

# Synthesis and Reactivity of the Phospha-Grignard Reagent $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)\text{Br}(\text{thf})$

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The novel phospha-Grignard reagent  $\text{Mg}(\text{PR}'_2)\text{X}(\text{thf})$  [ $\text{R}' = \text{SiMe}_3$ ,  $\text{X} = \text{Br}$  (**1**)/ $\text{Me}$  (**1'**)] was synthesized and structurally characterized as the phosphide-bridged dimer  $[\textbf{1}]_2$ . The potential for this compound to behave as a redox-friendly phos-

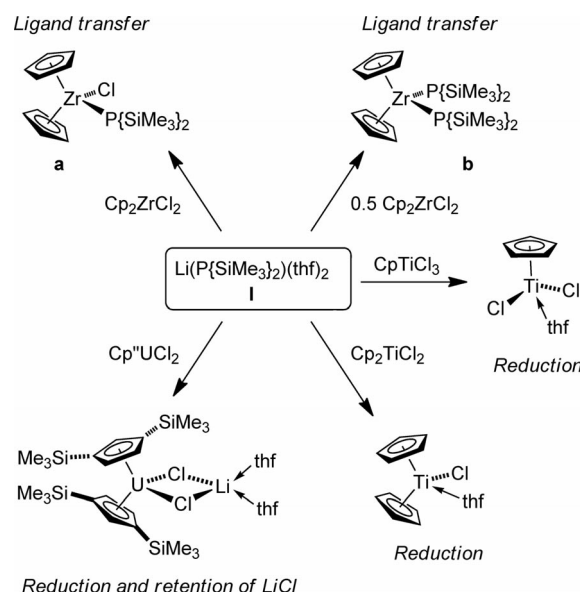
phide transfer reagent was probed by its reaction with group 4 metallocene compounds  $\text{Cp}_2\text{MCl}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ), resulting in phosphide transfer to zirconium, but reduction of the titanium centre to  $\text{Ti}^{\text{III}}$ .

## Introduction

One of the most commonly used synthetic methods for introducing anionic ligands to a metal centre is salt metathesis between a metal halide and the lithium salt of the pro-ligand. This approach has served organometallic chemists for many years, although there are many instances when lithium reagents are unsuitable due to their ability to simultaneously act as reducing agents, and the possible retention of lithium halide in the final product. In these cases an alternative procedure utilizes the corresponding magnesium reagent, which for organometallic complexes involves the ubiquitous Grignard reagents  $\text{RMgX}$  ( $\text{R}$  = pro-ligand,  $\text{X}$  = halide).

The synthesis of metal phosphide compounds is an interesting case as, prior to this study, alternatives to lithium phosphide reagents were scarce in the literature. The aforementioned limitations of  $\text{LiPR}'_2$  are illustrated clearly in a study conducted by Lappert et al., in which it was reported that, although the reaction of 1 or 2 equiv. of  $\text{Li}(\text{P}\{\text{SiMe}_3\}_2)(\text{thf})_2$  (**I**) with  $\text{Cp}_2\text{ZrCl}_2$  gave the desired phosphide transfer products  $\text{Cp}_2\text{Zr}(\text{P}\{\text{SiMe}_3\}_2)\text{Cl}$  (**a**) and  $\text{Cp}_2\text{Zr}(\text{P}\{\text{SiMe}_3\}_2)_2$  (**b**), the analogous reaction with  $\text{Cp}_2\text{TiCl}_2$  gave the  $\text{Ti}^{\text{III}}$  species  $\text{Cp}_2\text{TiCl}(\text{thf})$ .<sup>[1]</sup> It was also found during this study that **I** reduced both  $\text{CpTiCl}_3$  and  $\text{Cp}''_2\text{UCl}_2$  ( $\text{Cp}'' = 1,3\text{-}\{\text{SiMe}_3\}_2\text{C}_5\text{H}_3$ ) to  $\text{CpTiCl}_2(\text{thf})$  and  $\text{Cp}''_2\text{U}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2$ , respectively (Scheme 1).

Since the first magnesium phosphide compounds were reported over 40 years ago,<sup>[2]</sup> only a handful of further examples have been synthesized, and most examples are comprised of bis(phosphides),  $\text{Mg}(\text{PR}'_2)_2$  (Figure 1). In 1987, Hey et al. described the secondary phosphide  $\text{Mg}(\text{PPh})_2(\text{tmeda})$  (**II**), which was the first Mg phosphide to be crystallographically characterised.<sup>[3]</sup> Other examples of magne-



Scheme 1. Reactions of  $\text{Li}(\text{P}\{\text{SiMe}_3\}_2)(\text{thf})_2$  (**I**) with metallocene compounds showing reductive reaction pathways.

sium phosphides include  $\text{Mg}_4(\text{PPh})_8(\text{thf})_6$  (**III**),<sup>[4]</sup>  $[\text{Mg}(\text{P}\{\text{SiH}_2\text{Pr}_2\})_2]_2$  (**IV**),<sup>[5]</sup> polymeric  $[\text{Mg}(\text{PPh})_2]_\infty$ <sup>[2]</sup> and  $[\text{Mg}(\text{PPh}_2)_2(\text{thf})_4]_2$ .<sup>[2]</sup>

Several permutations of magnesium compounds incorporating the bis(trimethylsilyl)phosphide group have since been reported. The ether adducts  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)(\text{dme})$  (**V**)<sup>[6]</sup> and  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)_2(\text{thf})_2$  (**VI**)<sup>[7]</sup> have both been structurally characterized as the monomer in the solid state. In contrast, aggregates are formed under base-free conditions, exemplified by the crystallographically determined trimetallic example  $[(\{\text{Me}_3\text{Si}\}_2\text{P})\text{Mg}(\mu\text{-P}\{\text{SiMe}_3\}_2)_2\text{Mg}(\text{VII})]$ .<sup>[5]</sup>

There is an even greater paucity of heteroleptic magnesium phosphides in the literature, with the only structurally characterized examples being  $[\text{MgEt}(\text{PPh}_2)(\text{L})]_\infty$  ( $\text{L} =$

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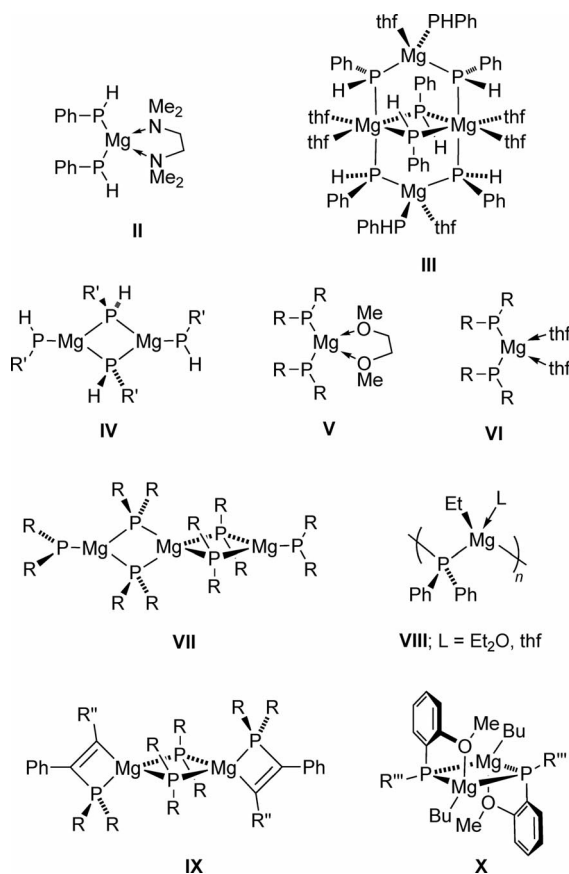


Figure 1. Previously reported magnesium phosphides [R = SiMe<sub>3</sub>, R' = Si(H)Pr<sub>2</sub>, R'' = C≡CPh, R''' = C(H)(SiMe<sub>3</sub>)<sub>2</sub>]. See text for references.

Et<sub>2</sub>O<sup>[2]</sup> or thf<sup>[4]</sup>) (VIII), [ $\{\text{PhC}(\text{P}\{\text{SiMe}_3\}_2)(\text{CC}\equiv\text{CPh})\}\text{Mg}\{\mu\text{-P}(\text{SiMe}_3)_2\}_2$ ] (IX)<sup>[8]</sup> and  $[\text{BuMg}\{\text{P}(\text{CH}\{\text{SiMe}_3\}_2)\text{-Ar}\}_2]$  (X; Ar = C<sub>6</sub>H<sub>4</sub>-2-OMe, C<sub>6</sub>H<sub>3</sub>-2-OMe-3-Me).<sup>[9]</sup> In this contribution we report the synthesis and structure of the phospho-Grignard reagent  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)\text{X}(\text{thf})$  (X = Br/Me), examine the solution-state behaviour of this class of compounds and discuss the reactivity towards group 4 metallocene compounds.

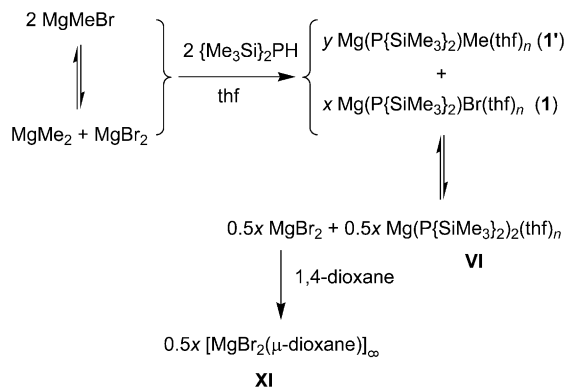
## Results and Discussion

A potentially clean method for the synthesis of the target phospho-Grignard reagents,  $\text{Mg}(\text{PR}_2)\text{X}(\text{L})_x$ , is protonolysis between an alkyl-Grignard reagent and a secondary phosphane in a coordinating solvent (L). A judicious choice of alkyl group in the starting Grignard reagent will afford a volatile side-product for easy removal and purification of the magnesium-containing product. Accordingly, we investigated the reaction of  $\text{MgMeBr}$  with  $\text{R}'_2\text{PH}$  (R' = Cy, Ph and SiMe<sub>3</sub>).

No reaction occurred when  $\text{Cy}_2\text{PH}$  was added to a solution of  $\text{MgMeBr}$  in Et<sub>2</sub>O, indicated by a single resonance in the <sup>31</sup>P NMR spectrum corresponding to unreacted phosphane. In contrast, the reaction of  $\text{Ph}_2\text{PH}$  with  $\text{MgMeBr}$  in Et<sub>2</sub>O yielded a white precipitate that was insol-

uble in most common solvents, except for thf. The main resonance in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the crude product ( $\delta_{\text{P}} = -47.3$  ppm) is in the expected region for an  $\text{Mg-PPh}_2$ -containing species [e.g. VIII, L = thf,  $\delta_{\text{P}} = -45.2$  ppm;  $\text{Mg}(\text{PPh}_2)_2(\text{thf})_4$ ,  $\delta_{\text{P}} = -39.7$  ppm<sup>[4]</sup>]. Additional resonances in the spectrum are assigned to unreacted  $\text{Ph}_2\text{PH}$  ( $\delta_{\text{P}} = -40.3$  ppm), tetraphenyldiphosphane ( $\delta_{\text{P}} = -15.4$  ppm), with two minor unidentified phosphorus-containing species ( $\delta_{\text{P}} = -16.5$  and  $-40.9$  ppm, ca. 10% by integration). All attempts at purification by crystallization were frustrated by poor solubility, likely due to the formation of polymeric material upon isolation of the solid product.

The reaction between  $\{\text{Me}_3\text{Si}\}_2\text{PH}$  and  $\text{MgMeBr}$  in Et<sub>2</sub>O produced a white precipitate that was crystallized from toluene/thf to afford colourless crystals. Combustion analysis was consistent with the formula  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)\text{Br}(\text{thf})$  (1). The <sup>1</sup>H NMR spectrum in [D<sub>8</sub>]thf, however, showed that in addition to a broad resonance at  $\delta_{\text{H}} = 0.15$  ppm assigned to SiMe<sub>3</sub> protons, a singlet at  $\delta_{\text{H}} = -1.62$  ppm was present (relative intensity SiMe<sub>3</sub>/MgMe = 20:1), which is in the region associated with magnesium-methyl groups.<sup>[10]</sup> The NOESY experiment confirmed that the MgMe and SiMe<sub>3</sub> groups are spatially related, suggesting the presence of  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)\text{Me}(\text{thf})$  (1') in solution. We believe methyl compound 1' is generated from the reaction of the phosphane with the dimethylmagnesium component of the MeMgBr solution (which is present as a product of the well-known Schlenk equilibrium of Grignard reagents in coordinating solvents;<sup>[11]</sup> Scheme 2), although exchange of the bromide ligand in compound 1 with methyl groups from MgMeBr or  $\text{MgMe}_2$  would also generate 1'.



Scheme 2. Postulated equilibria present during the reaction of  $\{\text{Me}_3\text{Si}\}_2\text{PH}$  and  $\text{MgMeBr}$ .

The corresponding <sup>31</sup>P{<sup>1</sup>H} spectrum of the isolated crystals in [D<sub>8</sub>]thf showed two broad resonances centred at  $\delta_{\text{P}} \approx -296.9$  and  $-305.1$  ppm, in an approximate 2:3 ratio by integration [spectrum (a), Figure 2 – slight shifts in  $\delta_{\text{P}}$  due to sample in thf/[D<sub>6</sub>]benzene]. The low-field resonance corresponds closely with that previously reported for a thf solution of the bis(phosphide)  $\text{Mg}(\text{P}\{\text{SiMe}_3\}_2)_2(\text{thf})_n$  (VI;  $\delta_{\text{P}} = -294.7$  ppm<sup>[7]</sup>), and the remaining peak is assigned to a coincidence of the phosphorus resonances from 1 and 1'.

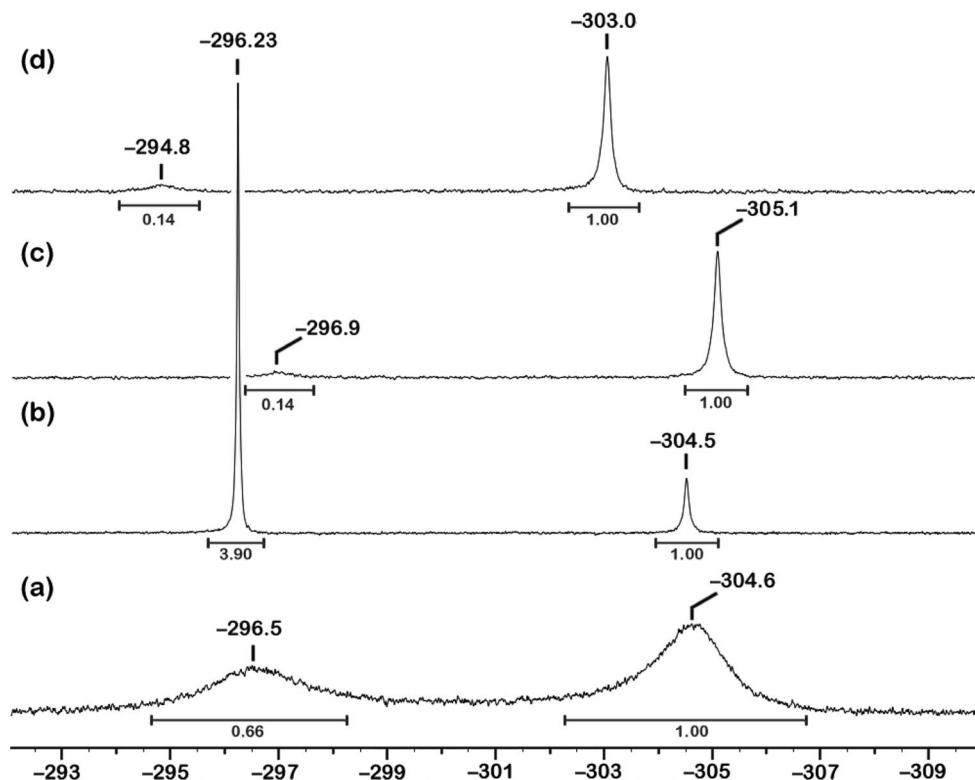


Figure 2. (a)  $^{31}\text{P}$  NMR spectrum of a bromide-enriched sample (**1**; 161 MHz,  $\text{thf}/[\text{D}_6]\text{benzene}$ ); (b)  $^{31}\text{P}$  NMR spectrum of sample (a) after addition of excess 1,4-dioxane; (c)  $^{31}\text{P}$  NMR spectrum of a methyl-enriched sample (**1'**; 161 MHz,  $[\text{D}_8]\text{thf}$ ); (d)  $^{31}\text{P}$  NMR spectrum of sample (c) after addition of excess 1,4-dioxane.

Whilst the presence of bis(phosphide) may be explained from the reaction of **1'** with a second equivalent of phosphane, an alternative explanation is the establishment of an additional Schlenk equilibrium between **1** and **VI**/ $\text{MgBr}_2$  (Scheme 2).

To probe this theory an excess of 1,4-dioxane was added to an NMR sample of the isolated crystals in  $\text{thf}/[\text{D}_6]\text{benzene}$ . We predicted that the dioxane would react with the  $\text{MgBr}_2$  component of the mixture, producing  $[\text{MgBr}_2(\mu\text{-dioxane})]_n$  (**XI**) and shifting the equilibrium to enrich the bis(phosphide) component **VI**. This exploits an established technique for the preparation of dialkylmagnesium compounds from Grignard reagents.<sup>[12]</sup> On addition, a white precipitate immediately formed suggesting the formation of insoluble, polymeric **XI**. This was shown as a sharpening of both resonances in the  $^{31}\text{P}$  NMR spectrum, with a significant change in the relative integrals such that the peak assigned as the bis(phosphide) increased in relative intensity [spectrum (b), Figure 2].

Repeating the reaction between the phosphane and the Grignard reagent and analysing sequential batches of crystals showed that subsequent crops were enriched in the proportion of methyl compound **1'**. In contrast to the data for the initially isolated crystals, the  $^{31}\text{P}$  NMR spectrum of the **1'**-enriched sample in  $[\text{D}_8]\text{thf}$  showed a major resonance at  $\delta_{\text{P}} = -305.1$  ppm, with a minor broad peak at  $\delta_{\text{P}} = -296.9$  ppm with relative intensity 0.14 [spectrum (c), Figure 2]. Addition of excess 1,4-dioxane to this sample did

not significantly change the relative intensities of the peaks [spectrum (d), Figure 2]. These data suggest that, whilst the bromide compound **1** is present as a Schlenk equilibrium with the bis(phosphide) and  $\text{MgBr}_2$ , the methyl compound is more stable to ligand exchange.

The solid-state structure of the initially isolated crystals was shown by single-crystal X-ray diffraction to be the phosphide-bridged dimer  $[\text{Mg}(\mu\text{-P}(\text{SiMe}_3)_2)\text{Br}(\text{thf})]_2$  (**[1]<sub>2</sub>**; Figure 3), which is the only structurally characterized exam-

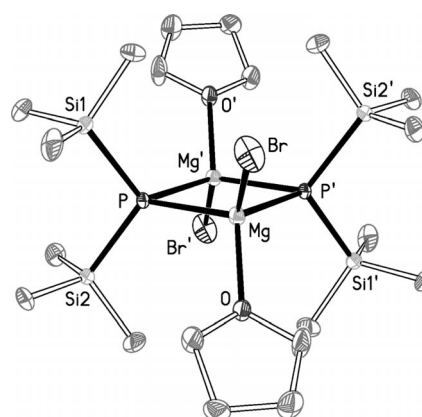


Figure 3. Thermal ellipsoid plot (30% probability; hydrogen atoms omitted;  $' = -x, -y + 1, -z$ ) of  $[\text{Mg}(\mu\text{-P}(\text{SiMe}_3)_2)\text{Br}(\text{thf})]_2$  (**[1]<sub>2</sub>**).

ple of a phosphidomagnesium halide (i.e. a true phosphorus analogue of a Grignard reagent). Selected bond lengths and angles are collected in Table 1 and crystal-structure and refinement data in Table 2.

Table 1. Selected bond lengths [Å] and angles [°] for [1]<sub>2</sub>.

Mg–P	2.5624(16)	Mg–P'	2.5631(16)
P–Si1	2.2245(14)	P–Si2	2.2362(14)
Mg–Br	2.4235(15)	Mg–O	2.026(3)
Mg–P–Mg'	85.73(5)	P–Mg–P'	94.27(5)
Si1–P–Si2	108.94(5)	Si1–P–Mg	108.69(6)
Si1–P–Mg'	120.78(6)	Si2–P–Mg	122.39(5)
Si2–P–Mg'	109.60(6)	O–Mg–Br	103.31(12)
O–Mg–P	108.84(11)	O–Mg–P'	112.73(11)
Br–Mg–P	118.95(6)	Br–Mg–P'	118.81(6)

Symmetry transformation: ' = -x, -y + 1, -z

The molecule lies on an inversion centre with a planar Mg<sub>2</sub>P<sub>2</sub> metallacycle and internal angles of 94.27(5)° and 85.73(5)° at the magnesium and phosphorus atoms, respectively. The Mg–P distances are essentially identical [2.5624(16) Å and 2.5631(16) Å] and in close agreement with those found for the bridging phosphides in **VII** [range: 2.536(3)–2.678(2) Å],<sup>[5]</sup> and **IX** [2.559(2) Å and 2.569(2) Å].<sup>[8]</sup> All other parameters are within normal ranges for magnesium bis(trimethylsilyl)phosphide complexes.

To assess the potential for 1/1' to act as a phosphide transfer reagent and to enable easy comparison with the lithium analogue **I**,<sup>[1]</sup> the reactivity of **1** with the group 4 metallocenes Cp<sub>2</sub>MCl<sub>2</sub> (M = Zr, Ti) was examined. Initial work employed 1 equiv. of zirconocene dichloride and was performed on an NMR scale in thf. An immediate reaction

was observed on mixing the two colourless solutions of starting reagents, indicated by the formation of a purple solution. The reaction was analysed by NMR spectroscopy following removal of the solvent and dissolving the residue in [D<sub>6</sub>]benzene. The <sup>31</sup>P NMR spectrum showed three new phosphorus environments at δ<sub>P</sub> = -109.8 (i), -78.4 (ii) and -72.4 ppm (iii). Resonances (i) and (iii) are consistent with the previously reported zirconium phosphide species Cp<sub>2</sub>Zr(P{SiMe<sub>3</sub>}<sub>2</sub>)Cl (**a**; δ<sub>P</sub> = -108.9 ppm in [D<sub>8</sub>]toluene)<sup>[13]</sup> and Cp<sub>2</sub>Zr(P{SiMe<sub>3</sub>}<sub>2</sub>)<sub>2</sub> (**b**; δ<sub>P</sub> = -72.2 ppm in [D<sub>6</sub>]benzene),<sup>[14]</sup> demonstrating that **1** is effective as a phosphide transfer reagent. Mass spectral analysis (EI<sup>+</sup>) showed molecular ion peaks at *m/z* = 432 (**a**) and 575 (**b**) in addition to a peak at *m/z* = 478 corresponding to the bromide species Cp<sub>2</sub>Zr(P{SiMe<sub>3</sub>}<sub>2</sub>)Br, to which we attribute the <sup>31</sup>P NMR resonance (ii). These data indicate that, in addition to phosphide transfer from magnesium to zirconium, halide transfer also occurs when using 1/1' in this context. The formation of a mixture of mono- and bis(phosphides) may be an indication of a lack of control due to the presence of different magnesium phosphide species in solution (vide infra), which react with the metallocene at different rates.

The reaction of **1** with Cp<sub>2</sub>TiCl<sub>2</sub> was initially performed on an NMR scale in [D<sub>6</sub>]benzene. An immediate colour change from red to orange/brown was observed, indicating a rapid reaction. NMR analysis of the reaction mixture showed a single phosphorus environment at δ<sub>P</sub> = -217.0 ppm, attributed to the diphosphane {Me<sub>3</sub>Si}<sub>2</sub>P–P–{SiMe<sub>3</sub>}<sub>2</sub>.<sup>[15]</sup> To investigate this reaction further it was repeated on a preparative scale in thf. Removal of the solvent and washing of the residue in pentane gave a green solution after filtering, from which no clean product was isolated. However, a small number of pale blue single crystals of **2**

Table 2. Crystal and structure refinement parameters for [1]<sub>2</sub> and **2**.

	[1] <sub>2</sub>	<b>2</b>
Empirical formula	C <sub>20</sub> H <sub>32</sub> Br <sub>2</sub> Mg <sub>2</sub> O <sub>2</sub> P <sub>2</sub> Si <sub>4</sub>	C <sub>44</sub> H <sub>68</sub> Br <sub>1.38</sub> Cl <sub>8.62</sub> Mg <sub>4</sub> O <sub>6</sub> Ti <sub>2</sub> ·3C <sub>6</sub> D <sub>6</sub>
M <sub>r</sub>	707.34	1536.22
T /K	173(2)	173(2)
Crystal system	triclinic	triclinic
Space group	P $\bar{1}$	P $\bar{1}$
a /Å	9.8043(3)	10.4377(4)
b /Å	10.5677(3)	13.3478(5)
c /Å	10.6452(4)	14.2036(3)
α /°	108.981(2)	112.145(2)
β /°	90.799(2)	90.776(2)
γ /°	115.446(2)	102.443(2)
V /Å <sup>3</sup>	926.41(5)	1779.97(10)
Z	1	1
d <sub>calcd.</sub> /Mg m <sup>-3</sup>	1.27	1.43
Absorption coefficient /mm <sup>-1</sup>	2.45	1.40
θ range /°	3.43–27.47	3.49–26.72
Reflections measured	15157	28206
Independent reflections	4202	7527
[I > 2σ(I)], R <sub>int</sub>	3645, 0.044	5292, 0.064
Data/restraints/parameters	4202/0/151	7527/0/382
Final R indices [I > 2σ(I)] R <sub>1</sub> , wR <sub>2</sub>	0.068, 0.276	0.048, 0.095
Final R indices (all data), R <sub>1</sub> , wR <sub>2</sub>	0.077, 0.289	0.081, 0.107
Goof on F <sup>2</sup>	1.299	0.930
Largest diff. peak/hole /e Å <sup>-3</sup>	1.39/–1.71	0.97/–0.75



were deposited from a  $[\text{D}_6]\text{benzene}$  NMR sample of the solid residue, that were analyzed by X-ray diffraction.

The crystal structure of **2** is consistent with the formula  $\text{Cp}_2\text{TiMg}_2\text{X}_5(\text{thf})_3$  ( $\text{X} = \text{halogen}$ ). The molecule is located on an inversion centre generating the hexametallic dimer  $[\text{Cp}_2\text{Ti}(\mu\text{-X})_2\text{Mg}(\text{thf})(\mu\text{-X})_2\text{Mg}(\text{thf})_2(\mu\text{-X})]_2$ ; there are also three molecules of  $\text{C}_6\text{D}_6$  in the unit cell. Initial refinement of all of the halides as chloride gave unreasonably small atomic displacement parameters for the atoms bridging between titanium and magnesium, suggesting heavier atoms at these positions. Given the presence of bromide in starting reagent **1**, and the observation of  $\text{Cp}_2\text{Zr}(\text{P}(\text{SiMe}_3)_2)\text{Br}$  in the corresponding reaction with zirconocene dichloride, we assumed contamination at these positions by Br atoms, and reanalyzed the structure allowing each halide position to freely refine as a mixture of Cl/Br. The resultant occupancies (see caption to Figure 4) show that the bromine atoms are predominantly located in the  $\text{Ti}(\mu\text{-X})\text{Mg}$  positions (av. 27% Br), whereas the remaining halide positions are only fractionally contaminated by bromide (av. 4.9% Br).

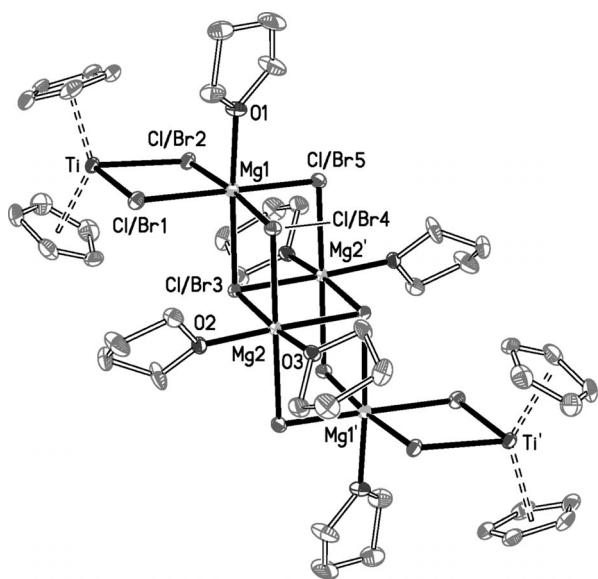


Figure 4. Thermal ellipsoid plot (30% probability; hydrogen atoms omitted;  $' = -x + 1, -y, -z + 1$ ) of **2**. Relative percentages of halides: 1 = 76.5% Cl, 23.5% Br; 2 = 69.0% Cl, 31.0% Br; 3 = 98.0% Cl, 2.0% Br; 4 = 93.2% Cl, 6.8% Br; 5 = 94.2% Cl, 5.8% Br.

Regarding the formation of **2**, work by Stephan in the early 1990s described the closely related compounds  $\{\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\}_2\text{Mg}(\text{thf})_2$  (**XII**) and  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{Mg}(\text{thf})_2(\mu\text{-Cl})]_2$  (**XIII**) as intermediates in the reduction of titanocene dichloride by magnesium (Figure 5).<sup>[16]</sup> It is curious to note that **XII** and **XIII** arise from the reaction between  $\text{Cp}_2\text{TiCl}_2$  with magnesium in the presence of phosphorus species  $\text{P}_4$  and  $\text{RPH}_2$  ( $\text{R} = \text{Ph}, \text{Cy}$ ), respectively. This is in contrast to the reduction of  $\text{Cp}_2\text{TiCl}_2$  with Mg in the presence of excess  $\text{PMe}_3$ , which affords the  $\text{Ti}^{\text{II}}$  compound  $\text{Cp}_2\text{Ti}(\text{PMe}_3)_2$  (**XIV**) in excellent yield.<sup>[17]</sup> On the basis of

Stephan's results, it is suggested that during the formation of **XIV**, Ti/Mg aggregates are formed during the initial reduction of  $\text{Ti}^{\text{IV}}$  to  $\text{Ti}^{\text{III}}$  and that these react rapidly with  $\text{PMe}_3$  to give  $\text{Cp}_2\text{TiCl}(\text{PMe}_3)$ . This reacts further with Mg to afford the phosphane-stabilized titanocene. Compound **2** may represent another example of a potential intermediate in the formation of these reagents. However, it is not clear during the preparation of **XII** and **XIII** whether there is a reaction taking place between the phosphorus component and the Mg prior to reaction with titanocene dichloride, and it is a magnesium phosphide reagent that is responsible for the formation of the reduced species.<sup>[18]</sup> We are currently conducting additional experiments to shed further light on this reaction.

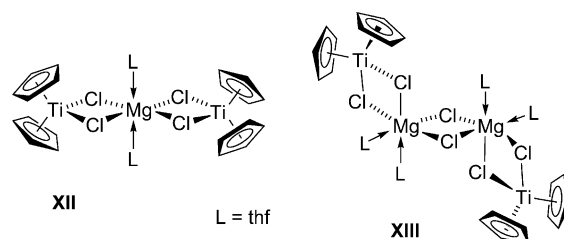


Figure 5. Previously reported titanium/magnesium structures  $\{\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\}_2\text{Mg}(\text{thf})_2$  (**XII**) and  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2\text{Mg}(\text{thf})_2(\mu\text{-Cl})]_2$  (**XIII**).

## Conclusions

We have demonstrated that the reaction of  $\{\text{Me}_3\text{Si}\}_2\text{PH}$  with  $\text{MgMeBr}$  affords a mixture of  $\text{Mg}(\text{P}(\text{SiMe}_3)_2)\text{Br}(\text{thf})$  (**1**) and  $\text{Mg}(\text{P}(\text{SiMe}_3)_2)\text{Me}(\text{thf})$  (**1'**). Data indicate that the bromide forms a Schlenk equilibrium with the bis-(phosphide)  $\text{Mg}(\text{P}(\text{SiMe}_3)_2)_2(\text{thf})_n$  and  $\text{MgBr}_2$ , whereas the methyl compound is more stable towards ligand exchange processes. The reaction between a bromide-enriched sample of **1/1'** and  $\text{Cp}_2\text{ZrCl}_2$  generated the mono- and bis-(phosphide) species  $\text{Cp}_2\text{Zr}(\text{P}(\text{SiMe}_3)_2)\text{Cl}$  and  $\text{Cp}_2\text{Zr}(\text{P}(\text{SiMe}_3)_2)_2$ , as well as the halide exchange product,  $\text{Cp}_2\text{Zr}(\text{P}(\text{SiMe}_3)_2)\text{Br}$ .

In contrast, no phosphide transfer to the titanium atom was observed in the reaction between **1/1'** and  $\text{Cp}_2\text{TiCl}_2$ , with the bis(phosphane)  $\{\text{Me}_2\text{Si}\}_2\text{P-P}(\text{SiMe}_3)_2$  identified as the only phosphorus-containing species. An isolated metallic component **2** of the reaction contained reduced titanium(III) centres bridged to magnesium atoms by halide atoms.

The initial goal of this work was to find an alternative milder reagent for the introduction of phosphide groups at metal centres, compared with previously utilized lithium phosphides. Unfortunately, the presence of solution equilibria, the retention of redox pathways during reaction with transition metals and an additional source of halide mean that the magnesium phosphide does not behave as a simple reagent for this transformation.

## Experimental Section

**General:** All manipulations were carried out under dry nitrogen by using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried with appropriate drying agents and degassed prior to use. NMR spectra were recorded by using a Varian VNMRs 400 MHz spectrometer at 400.1 ( $^1\text{H}$ ), 100.4 ( $^{13}\text{C}\{^1\text{H}\}$ ) and 161.4 ( $^{31}\text{P}\{^1\text{H}\}$ ) MHz and 79.4 MHz ( $^{29}\text{Si}\{^1\text{H}\}$ ) from samples at 303 K in  $[\text{D}_6]\text{thf}$ , unless otherwise stated.  $^{29}\text{Si}$  chemical shifts were extracted from two-dimensional  $^{29}\text{Si}/^1\text{H}$  HMBC experiments. Coupling constants are quoted in Hz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances; phosphorus chemical shifts were referenced externally to  $\text{H}_3\text{PO}_4$  (aq.); silicon chemical shifts were referenced externally to  $\text{SiMe}_4$ . Low-resolution electron impact mass spectrometry was carried out with VG Autospec Fisons instruments by Dr. Ali Abdul-Sada at the University of Sussex. Elemental analyses were performed by S. Boyer at the London Metropolitan University. Methylmagnesium bromide was purchased from Aldrich as a 3.0 M solution in  $\text{Et}_2\text{O}$ ;  $\{\text{Me}_3\text{Si}\}_2\text{PH}$  was kindly donated by Dr I. Crossley.

**Synthesis of  $\text{Mg}(\text{P}(\text{SiMe}_3)_2\text{X}(\text{thf}))$  [ $\text{X} = \text{Br}$  (**1**)/ $\text{Me}$  (**1'**)]:** A solution of  $\text{MgMeBr}$  (3.1 mL of a 3.0 M solution, 9.3 mmol) in  $\text{Et}_2\text{O}$  was added dropwise through a syringe to a solution of  $\{\text{Me}_3\text{Si}\}_2\text{PH}$  (2.0 mL, 9.2 mmol) in  $\text{Et}_2\text{O}$  (ca. 10 mL) at  $-78^\circ\text{C}$ . The solution was stirred and warmed to ambient temperature. After stirring for 3 h, a white precipitate formed that was isolated by filtration and washed with a small amount of cold  $\text{Et}_2\text{O}$  (ca. 10 mL). Slow cooling of a warm ( $60^\circ\text{C}$ ) toluene/thf solution to ambient temperature yielded colourless crystals, which proved to be a mixture of  $\text{Mg}(\text{P}(\text{SiMe}_3)_2\text{Br}(\text{thf}))$  (**1**) and  $\text{Mg}(\text{P}(\text{SiMe}_3)_2\text{Me}(\text{thf}))$  (**1'**). Overall yield 2.14 g (4 crops). Initial batches of crystals were consistent with a sample high in bromide **1**, whilst subsequent batches showed a higher proportion of methyl compound **1'**. Analysis of **1**:  $\text{C}_{10}\text{H}_{26}\text{BrMgOPSi}_2$  (353.67): calcd. C 33.96, H 7.41; found C 33.82, H 7.50. NMR of **1**:  $^1\text{H}$  NMR:  $\delta = 0.15$  (br. s,  $\text{SiMe}_3$ ).  $^{13}\text{C}$  NMR:  $\delta = 7.2$  (br. s,  $\text{SiMe}_3$ ) ppm.  $^{31}\text{P}$  NMR:  $\delta = -296.9$  (br.),  $-305.1$  (br.) ppm.  $^{29}\text{Si}$  NMR  $\delta = 2.9$  (br.,  $\text{SiMe}_3$ ) ppm. NMR of **1'**:  $^1\text{H}$  NMR:  $\delta = 0.14$  (br. s,  $\text{SiMe}_3$ ),  $-1.62$  (s,  $\text{MgMe}$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta = 7.2$  ( $^2J_{\text{CP}} = 9$  Hz,  $\text{SiMe}_3$ ),  $-14.6$  ( $\text{MgMe}$ ) ppm.  $^{31}\text{P}$  NMR:  $\delta = -305.1$  (br.) ppm.  $^{29}\text{Si}$  NMR:  $\delta = 1.4$  (d,  $^1J_{\text{SiP}} = 39$  Hz,  $\text{SiMe}_3$ ) ppm.

**NMR Reaction of **1** with  $\text{Cp}_2\text{ZrCl}_2$ :** **1** (20.8 mg, 0.059 mmol) was dissolved in thf (ca. 0.3 mL) and added to a solution of  $\text{Cp}_2\text{ZrCl}_2$  (17.2 mg, 0.059 mmol) in  $[\text{D}_6]\text{benzene}$  (ca. 0.3 mL) in a vial in an inert atmosphere glovebox. An instant colour change from colourless to red/purple was observed. An NMR tube was charged with the solution, and NMR spectra were recorded. After 24 h, the solvent was removed and the residue dissolved in pure  $[\text{D}_6]\text{benzene}$ , and the final products were analysed by NMR spectroscopy.

**NMR Reaction of **1** with  $\text{Cp}_2\text{TiCl}_2$ :**  $\text{Cp}_2\text{TiCl}_2$  (12.3 mg, 0.049 mmol) was dissolved in  $[\text{D}_6]\text{benzene}$  (ca. 0.3 mL) and added to **1** (17.5 mg, 0.049 mmol) in a vial in an inert atmosphere glovebox. The reaction mixture was swirled until **1** had completely dissolved. A colour change from red to orange/brown was observed. An NMR tube was charged with the solution, and NMR spectra were recorded.

**Preparative Scale Reaction of **1** with  $\text{Cp}_2\text{TiCl}_2$ :** **1** (100.9 mg, 0.285 mmol) was dissolved in thf (ca. 10 mL) and added dropwise to a stirred solution of  $\text{Cp}_2\text{TiCl}_2$  (71 mg, 0.285 mmol) in thf (ca. 10 mL). The solution gradually turned dark green over a period of 2 h. The solvent was removed in vacuo and the residue washed with pentane to afford a green solution. Despite trying numerous

conditions, no clean product could be obtained from this mixture. A sample of the residue was dissolved in  $[\text{D}_6]\text{benzene}$ , from which crystals of **2** were deposited over a period of 2 d. As both the composition of reagent **1** (mixed Br/Me) and the product **2** (mixed Br/Cl) are variable, and the reaction between **1** and  $\text{Cp}_2\text{TiCl}_2$  leading to **2** is non-stoichiometric, we are unable to report a reliable synthesis of **2** in this work. In addition further characterization of **2** by elemental analysis is not viable (due to the variable Br/Cl composition of the crystals), and NMR analysis is hampered by the paramagnetic nature of the  $\text{Ti}^{\text{III}}$  centres.

**Crystallographic Data Collection and Refinement Procedures:** Details of the crystal data, intensity collection and refinement for complexes [**1**]<sub>2</sub> and **2** are given in Table 2. Crystals were covered with an inert oil, and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. Data was collected at 173(2) K by using  $\text{Mo-K}_\alpha$  radiation at 0.71073 Å. The structures were refined with SHELXL-97.<sup>[19]</sup> **Compound 2:** The halide positions are modelled as disordered between Br/Cl atoms, with free refinement of the occupancy of each atom, and EADP/EXYZ restraints. Two of the thf molecules are disordered, and one of the benzene solvate molecules was refined as a rigid body; the disordered atoms were left isotropic. CCDC-785516 ([**1**]<sub>2</sub>) and -785517 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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