Hydrophosphinylation of Styrenes Catalysed by Well-Defined s-Block Bimetallics

Andrew W. J. Platten,[a] Andryj M. Borys,[a] and Eva Hevia*[a]

Advancing the applications of s-block heterobimetallic complexes in catalysis, we report the use of potassium magnesiate (PMDETA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$ [PMDETA = N,N,N',N',N''-pentamethyldiethylenetriamine] for the catalytic hydrophosphinylation of styrenes under mild conditions. Exploiting chemical cooperation, this bimetallic approach offers greater catalytic activity and chemoselectivity than the single-metal components KCH$_2$SiMe$_3$ and Mg(CH$_2$SiMe$_3$)$_2$. Stoichiometric studies between (PMDETA)$_2$K$_2$Mg(CH$_2$SiMe$_3$)$_4$ and Ph$_2$P(O)H help to elucidate the constitution of the active catalytic species, and illustrate the influence of donors on the potassium cation coordination, and how this may impact catalytic activity. Mechanistic investigations support that the rate determining step is the insertion of the olefinic substrate.

Introduction

Organophosphorus compounds are ubiquitous amongst the chemical sciences, being highly valued for their widespread application as ligands in catalysis,[1] or in the agrochemical industry,[2] to name just a few. Despite this, the synthetic methods frequently employed to prepare organophosphorus compounds still rely on salt-metathesis routes using toxic, halogenated precursors such as PCl$_3$.[3,4] These routes also suffer from poor functional group tolerance, and often require protecting groups to prevent over-substitution. The direct addition of P–H bonds to unsaturated substrates is an attractive synthetic strategy since it is 100% atom-economical, but nevertheless often necessitates the use of precious transition-metal catalysts or radical initiators to enable the transformation.[5] Within this context, there has been significant interest in developing earth-abundant and sustainable catalysts to promote a range of hydroelementation reactions.[6,7] Although many transition-metal free methods for the hydrophosphination (*i.e.* P^{III}-H addition) of unsaturated species have been reported,[8] the hydrophosphinylation reaction (*i.e.* P^{V}-(O)–H addition) is considerably less explored.[9]

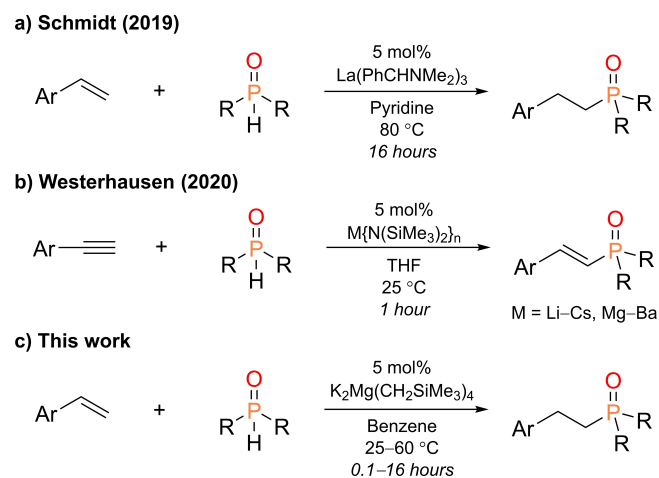Whilst catalyst-free methods have shown some success for the hydrophosphinylation of activated unsaturated substrates

such as isocyanates,[10] there has been encouraging developments using s-[11–17] or f-block[18–21] organometallics to extend the scope of this reaction. Unlike transition-metal catalysis which relies on oxidative addition of the P–H bond or activation of the unsaturated substrate itself,[8,9] s- and f-block metal (pre)catalysts operate by deprotonation of HP(O)R$_2$ to generate a nucleophilic M-OPR$_2$ species which in turn can undergo insertion of the unsaturated organic substrate. Polarised unsaturated compounds including styrenes, alkynes, nitriles and heterocumulenes are typical substrates for these transformations, which in turn provides selective access to the anti-Markovnikov addition products due to the stabilisation of the transition-states in the addition step. Notable examples include the use of organo-lanthanum pre-catalysts which are effective for the hydrophosphinylation of styrenes, albeit under forcing conditions and using pyridine as the reaction solvent (Scheme 1a).[21] Westerhausen and co-workers have explored the use of alkali- and alkaline-earth metal amides [M{N(SiMe$_3$)$_2$}$_n$; M = group 1 (n = 1); M = group 2 (n = 2)] for the hydrophosphi-

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Scheme 1. Hydrophosphinylation of unsaturated compounds using s- and f-block catalysts.

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nylation of arylacetylenes (Scheme 1b).[16] These comprehensive studies revealed that the heavy alkali-metal amides were the most effective catalysts for this transformation, whilst the lighter congeners of both groups 1 and 2 showed poor activity. The double hydrophosphinylation of alkynes and nitriles using s- and f-block catalysts has also been explored.[14,19,20]

A powerful strategy to upgrade the catalytic activity of lighter group 2 metals such as magnesium is through co-complexation with a group 1 metal, affording heterobimetallic 'ate' complexes.[22,23] These heterobimetallics have been widely used for many stoichiometric transformations,[24] and this has more recently been expanded to catalytic regimes. In particular, they have been employed in several catalytic hydroelementation and addition reactions,[25–29] showing superior catalytic activity when compared to the monometallic components, and in many cases even outperform the heavier group 2 congeners. The use of heterobimetallic s-block catalysts has been explored by Westerhausen for the hydrophosphinylation of isocyanates,[30] but in this case, the activity of the heterobimetallic catalyst was comparable to that of the monometallic calcium catalyst. Within our group, we have successfully employed alkali-metal magnesiates as catalysts for hydroamination, hydroalkoxylation and hydrophosphination reactions,[25–28] and therefore anticipated that they would be suitable candidates for the hydrophosphinylation of styrene derivatives (Scheme 1c).
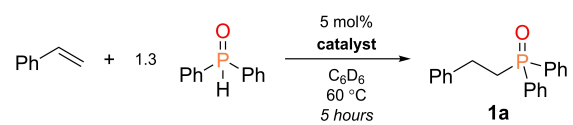
Results and Discussion

Styrene and $Ph_2P(O)H$ were used as benchmark substrates to optimise the catalytic reaction conditions (Table 1). Starting with 5 mol% of $(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4$ [TMEDA = N,N,N',N'-tetramethylethylenediamine] as the pre-catalyst, a 23% yield of the desired hydrophosphinylation product **1a** was formed after 5 hours of heating at 60 °C (entry 1). Moving to the heavier alkali-metal magnesiates led to a significant improvement in yield, with 88% yield using $(TMEDA)_2Na_2Mg(CH_2SiMe_3)_4$ and >99% using $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ [PMDETA =

N,N,N',N',N''-pentamethyldiethylenetriamine], illustrating a marked alkali-metal effect (entries 2–3). In the absence of a catalyst, no product is observed even after 20 hours of heating at 60 °C (entry 4). Using $Mg(CH_2SiMe_3)_2$, only 3% yield of **1a** is formed after 5 hours, illustrating the superior catalytic activity of the heterobimetallic magnesiates (entry 5). The monometallic group 1 alkyls (AM-CH_2SiMe_3; AM = Li, Na, K) however showed comparable activity to the heterobimetallic magnesiates containing the same alkali-metal (entries 6–8), and followed the trend K > Na > Li. It should be noted however, that whilst KCH_2SiMe_3 gave quantitative yield of the styrene hydrophosphinylation product **1a** in just 2 hours, it showed poor selectivity for many other styrene derivatives, leading to undesirable side-reactions such as polymerisation (*vide infra*). Whilst sufficiently basic to deprotonate $Ph_2P(O)H$ (pKa = 28.0),[31] KO^tBu was found to be an ineffective catalyst for this particular transformation under these conditions (entry 9), despite finding success for reductive addition of phosphine oxides to terminal alkynes.[13] The hydrophosphinylation of styrenes using simple alkali-metal base pre-catalysts, including ^nBuLi and KOH, is possible however provided the reaction is carried out in an appropriate coordinating solvent.[17]
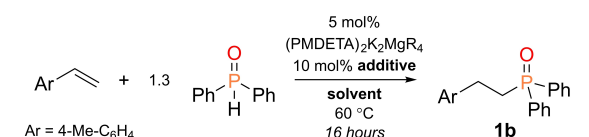
Using $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ as the optimal pre-catalyst, the role of the alkali-metal within these heterobimetallic magnesiates was investigated through the addition of different donor additives, which could modify the potassium cation coordination environment. To make these influences more apparent, a more challenging substrate, namely 4-methylstryene, was selected (Table 2). Without any donor additives, an 84% yield of hydrophosphinylation product **1b** was formed after 16 hours of heating at 60 °C (entry 1). No differences were observed when performing the reaction in THF-d_8 (entry 2). A comparable yield (85%) was obtained with the addition of 10 mol% 18-crown-6 (entry 3), although a slight increase in the initial rate of the reaction was nevertheless observed (see Figures S1–2). Moving to [2.2.2]-cryptand, a macrocyclic donor which sequesters K^+ ions, a reduced yield of 40% was found (entry 4). Whilst this illustrates the superior catalytic ability of the heterobimetallic system and the beneficial role of the alkali-metal cation, it also demonstrates

Table 1. Catalyst optimisation for the hydrophosphinylation of styrene.

Entry	Catalyst	NMR Yield [%][a]
1	$(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4$	23
2	$(TMEDA)_2Na_2Mg(CH_2SiMe_3)_4$	88
3	**$(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$**	**>99**
4	No catalyst	0[b]
5	$Mg(CH_2SiMe_3)_2$	3
6	$LiCH_2SiMe_3$	19
7	$NaCH_2SiMe_3$	81
8	KCH_2SiMe_3	>99[c]
9	KO^tBu	0

[a] NMR yields of **1a** determined by ^1H NMR spectroscopic data using adamantane as an internal standard, [b] No product observed after 20 hours at 60 °C, [c] Reaction complete in 2 hours at 60 °C.

Table 2. Influence of donor additives on the hydrophosphinylation reaction.

Entry	Solvent	Additive	NMR Yield [%][a]
1	C_6D_6	–	84
2	THF-d_8	–	84
3	C_6D_6	18-Crown-6	85
4	C_6D_6	[2.2.2]-Cryptand	40
5	C_6D_6	$Ph_2P(O)OH$	12

[a] NMR yields of **1b** determined by ^1H NMR spectroscopic data using adamantane as an internal standard.

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that the increased nucleophilicity of a formally dianionic magnesiate $[MgR_4]^{2-}$ also plays an important role.

When monitoring the catalytic reaction in THF-d_8 or with 10 mol% 18-crown-6 by ^{31}P NMR spectroscopy, it was found that small amounts of both diphenylphosphine (Ph₂PH) and diphenylphosphinic acid (Ph₂P(O)OH) slowly formed over time. This has been previously identified to originate from a disproportionation of Ar_2P^{III}–O–M into $Ar_2P^{IV}(O)$–O–M and Ar_2P^{III}-M, and furthermore is accelerated by ethereal donors or solvents.[30] The diphenylphosphinic acid formed has a detrimental impact on the catalytic reaction, and the addition of 10 mol% Ph₂P(O)OH resulted in a dramatic decrease in the yield (12%) of **1b** formed (Table 2, entry 5).

To shed light on the constitution of the metallated intermediates and to further assess the impact of donor additives, stoichiometric experiments between (PMDETA)₂K₂Mg-(CH₂SiMe₃)₄ and Ph₂P(O)H (1:4 ratio) were carried out (Figure 1a). In the absence of any additional donors, the Ph₂P(O)H itself can act as a neutral donor to give $[K_2Mg(OPPh_2)_4\{Ph_2P-(O)H\}_2]_\infty$ (**2**). The solid-state structure of **2** reveals a Weiss-type

motif[32] – a distorted tetrahedral Mg centre in close proximity to two peripheral K cations *via* four diphenylphosphinite bridges (Figure 1b). This extends into a 1D-polymer through bridging K···O···K interactions from the diphenylphosphine oxide donor. Incorporation of free Ar2P(O)H within the crystal structure is also observed in a related dipotassium calciate, however in this case, a single phosphine oxide coordinates to the Ca centre, and the potassium cations are stabilised by π-arene interactions.[30] When two equivalents of 18-crown-6 are added, a *pseudo*-solvent separated structure is obtained, [(18-C-6)₂K₂Mg(OPPh₂)₄]∞ (**3**). In the solid-state (Figure 1c), the potassium cations are now removed away from the $[Mg(OPPh_2)_4]^{2-}$ core and show no K···O interactions with the diphenylphosphinite ligands. The K cations do nevertheless show weak interactions to the formal dianion, albeit through peripheral η²-arene interactions, with additional K···P interactions (3.4619(8) Å) between neighbouring molecules leading to an infinite 2D-lattice. Finally, the addition of [2.2.2]-cryptand results in complete sequestering of the potassium cations to give a solvent-separated ion triple, {Mg(OPPh₂)₄}{K[2.2.2]-cryptand}₂ (**4**)
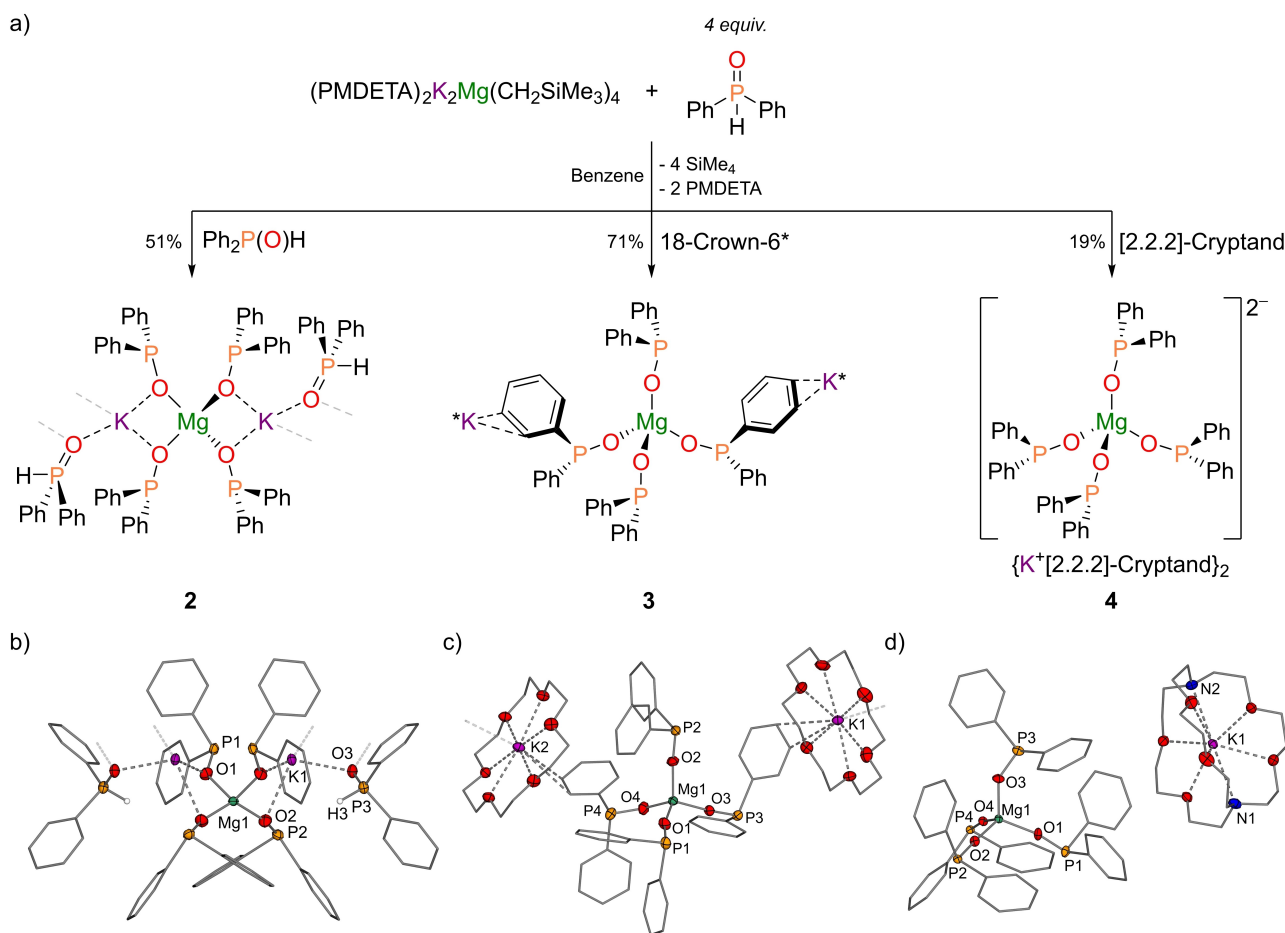

Figure 1. a) Synthesis of tetra-phosphinite dipotassium magnesiates **2**–**4**; b) Solid-state structure of **2**. Thermal ellipsoids shown at 30% probability and hydrogen atoms, except for P–H bonds, omitted for clarity. Selected bond lengths [Å]: Mg1-O1 1.931(1), Mg1-O2 1.901(1), O1-P1 1.572(1), O2-P2 1.558(1), O1-K1 2.853(1), O2-K1 2.866(1), O3-K1 2.690(1), O3-P3 1.493(1); c) Solid-state structure of **3**. Thermal ellipsoids shown at 30% probability. Selected bond lengths [Å]: Mg1-O1 1.904(2), Mg1-O2 1.912(2), Mg1-O3 1.916(1), Mg1-O4 1.927(2), O1-P1 1.533(2), O2-P2 1.546(1), O3-P3 1.547(1), O4-P4 1.560(1); d) Solid-state structure of **4**. Thermal ellipsoids shown at 30% probability. Only one of the two {K⁺[2.2.2]-cryptand} cations are shown. Selected bond lengths [Å]: Mg1-O1 1.907(1), Mg1-O2 1.922(1), Mg1-O3 1.939(1), Mg1-O4 1.922(1), O1-P1 1.549(1), O2-P2 1.547(1), O3-P3 1.558(1), O4-P4 1.549(1).

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(Figure 1d). Compounds **2–4** are poorly soluble in most organic solvents but display a characteristic downfield shifted signal relative to $Ph_2P(O)H$ in the ^{31}P NMR spectrum [δ: ≈84 ppm (C_6D_6); ≈77 ppm (DMSO-d_6)]. These spectroscopic signals can be unambiguously observed during catalytic trials, and isolated **2** shows comparable catalytic activity to $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$, illustrating that this is likely an on-cycle species (*vide infra*).

Having gained some insights into the constitution of the metalated intermediates, we then went on to explore the scope of the hydrophosphinylation reaction (Figure 2). Styrenes containing halogen atoms (F, Cl, Br) at the *para*-position were well tolerated to give compounds **1c–e** in high yields (77–93%). Using the electron-withdrawing *para*-CF_3 substituted styrene gave the corresponding hydrophosphinylation product **1f** in 96% yield after just 5 minutes at room temperature, whilst 4-vinylbiphenyl took 2 hours at 60°C to give **1g** in 93% yield. *Meta*-OMe substituted styrene gave hydrophosphinylation product **1h** in 97% yield after 6 hours at 60°C. Vinyl-substituted heteroaryls (4-vinylpyridine and 2-vinylthiophene) reacted smoothly to give **1i** and **1j** respectively in excellent yields. The use of 5 mol% KCH_2SiMe_3 as a pre-catalyst was also tested for each of the styrene substrates (yields shown in brackets in Figure 2). Although comparable or improved yields could be obtained in shorter reaction times for three of the substrates (**1a**, **1b** and **1i**), no or trace hydrophosphinylation product was

obtained for the rest of the series, reflecting the greater efficiency and improved functional group tolerance of the bimetallic potassium magnesiate over the monometallic species. Diarylphosphine oxides, $Mes_2P(O)H$ (Mes = 2,4,6-trimethylphenyl) and $Naph_2P(O)$ (Naph = 1-naphthyl), reacted cleanly with styrene to give the corresponding hydrophosphinylation products **1k** and **1l** in 91% and 74% yield, respectively. The use of $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ as a pre-catalyst was also effective for the hydrophosphination of styrene using Ph_2PH, giving **1m** in 95% yield after just 1 hour at 25°C. Phosphinates $\{R(OR')P(O)H\}$ and phosphites $\{(OR)_2P(O)H\}$ were unsuccessful substrates for this transformation however. This is largely attributed to the reduced acidity of these P(V)-compounds in comparison to the diarylphosphine oxides, but evidence of undesirable nucleophilic substitution reactions were also observed by ^1H and ^{31}P NMR spectroscopy.

Insights into the reaction mechanism *via* kinetic studies were hampered by the poor solubility of the proposed active tetra-phopshinite dipotassium magnesiate, **2**. Increasing the concentration of $Ph_2P(O)H$ was found to improve the solubility of **2**, leading to an apparent increase in the reaction rate (Figure S3), however only a small kinetic isotope effect of ≈1.15 was found when using $Ph_2P(O)D$ (either through comparison of rates or in competition reactions), suggesting that the initial deprotonation or protonolysis steps were not rate-determining (Figures S4–5). This instead supports that it is the insertion of
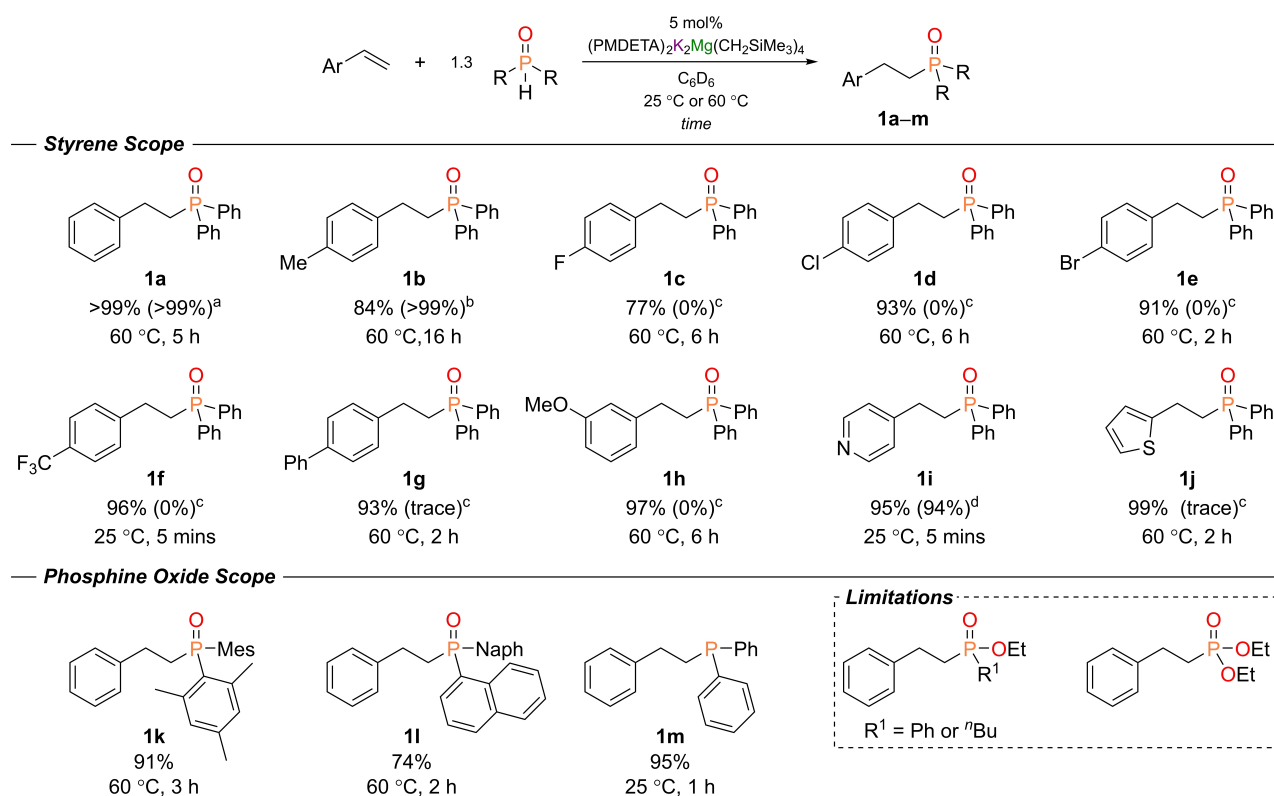

Figure 2. Substrate scope for the hydrophosphinylation of styrene derivatives using 5 mol% $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ as the pre-catalyst. Yields determined by ^1H NMR spectroscopic data using adamantane as an internal standard. All reactions were performed in duplicate, and the average value is shown. Yields in brackets refer to catalytic trials attempted using 5 mol% KCH_2SiMe_3 as the pre-catalyst. [a] After 1 hour at 60°C. [b] After 2 hours at 60°C. [c] After 5 hours at 60°C. [d] After 5 minutes at 25°C.

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styrene that is the rate-determining step, which is consistent with our previous studies using alkali-metal magnesiates for catalytic hydroelementation and addition reactions.[25–29] The marked alkali-metal effect (K > Na > Li) and donor influence suggests that coordination of the alkene *via* the π-bond to the soft potassium cation also plays a key step in the reaction mechanism. Based on these observations and literature precedent,[16,21] a proposed catalytic cycle for the hydrophosphinylation of styrenes using potassium magnesiates can be constructed (Figure 3).

Conclusions

In conclusion, we have demonstrated the use of s-block bimetallics for the catalytic hydrophosphinylation of styrenes. The reaction operates under mild conditions to afford a range of organophosphorus compounds in good to excellent yields. Stoichiometric and crystallographic studies between the potassium magnesiate pre-catalyst and $Ph_2P(O)H$ has shed light on the constitution of the metalated intermediates, as well as providing insights into the role of donors on the potassium cation coordination environment, which is implicated to influence the catalytic activity of the bimetallic complexes. Underpinned by the special cooperation between potassium and magnesium, this bimetallic approach offers greater activity, functional group tolerance and chemoselectivity than when using the single-metal alkyl components as pre-catalysts.
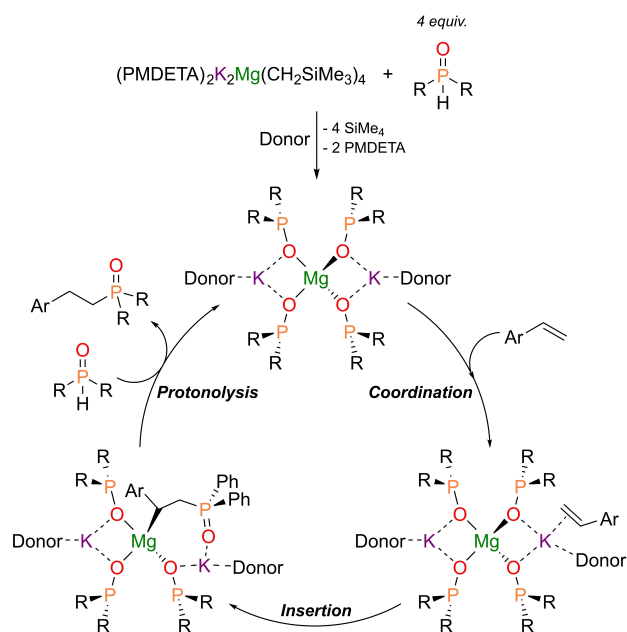

Figure 3. Proposed catalytic cycle for the hydrophosphinylation of styrenes catalysed by potassium magnesiates.

Experimental

General Considerations

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line[33] or glove-box techniques (MBraun UNILab Pro ECO, < 0.5 ppm H_2O and O_2). Solvents were dried using a MBraun MBSPS 5 and stored over 4 Å molecular sieves. C_6D_6 and THF-d_8 were dried and distilled over NaK alloy and stored over 4 Å molecular sieves. DMSO-d_6 was degassed and stored over 4 Å molecular sieves. $CDCl_3$ was stored over 4 Å molecular sieves. Solid $LiCH_2SiMe_3$ was obtained by removal of pentane from commercially available solutions. $NaCH_2SiMe_3$, KCH_2SiMe_3, $Mg(CH_2SiMe_3)_2$, $(TMEDA)_2Li_2Mg(CH_2SiMe_3)_4$, $(TMEDA)_2Na_2Mg(CH_2SiMe_3)_4$ and $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ were prepared according to literature procedures.[34–37] Diphenylphosphine oxide was used as supplied from Sigma Aldrich or Combi-Blocks (98% purity), whilst all other phosphine oxides were prepared according to literature procedures.[38] Styrene and 4-methylstyrene were distilled over CaH_2 and degassed prior to use. All other styrene substrates were used directly as supplied from commercially available sources. 18-Crown-6 was sublimed *in vacuo* prior to use. All other compounds were used as supplied from commercially available sources. NMR spectra were recorded on Bruker Avance III HD 300 or 400 MHz spectrometers. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to residual solvent peaks. CHN elemental microanalyses were performed on a Flash 2000 Organic Elemental Analyser (Thermo Scientific). Single crystal X-ray diffraction measurements were made on a *RIGAKU Synergy S* area-detector diffractometer using mirror optics monochromated Cu $K\alpha$ radiation ($\lambda = 1.54184$ Å. The crystal structures of compounds **2–4** have been deposited into the Cambridge Crystallographic Data Centre (CCDC) and have been assigned the following numbers: **2** – 2124454; **3** – 2124455; **4** – 2124456.

Synthesis of [K$_2$Mg(OPPh$_2$)$_4${Ph$_2$P(O)H}$_2$]$_∞$ (2)

$(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ (80 mg, 0.1 mmol) was dissolved in benzene (2 mL) and frozen in a −30 °C glovebox freezer. Diphenylphosphine oxide (121 mg, 0.6 mmol) was added and the reaction mixture was thawed to room temperature with stirring. Leaving the solution undisturbed for 24 hours afforded colourless crystals that were separated from the mother liquor, washed with hexane (1 mL) and dried. Yield – 67 mg (51%). ^{31}P NMR (121.5 MHz, DMSO-d_6): δ 76.8 (br), 18.4 (br d, $^1J_{P-H} = 456$ Hz). Elemental analysis: Calculated for $C_{72}H_{62}K_2MgO_6P_6$: C, 65.90; H, 4.73. Found: C, 66.31; H, 5.01.

Synthesis of [(18-C-6)$_2$K$_2$Mg(OPPh$_2$)$_4$]$_∞$ (3)

$(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ (80 mg, 0.1 mmol) was dissolved in benzene (2 mL) and frozen in a −30 °C glovebox freezer. Diphenylphosphine oxide (121 mg, 0.6 mmol) was added and the reaction mixture was thawed to room temperature with stirring. 18-Crown-6 (53 mg, 0.2 mmol) was added and the solution was layered with hexane (4 mL). After complete diffusion (*ca.* 4 days), the colourless needles were separated from the mother liquor, washed with hexane (1 mL) and dried. Yield – 115 mg (71%). Elemental analysis: Calculated for $C_{72}H_{87}K_2MgO_{16}P_4$: C, 60.23; H, 6.18. Found: C, 60.13; H, 6.13.

Synthesis of [Mg(OPPh$_2$)$_4$][K{2.2.2}-Cryptand]$_2$ (4)

$(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ (20 mg, 0.025 mmol) was dissolved in benzene (1 mL) and frozen in a −30 °C glovebox freezer. Diphenylphosphine oxide (20 mg, 0.1 mmol) was added and the reaction

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mixture was thawed to room temperature with stirring. [2.2.2]-Cryptand (18 mg, 0.05 mmol) was added and the solution was allowed to partially evaporate over the course of 24 hours to give colourless crystals that were separated from the mother liquor, washed with hexane (0.5 mL) and dried. Yield – 8 mg (19%). Crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane into a saturated THF solution of **4**. Elemental analysis: Calculated for $C_{84}H_{112}K_2MgN_4O_{16}P_4$: C, 60.77; H, 6.80; N, 3.37. Found: C, 60.25; H, 6.74; N, 3.05.

Catalytic Reactions

A J. Young's NMR tube was charged with phosphine oxide (0.325 mmol, 1.3 eq), styrene substrate (0.25 mmol), adamantane (5.7 mg, 0.042 mmol), and dissolved in C_6D_6 (0.5 mL). A ^1H NMR spectrum was recorded to determine the ratio of styrene with respect to the internal standard. $(PMDETA)_2K_2Mg(CH_2SiMe_3)_4$ (10 mg, 0.0125 mmol, 5 mol%) was added and the reaction was heated to 60°C (or kept at 25°C) for the required time, with periodic monitoring by ^1H and ^{31}P NMR spectroscopy. After reaction completion, the C_6D_6 was removed *in vacuo* and the sample was redissolved in $CDCl_3$ (0.5 mL) for characterisation and to confirm that the hydrophosphinylation products matched reported litera-ture values. All reactions were performed in duplicate.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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