other hand, the computed δ(31P) of the plane isomer is deshielded by 1.6 ppm compared to the experimental values found for both isomers.

![Scheme 4](image.png)

Scheme 4 Reactivity of 3 with n-Bu₂Mg and MeMgBr.

Finally, the reactivity of potentially monoanionic phosphane 3 was studied for comparison as in this case no tautomerization is possible. Thus, the reaction between 3 and n-Bu₂Mg in 1:0.5 molar ratio in hexane smoothly gave [PhP(NEt₂)₂Mg (11) (in yield of 49 %) as colourless crystals soluble in aromatic and moderately in aliphatic solvents. The 31P NMR spectrum of 11 revealed one signal at 122.1 ppm significantly shifted in comparison with the value found for the starting phosphane 3 [δ(31P) = 82.5 ppm]. The 1H and 13C(1H) NMR spectra of 3 revealed one set of relatively broad signals for both DipN and NEt₂ groups. The treatment of 3 with one molar equivalent of MeMgBr (Scheme 3) in THF produced compound [{PhP(NEt₂)₂Mg(µ-Br)(THF)}₂ (12) in 69% yield as a colourless solid soluble in aromatic solvents and THF. The 31P NMR spectrum of 12 revealed one signal at 127.6 ppm close to the value found for 11. The 1H and 13C(1H) NMR spectra of 12 revealed signals of coordinated THF [δ(1H) = 1.07 and 3.57 ppm; δ(13C) = 25.2 and 70.5 ppm] and one set of relatively broad signals for both DipN and NEt₂ groups.

Solid state structures

The molecular structures of 5, 7-12 were determined using single-crystal X-ray diffraction analysis (Figures 7-14) and the crystallographic data are summarized in the Experimental section.
The Mg(1) atom in 5 is four-coordinated and adopts a distorted tetrahedral coordination environment (Figure 7). The Mg(1)-N(2) and Mg(1)-N(22) bond lengths of 1.9864(18) and 1.9879(15) Å, respectively, are slightly shorter than the Σ_{cov}(N, Mg) = 2.10 Å.13 In contrast, the Mg(1)-N(1) and Mg(1)-N(11) bond lengths [2.2079(15) and 2.1835(15) Å] are longer and indicate the presence of strong N→Mg intramolecular interaction rather than a covalent bond. This fact is further reflected by the geometry around respective nitrogen atoms, which is essentially trigonal planar for N(2) and N(22), while it is tetrahedral in the case of NH groups [N(1) and N(11) atoms].

Similar difference is also observed for P-N bonds, because P(1)-N(2) and P(2)-N(22) bond lengths [1.6590(15) and 1.6722(14) Å] are significantly shorter than P(1)MN(1) and P(1)MN(2) bond lengths [1.7241(14) and 1.6985(15) Å], which is essentially trigonal planar for N(2) and N(22), while it is tetrahedral in the case of NH groups [N(1) and N(11) atoms].

Compound 7 crystallized in the centrosymmetric C2/c space group and its molecular structure proved the presence of PH group and the formation of a phosphinate backbone (Figure 8). The central Mg(1) atom is tetrahedrally coordinated. In contrast to 5, the Mg(1)-N(1) and Mg(1)-N(2) bond lengths of 2.0546(13) and 2.0453(18) Å, respectively, are nearly identical and correspond to the Σ_{cov}(N, Mg) = 2.10 Å.13 Analogously, the P(1)-N(1) and P(1)-N(2) distances [1.597(2) and 1.5989(15) Å] are very similar suggesting effective delocalization of the negative charge across the NPN phosphinate backbone and its symmetrical bonding to the central Mg(1) atom. The Σ_{cov}(N, P) = 1.82 Å is also reflected by the geometry around respective nitrogen atoms, which is essentially trigonal planar for N(2) and N(22), while it is tetrahedral in the case of NH groups [N(1) and N(11) atoms].

Compound 8 forms a centrosymmetric dimer in the solid state (Figure 9) via two strong intermolecular contacts with the distances Mg(1)-N(1a) and Mg(1)-N(1) of 2.1409(14) Å approaching Σ_{cov}(N, Mg) = 2.10 Å.13 The central Mg(1) atom is coordinated by the ligand in a non-symmetric fashion as demonstrated by fairly different distances Mg(1)-N(1) 2.2978(16) Å vs. Mg(1)-N(2) 2.0680(15) Å. This fact is also reflected in slightly different P(1)-N(1) and P(1)-N(2) bond lengths of 1.7241(14) and 1.6985(15) Å, respectively. The coordination sphere of the Mg(1) atom is further saturated by two THF molecules [Mg(1)-O(1) 2.0852(12) and Mg(1)-O(2) 2.1346(14) Å; Σ_{cov}(O, Mg) = 1.99 Å].13 The Mg(1) atom is, thus, five-coordinated and resulting polyhedron may be described as an intermediate between the square pyramid and the trigonal bipyramid with the τ value of 0.65.14 All three four-membered Mg₂N₂ and Mg₂nP rings are essentially planar and share their edges with formation of a ladder-like structure. Similar structural motif with three mutually connected four-membered rings was determined for the magnesium amidinate [{[MeC(NEt)(N₂)]₂Mg}₂ by Winter et al.15

![Figure 8](image)

Figure 8 Molecular structure of 7 (40% probability displacement ellipsoids). Hydrogen atoms except of PH groups are omitted for clarity. The symmetry operator a = -x, y, ½-z. Selected bond lengths [Å] and bonding angles [deg]: Mg(1)-N(1) 2.0546(13), Mg(1)-N(2) 2.0453(18), P(1)-N(1) 1.597(2), P(1)-N(2) 1.5989(15), N(3)-Mg(1)-N(2) 73.55(7), N(1)-Mg(1)-N(1a) 129.53(7), N(3)-Mg(1)-N(1a) 127.65(8), N(2)-Mg(1)-N(1a) 134.79(7), N(2)-Mg(1)-N(1a) 127.65(8), N(1)-P(1)-N(2) 100.37(8).
Although compound 8 crystallizes as a dimer from benzene (vide supra), occasionally single-crystals were also obtained from a saturated THF solution and showed a monoclinic structure (8a, Figure 10). The unit cell of 8a contains two independent molecules, but they are closely structurally related and only one of them is discussed here in detail. The central Mg(1) atom is five-coordinated in 8a by the ligand and three oxygen atoms coming from coordinated THF molecules [Mg(1)-O(1) 2.035(4), Mg(1)-O(2) 2.053(3) and Mg(1)-O(3) 2.104(4) Å; Σ_{cov}(O, Mg) = 1.99 Å]. The Mg(1)-N(1) and Mg(1)-N(2) [2.048(4) and 2.058(4) Å] as well as P(1)-N(1) and P(1)-N(2) [1.699(4) and 1.703(5) Å] bond lengths are nearly identical and slightly shorter than values expected for single bonds [Σ_{cov}(N, P) = 1.82 Å and Σ_{cov}(N, Mg) = 2.10 Å]. The central MgN_{2}P is again essentially planar. The coordination polyhedron of the central atom is again strongly distorted, but closer to the square pyramid than to the trigonal bipyramid as indicated by the value τ = 0.30. Chivers et al. reported on an analogous monomeric four-membered ring compound stabilized by a boramidinate ligand PhB(NDip)_{2}Mg(THF)_{2}, but in this case the central atom is only four-coordinated and adopts a tetrahedral shape. Similarly, compound Ph_{2}Si(NDip)_{2}Mg(THF)_{2} contains a four-membered ring system. The presence of bulky Dip groups in the later compounds is most probably responsible for the coordination of only two THF molecules in contrast to 8a, where three THF donors are present.

Compound 10 exists in solution as two isomers that are in a dynamic equilibrium (anti-10 and syn-10, vide supra) and from this solution single-crystals of syn-10 were obtained preferably in all cases and its structure is shown in Figure 12. The central MgN_{2}P core remains essentially planar and the phenyl group and the bromine atom are located in syn fashion. The Mg(1)-N(1) and Mg(1)-N(2) bond lengths [2.150(2) and 2.087(3) Å] are mutually a bit more different in comparison with phosphinates 7 and 9. Nevertheless, the P(1)-N(1) and P(1)-N(2) distances [1.606(2) and 1.602(2) Å] within the phosphinate backbone are essentially identical and also the N(1)-P(1)-N(2) bonding angle [98.86(12)°] resembles those established for 7 and 9. The Mg(1)-Br(1) bond length of 2.491(7) Å corresponds to the Σ_{cov} (Br, Mg) = 2.53 Å. The central Mg(1) atom is further coordinated by two THF molecules [Mg(1)-O(1) 2.061(2) and Mg(1)-O(2) 2.115(2) Å; Σ_{cov}(O, Mg) = 1.99 Å]. The value τ of 0.48° for syn-10...
indicates an intermediate coordination geometry around Mg(1) atom between the square pyramid and the trigonal bipyramid. syn-10 is rare example of a heteroleptic magnesium(II) phosphinate. To the best of our knowledge, the only analogues Ph3P(NDip)2MgX(Et2O) (where X = Br or I) have recently been synthesized by Stasch.10 Nevertheless, there is a number of related magnesium ammimates: for example R(C(NR’))2MgX(L) (R = CCPh, PPh2, PCy2; R’ = i-Pr, Cy; X = Cl, Br; L = THF, Et2O) have recently been characterized.18

![Figure 12](image_url)

**Figure 12** Molecular structure of syn-10 (40% probability displacement ellipsoids). Hydrogen atoms except of Ph groups are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: Mg(1)-N(1) 2.150(2), Mg(1)-N(2) 2.087(3), Mg(1)-Br(1) 2.4917(12), Mg(1)-O(1) 2.061(2), Mg(1)-O(2) 2.115(2), P(1)-N(1) 1.606(2), P(1)-N(2) 1.602(2), N(1)-Mg(1)-N(2) 70.21(9), N(1)-Mg(1)-Br(1) 105.83(8), N(1)-Mg(1)-O(1) 96.14(8), N(1)-Mg(1)-O(2) 156.63(11), N(2)-Mg(1)-Br(1) 126.06(7), N(2)-Mg(1)-O(1) 128.08(10), N(2)-Mg(1)-O(2) 90.07(10), Br(1)-Mg(1)-O(1) 105.84(8), Br(1)-Mg(1)-O(2) 95.81(7), O(1)-Mg(1)-O(2) 86.11(8), N(1)-P(1)-N(2) 98.86(12).

Molecular structure of 11 is shown in Figure 13 and is structurally related to 5. The central Mg(1) atom is tetrahedrally coordinated by two chelating phosphanes. The Mg(1)-N(1) and Mg(1)-N(3) bond lengths [2.0202(13) and 2.0220(14) Å] are shorter in comparison with Mg(1)-N(2) and Mg(1)-N(4) distances [2.2262(14) and 2.1796(14) Å] indicating the presence of a strongEt3N→Mg intramolecular interaction rather than a covalent bond in the latter case (compare with the Σsyn(N, Mg) = 2.10 Å13). Analogously, the P(1)-N(2) and P(2)-N(4) distances [1.8443(13) and 1.8399(14) Å] are significantly elongated in comparison with the P(1)-N(1) and P(2)-N(3) bonds [1.6648(13) and 1.6756(13) Å]. The latter values coincide with the double bond Σsyn(N, P) = 1.62 Å13, while the former correspond better to the single bond Σsyn(N, P) = 1.82 Å.13 The N(1)-P(1)-N(2) and N(3)-P(1)-N(4) bonding angles of 93.45(6) and 93.77(6)°, respectively, well correspond to the values found in 5.

![Figure 13](image_url)

**Figure 13** Molecular structure of 11 (40% probability displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bonding angles [deg]: Mg(1)-N(1) 2.0026(13), Mg(1)-N(2) 2.2262(14), Mg(1)-N(3) 2.0220(14), Mg(1)-N(4) 2.1796(14), P(1)-N(1) 1.6648(13), P(1)-N(2) 1.6756(13), P(2)-N(4) 1.8399(14), N(1)-Mg(1)-N(2) 74.23(5), N(1)-Mg(1)-N(3) 128.84(5), N(1)-Mg(1)-N(4) 133.88(5), N(2)-Mg(1)-N(3) 136.25(5), N(2)-Mg(1)-N(4) 117.95(5), N(3)-Mg(1)-N(4) 75.27(5), N(1)-P(1)-N(2) 93.45(6), N(3)-P(1)-N(4) 93.77(6).

To summarize, it is evident from the determined molecular structures of 5, 7-12 that the tautomeric NH→P shift with the formation of a phosphinate backbone is reflected also in the main structural features of these complexes. Thus, the coordination of the NPN backbone to the central magnesium atom in phosphinates 7, 9 and syn-10 is essentially symmetrical regarding both Mg-N and P-N bonds pointing to a delocalization of the negative charge over this system. In contrast, there is a significant difference between respective Mg-N and P-N bonds found in amino-amidophosphanes 5, 11 and 12. Bis(amide)phophanes 8 and 8a represent special cases, in the first one the NPN core is strongly distorted by the formation of an intermolecular contact. The ligand in 8a exhibits symmetrical coordination similarly to phosphinates 7, 9 and syn-10, but P-N bond distances in 8a are elongated about 0.1 Å in comparison with 7, 9 and syn-10. There is also significant difference in the value of N-P-N bonding angles. This value falls into the interval 91.90(17)-94.98(10)° in 5, 8a, 11 and 12, while wider angles were observed in phosphinates 7, 9 and syn-10 [98.86(12)-100.37(8)°]. The presence of the lone pair at the phosphorus atom in 5, 8a, 11 and 12 is most probably responsible for this deviation as the phosphorus atom...
in phosphinates lacks it. In contrast, the N-Mg-N bonding angles lie in a narrow interval 70.21(9) (syn-10)-75.27(5)° (11) with no obvious trend among studied complexes.

**Conclusions**

We have demonstrated high potential of phosphines 1-3 as ligand-precursors for the preparation of magnesium compounds by a simple metallation using n-Bu₂Mg and MeMgBr. The structural versatility of isolated products is remarkable and importantly, an isolation of a particular structural motif may be controlled by a targeted substitution of the respective phosphine. Another approach is the utilization of the NH→PH tautomeric shift as a useful tool for the preparation of monoanionic NPN phosphinate backbone. Significant benefit of 1-3 and their derivatives is an easy and straightforward monitoring of experimental procedures by 31P NMR spectroscopy. The extension of utilization of 1-3 and related systems in the main group chemistry is a next target for us.

**Experimental**

**General procedures**

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. All solvents were dried using Pure Solv- Innovative Technology equipment. The starting compounds: n-Bu₂Mg (1 M solution in heptane) and MeMgBr (1.4 M solution in THF/toluene 3:1) were obtained from the commercial suppliers and used as delivered. The ligand-precursors 1 and 2 were prepared according to published procedures.11 1H, 13C{1H} and 31P NMR spectra were recorded on a Bruker Avance 500 or a Bruker Avance III 400 MHz spectrometers, using a 5 mm tunable broad-band probe. Appropriate chemical shifts in 1H and 13C{1H} NMR spectra were related to the residual signals of the solvent [CDCl₃]: δ(1H) = 7.16 ppm and δ(13C) = 128.39 ppm, THF-d₈: δ(1H) = 3.58 ppm and δ(13C) = 67.57 ppm. 31P NMR chemical shifts were referred to external 85% H₃PO₄.

Synthesis of PhP(NEt₃)(NHDip): (3): Et₃NH (5.88 mL, 56.1 mmol) was dissolved in diethyl ether (100 mL) and a solution of PhP(NHDip)Cl (7.9 g, 24.9 mmol) in diethyl ether (50 mL) was added at 0°C while stirring. A precipitate formed. Stirring continued overnight, the solid was removed by filtration and washed three times with 50 mL of diethyl ether. The solutions were combined and the solvent and the excess amine were removed in vacuo giving colourless crystals of 3. Yield 91%; m.p. 58-59°C. 1H NMR (400 MHz, CDCl₃, 25°C): δ = 0.81 (t, 3J_H-H = 7.2 Hz, 6H, CH₂CH₃), 1.25 (d, 3J_H-H = 6.8 Hz, 6H, CHCH₃), 1.27 (d, 3J_H-H = 6.8 Hz, 6H, CHCH₃), 2.87 (m, 4H, CH₂CH₃), 3.53 (sept, 3J_H-H = 6.8 Hz, 6H, CHCH₃), 4.28 (d, 3J_H-H = 5.6 Hz, 1H, NH), 7.16 (m, 4H, Ar-H), 7.28 (t, 2H, Ar-H), 7.84 (m, 2H, Ar-H) ppm. 13C{1H} NMR (100.61 MHz, CDCl₃, 25°C): δ = 15.6 (s, CH₂CH₃), 24.4 (s, CHCH₃), 24.8 (s, CHCH₃), 28.8 (s, CHCH₃), 43.2 (d, 3J_H-H = 16.1 Hz, CH₂CH₃), 124.3 (s, Ar-C), 124.4 (s, Ar-C), 128.8 (s, Ar-C), 129.0 (d, 3J_H-H = 3.8 Hz, Ar-C), 131.4 (d, 3J_H-H = 16.2 Hz, α-C(CH₃)), 140.3 (d, 3J_H-H = 10.8 Hz, ipso-C), 142.8 (d, 3J_H-H = 4.6 Hz, Ar-C), 143.4 ppm (Ar-C) ppm. 31P NMR (161.97 MHz, CDCl₃, 25°C): δ = 82.5 (s) ppm (Ar-C). Anal. calcd. for C₂₅H₃₅N₃P (356.50): C 74.1, H 9.3; found C 74.2, H 9.4.
(161.97MHz, C_{15}D_{15} 25°C): δ = 88.3 (s) ppm. Anal. calcd. for C_{14}H_{32}MgN_{2}P (332.76): C 65.0, H 10.0; found C 65.1, H 10.1.

**Synthesis of [PhP(NH-Bu)(Nt-Bu)]_2Mg (5):** n-BuMg (1.5 mL, 1.5 mmol, 1 mL solution in heptane) was added dropwise to a solution of I (0.762 g, 3.0 mmol) in hexane (20 mL) at -40°C while stirring. The reaction mixture was slowly warmed to room temperature and stirred for one hour. The slightly yellow solution was concentrated to approximately one third and stored at 6°C for one day, yielding colourless single-crystals of 5. Yield 414 mg, 52%; m.p. 166°C. 

\[^{1}H\] NMR (400MHz, C_{15}D_{15}, 25°C): δ = 1.05 (s broad, 18H, C(CH_{3})) ppm. Anal. calcd. for C_{31}H_{30}MgN_{2}P (494.84): C 63.7, H 9.1.

**Synthesis of [PhP(NH-Bu)(Nt-Bu)]_2MgBr (6):** MeMgBr (1.5 mL, 2.1 mmol, 1.4 M solution in THF/toluene 3:1) was added dropwise to a solution of I (0.522 g, 2.1 mmol) in THF (20 mL) at -40°C while stirring. Small bubbles of methane appeared and the solution turned yellow. The reaction mixture was slowly warmed to room temperature and stirred for one hour and the solution turned to colourless again. The solvent was removed under vacuo to yield colourless oil of 6. Yield 414 mg, 95%. 

\[^{1}H\] NMR (400MHz, C_{15}D_{15}, 25°C): δ = 1.14 ppm.

\[^{13}C\] NMR (100.61MHz, C_{15}D_{15}, 25°C): δ = 25.3 ppm. 1H NMR spectrum contained two sets of signals, major set: δ = 11.8 Hz, Ar-C), 130.1 (d, J_{F-P} = 82.4 Hz, ipso-C_{15}H_{10}) ppm. 

\[^{31}P\] NMR (161.97MHz, C_{15}D_{15}, 25°C): δ = 91.2 (s) ppm. Anal. calcd. for C_{32}H_{34}MgN_{2}O_{2}P (526.98): C 63.8, H 9.2; found C 63.9, H 9.2.

**[PhP(NPh)]_2Mg(THF)]_2 (8):** n-BuMg (1.5 mL, 1.5 mmol, 1 mL solution in heptane) was added dropwise to a solution of 2 (0.452 g, 1.5 mmol) in THF/toluene (1:1, 20 mL) at -70°C while stirring. The reaction mixture was slowly warmed to room temperature and stirred for one hour. Slightly yellow precipitate is formed during warming. The suspension was filtered and washed three times with 30 mL of THF at 50°C (to remove traces of a side product see discussion) giving slightly yellow powder of 8. Single-crystals of 8 were grown in benzene. Yield 419 mg, 59%; m.p. 175°C with decomposition.

\[^{1}H\] NMR (400MHz, C_{15}D_{15}, 25°C): δ = 1.10 (s broad, 8H, C(CH_{3})) ppm. 1H NMR spectrum contained two sets of signals, major set: δ = 11.8 Hz, Ar-C), 130.1 (d, J_{F-P} = 82.4 Hz, ipso-C_{15}H_{10}) ppm. 

\[^{13}C\] NMR (100.61MHz, C_{15}D_{15}, 25°C): δ = 25.5 (s, C_{15}H_{10}), 69.8 (s, C_{15}H_{10}), 116.6 (s, Ar-C), 121.6 (d, J_{F-P} = 19.9 Hz, Ar-C), 128.8 (s, p-C_{6}H_{5}), 131.0 (d, J_{F-P} = 20.0 Hz, &harr;C_{6}H_{5}), 131.1 (d, J_{F-P} = 17.2 Hz, m-C_{6}H_{5}), ipso-C not observed ppm. 

Synthesis of [PhP(NPh)]_2MgBr(THF) (9): n-BuMg (1.2 mL, 1.2 mmol, 1 mL solution in heptane) was added dropwise to a solution of 2 (0.694 g, 2.4 mmol) in THF (20 mL) at -10°C while stirring.

The reaction mixture was slowly warmed to room temperature and stirred for one hour. The solvent was removed under reduced pressure and the product was re-dissolved in toluene and stored at -30°C to give single crystals of 9. Yield 339 mg, 42%; m.p. 96°C. Yield 339 mg, 42%; m.p. 96°C. 

\[^{1}H\] NMR (400MHz, C_{15}D_{15}, 25°C): δ = 1.27 (s broad, 8H, C(CH_{3})) ppm. 1H NMR spectrum contained two sets of signals, major set: δ = 11.8 Hz, Ar-C), 130.1 (d, J_{F-P} = 82.4 Hz, ipso-C_{15}H_{10}) ppm. 

\[^{13}C\] NMR (100.61MHz, C_{15}D_{15}, 25°C): δ = 25.8 (s, C_{15}H_{10}), 68.9 (s, C_{15}H_{10}), 118.9 (s, Ar-C), 121.6 (d, J_{F-P} = 18.4 Hz, Ar-C), 129.6 (d, J_{F-P} = 12.7 Hz, Ar-C), 129.7 (d, J_{F-P} = 12.7 Hz, Ar-C), 130.8 (d, J_{F-P} = 12.7 Hz, Ar-C), 132.6 (s, Ar-C), 133.3 (d, J_{F-P} = 91.8 Hz, ipso-C_{15}H_{10}) ppm. 

\[^{31}P\] NMR (161.97MHz, C_{15}D_{15}, 25°C): δ = 89.1 (s) ppm. Anal. calcd. for C_{30}H_{32}MgN_{2}O_{2}P (579.05): C 63.7, H 9.1.
Hz, P/H ppm. The $^1$H NMR spectrum also contained: $\delta = 1.71$ (s broad, 8H, C$_8$H$_4$O), 3.58 (s broad, 8H, C$_8$H$_4$O), 6.11 (s broad, Ar-H), 6.47 (d, Ar-H), 6.64 (t, Ar-H) 6.77 - 7.03 (m, Ar-H), 7.25 - 7.39 (m, Ar-H), 7.59 (t, Ar-H) ppm. $^{13}$C($^1$H) NMR (100.61MHz, THF-d$_8$, 25°C): $\delta = 26.4$ (s, C$_2$H$_2$O), 68.4 (s, C$_2$H$_2$O), 117.3 (d, J$_{P-C}$ = 12.4 Hz, Ar-C), 118.4 (d, J$_{P-C}$ = 41.1 Hz, Ar-C), 119.8 (s, Ar-C), 121.7 (d, J$_{P-C}$ = 18.5 Hz, Ar-C), 122.8 (d, J$_{P-C}$ = 16.8 Hz, Ar-C), 129.3 (d, J$_{P-C}$ = 17.9 Hz, Ar-C), 129.7 (s, Ar-C), 130.9 (d, J$_{P-C}$ = 17.9 Hz, Ar-C), 131.4 (d, J$_{P-C}$ = 11.7 Hz, Ar-C), 132.6 (d, J$_{P-C}$ = 2.6 Hz, Ar-C), 132.8 (d, J$_{P-C}$ = 2.5 Hz, Ar-C), 134.1 (d, J$_{P-C}$ = 91.0 Hz, ipso-C$_8$H$_7$P), 150.4 (d, J$_{P-C}$ = 53.5 Hz, ipso-C$_8$H$_7$N) ppm. $^{31}$P NMR (161.97MHz, THF-d$_8$, 25°C): $\delta = 127.6$ (s broad) ppm. Anal. calc'd for C$_{26}$H$_{48}$BrMgNO$_5$P (539.75): C 57.9, H 6.0; found C 58.0, H 6.1.

**Computational Details**

All the calculations were performed with the Gaussian 09 program$^{20}$ using the dispersion-corrected B3LYP-D functional$^{21}$ together with the Dunning’s correlation consistent basis sets.$^{22}$ The Grimme D dispersion correction$^{23}$ was applied throughout. The geometries of all species were fully optimized and characterized by harmonic vibrational frequency computations at the B3LYP-D/aug-cc-pVQZ level. Thermal contributions to the enthalpy and Gibbs free energy at 298 K were obtained by standard thermodynamics calculations at the B3LYP-D/aug-cc-pVQZ level. More reliable relative energies were obtained from single-point calculations at the B3LYP-D/aug-cc-pVTZ level. The performance of the B3LYP-D hybrid functional on the geometries and relative energies of isomers of 10 was assessed by comparison with experiment. We also performed all calculations with the M06 functional$^{24}$ and BP86-D functional.$^{25}$

Implicit solvent effects were computed using the polarizable continuum model (PCM) with radii and non-electrostatic terms from Truhlar and co-workers’ SMD model$^{26}$ at the B3LYP-D/aug-cc-pVTZ level of theory. The $^{31}$P magnetic shielding tensors of the optimized structures in THF were computed with the Gauge-Independent Atomic Orbital (GIAO) method at the B3LYP/cc-pVQZ level of theory. To compare isotropic shielding with the experimentally observed $^{31}$P chemical shifts, the NMR parameters for H$_2$PO$_4$ were calculated at the same level of theory and used as the reference molecule.

**X-ray crystallography**

The suitable single crystals of 5 and 7-12 were mounted on a glass fibre with an oil and measured on a four-circle diffractometer KappaCCD with a CCD area detector by monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 150(1) K. The numerical$^{28}$ absorption corrections from the crystal shape were applied for all crystals. The structures were solved by the direct method (SIR92)$^{29}$ and refined by a full matrix least squares procedure based on $F^2$ (SHELXL97).$^{30}$ Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $B_{eq}$(H) = 1.2 $U_{eq}$ (pivot atom) or of 1.5 $U_{eq}$ for the methyl moiety with C-H = 0.96, 0.97, 0.98 and 0.93 Å for methyl, methylene, methine and hydrogen atoms in the aromatic ring, respectively. The hydrogen atoms of NH and PH groups were refined from the Fourier difference map. Two carbon atoms of disorder THF molecule coordinated to the magnesium atom in 8a was split into two positions. There are disordered solvent molecules (THF) of 8a and 9. Attempts were made to model this disorder, but were unsuccessful. PLATON
Crystallographic data for 5. 

\[ \text{C}_{23} \text{H}_{48} \text{Mg}_4 \text{N}_4 \text{P}_2 \]  

\[ M = 526.95, \text{ monoclinic}, \ P_2_1/c, \ a = 17.4962(4), \ b = 11.4130(2), \ c = 18.2113(6) \ \text{Å}, \ \beta = 121.211(2)°, \ V = 3110.18(15) \ \text{Å}^3, \ Z = 4, \ T = 150(1) \ \text{K}, 24498 \ \text{total reflections}, 8686 independent \ (R_{int} = 0.029, R1 (obs. data) = 0.038, wR2 (all data) = 0.084), S = 1.156, \Delta_r, \Delta_p, \max., \min. [\text{e Å}^{-3}] = 0.332, -0.307, \text{CCDC 1039991}. 

Crystallographic data for 7. 

\[ \text{C}_{23} \text{H}_{48} \text{Mg}_4 \text{N}_4 \text{P}_2 \]  

\[ M = 526.95, \text{ monoclinic}, \ P_2_1/c, \ a = 25.7012(3), \ b = 8.6979(5), \ c = 18.7740(2) \ \text{Å}, \ \beta = 132.402(3)°, \ V = 3099.1(15) \ \text{Å}^3, \ Z = 4, \ T = 150(1) \ \text{K}, 10544 \ \text{total reflections}, 2959 independent \ (R_{int} = 0.028, R1 (obs. data) = 0.038, wR2 (all data) = 0.100), S = 1.174, \Delta_r, \Delta_p, \max., \min. [\text{e Å}^{-3}] = 0.339, -0.421, \text{CCDC 1039991}. 

Crystallographic data for 11. 

\[ \text{C}_{44} \text{H}_{92} \text{Mg}_8 \text{N}_8 \text{P}_2 \]  

\[ M = 1073.83, \text{ triclinic}, \ P-1, \ a = 10.9041(7), \ b = 11.0920(5), \ c = 12.5151(8) \ \text{Å}, \ \alpha = 97.658(5), \ \beta = 91.018(5), \ \gamma = 110.470(4)°, \ V = 1402.33(4) \ \text{Å}^3, \ Z = 1, \ T = 150(1) \ \text{K}, 27272 \ \text{total reflections}, 5404 independent \ (R_{int} = 0.024, R1 (obs. data) = 0.040, wR2 (all data) = 0.099), S = 1.087, \Delta_r, \Delta_p, \max., \min. [\text{e Å}^{-3}] = 0.493, -0.413, \text{CCDC 1039909}. 

Crystallographic data for 12. 

\[ \text{C}_{22} \text{H}_{48} \text{Br}_2 \text{Mg}_2 \text{N}_2 \text{O}_2 \text{P}_2 \]  

\[ M = 1063.58, \text{ triclinic}, \ P-1, \ a = 12.1820(9), \ b = 14.8989(10), \ c = 16.3201(11) \ \text{Å}, \ \alpha = 75.236(5), \ \beta = 71.290(4), \ \gamma = 82.394(6)°, \ V = 2708.8(3) \ \text{Å}^3, \ Z = 2, \ T = 150(1) \ \text{K}, 55308 \ \text{total reflections}, 9711 independent \ (R_{int} = 0.041, R1 (obs. data) = 0.037, wR2 (all data) = 0.074), S = 1.134, \Delta_r, \max., \min. [\text{e Å}^{-3}] = 0.421, -0.458, \text{CCDC 1039915}. 

Acknowledgements 

The authors thank the Grant agency of the Czech Republic project no. P207/12/0223. M. A. thanks the European Community for financial support through the postdoctoral fellowship FP7-PEOPLE-2010-IEF-273527. F. D. P wishes to thank the Fund for Scientific Research–Flanders (FWO) and the Free University of Brussels (VUB) for their continuous support.

Notes and references 

\* Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ - 532 10, Pardubice, Czech Republic Fax: +420466037068; Tel: +420466037163; E-mail: libor.dostal@upce.cz

\+ Eenheid Algemene Chemie (ALGC), Vrije Universiteit Brussel (VUB) Pleinlaan 2, B-1050 Brussels, Belgium

\† Research Institute for Organic Syntheses, Rybitvi 296, CZ-533 54 Pardubice, Czech Republic

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/


(b) J. Zak, S. Kudrnovský and M. Brabec, CrystEngComm, 2013, 15, 1960.


14 A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. 1984, 1349. This criterion was obtained using Platon software. The value $\tau = 0$ indicates the presence of ideal square pyramid, while $\tau = 1$ for ideal trigonal bipyramid.


The reactivity of bis(organoamino)phosphanes with magnesium(II) reagents is reported. The outcome of reactions is influenced by tautomeric H-shift in ligand backbones.