

Journal Pre-proofs

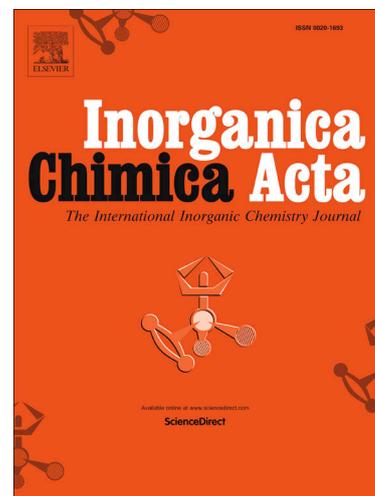
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Indium(III) Promoted Oxidative P-P Coupling of Silylphosphines

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Abstract

The reaction of indium(III) salts with $\text{Ph}_2\text{PSiMe}_3$ and $\text{PhP}(\text{SiMe}_3)_2$ gives rise to a one- and two-electron reductive P-P coupling respectively, with the formation of new P-P bonds resulting in the preparation of $(\text{Ph}_2\text{P})_2$ and the cyclicoligophosphane compounds $(\text{PhP})_4$ and $(\text{PhP})_6$.

Introduction

Indium(III) salts and silylated phosphines are archetypal reagents for the preparation of indium phosphide quantum dots.^{1,2} The two species are typically reacted together at high temperature and undergo a desilylation-type reaction, where the formation of InP is driven forward through the release of Me_3SiX ($\text{X} = \text{halide/carboxylate}$).³ Chemical reactions between indium(III) salts and phosphines have typically resulted in either the formation of InP ,⁴ or small molecules featuring In-P bonds⁵⁻⁹ with the exception of two examples witnessing the formation of large molecular clusters that mimic the structure of bulk InP .^{10,11} Motivated by this, we sought to probe the reactivity of silylphosphines of the type $\text{Ph}_x\text{P}(\text{SiMe}_3)_{3-x}$ with a variety of indium(III) salts.

We found that instead of the expected formation of In-P bonds we observed an oxidative P-P coupling resulting in the preparation of $(\text{Ph}_2\text{P})_2$, $(\text{PhP})_4$ and $(\text{PhP})_6$, which was accompanied by the reduction of In(III) to In(0) . We posit that this may be an alternative route to the formation of diphosphines, or cyclooligophosphanes which are otherwise prepared *via* treatment of a chlorophosphine with powerful reducing agents such as Na , or LiAlH_4 in the presence of a primary or secondary phosphine, or through the reaction of a secondary chlorophosphine with triethylsilane in the presence of trimethylsilyl trifluoromethanesulfonate.¹²⁻¹⁷

Results and Discussion

We prepared $\text{Ph}_2\text{PSiMe}_3$ through the reduction of Ph_3P with Li metal followed by treatment with Me_3SiCl ,¹⁸ and $\text{PhP}(\text{SiMe}_3)_2$ from treatment of PhPH_2 with $n\text{BuLi}$ then Me_3SiCl .^{19,20} The phosphines were then treated with various InX_3 ($\text{X} = \text{F, Cl, I, OAc}$) salts at different ratios in THF, toluene and $d_8\text{-THF}$.

The reaction of In(OAc)_3 (114 mg, 0.39 mmol) and $\text{Ph}_2\text{PSiMe}_3$ (0.2 ml, 0.78 mmol) in THF (5 ml) turned a transient yellow colour, before yielding a grey precipitate (ESI Figure S3.1) which was removed *via* cannula filtration. After concentration of the resulting filtrate *in vacuo*, followed by storage at -20°C , crystalline tetraphenyldiphosphine [$(\text{Ph}_2\text{P})_2$] was obtained which matched the phase, unit cell and NMR spectra of the previously reported molecule.²¹ This initial experiment suggested that an unexpected type of reactivity was occurring: instead of observing the

for atoms.

Motivated by this unexpected result, we conducted experiments in d_8 -THF to directly observe all the soluble products. The reaction of InCl_3 and $\text{Ph}_2\text{PSiMe}_3$ gave a remarkably clean ^{31}P NMR spectra (Figure 1). The only two (soluble) products of the reaction visible in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are tetraphenyldiphosphine and diphenylphosphine. This was supported by GC-MS analysis, which gave a $m/z = 370.1$, which matches $(\text{Ph}_2\text{P})_2$ at 77% yield, alongside water/oxidation products (Ph_2PH , $\text{Ph}_2\text{P}(\text{OSiMe}_3)_2$ and $(\text{Ph}_2\text{P}-(\text{O})\text{PPh}_2)$). These can be partially explained by the non-air sensitive capabilities of the GC-MS – confirmed by analysing $\text{Ph}_2\text{PSiMe}_3$, which was pure by NMR spectroscopy, but decomposed in the GC-MS vial. Trace amounts of Ph_2PH can be seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which we attribute to water from InCl_3 – we observe a reduction in this peak intensity by extended drying of the InCl_3 (see Figure S2.9 for “as received” InCl_3 experiments). Further evidence of hydrolysis comes from the occasional formation of small amounts of $\text{Ph}_2\text{POSiMe}_3$ (^{31}P $\delta = 95$ ppm).²² The solvents are anhydrous based upon a representative, clean ^{31}P NMR spectrum of neat $\text{Ph}_2\text{PSiMe}_3$ (ESI Figure S6).

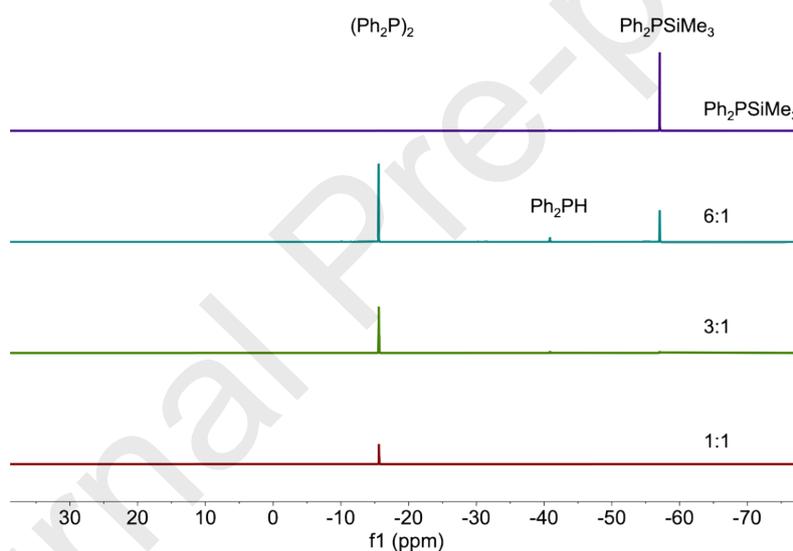


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reactions between $\text{Ph}_2\text{PSiMe}_3$ and InCl_3 at different ratios in d_8 -THF, labelled as P:In on the right-hand side.

This outcome was repeated when InF_3 , InI_3 and $\text{In}(\text{OAc})_3$ were used (ESI Figures S2.1-3), indicating a consistency between different indium salts. We also observe the formation of the corresponding Me_3SiX by-product in ^{29}Si NMR spectra and ^{19}F NMR spectra for InF_3 (ESI Figures S2.4 and S2.5). For all the NMR spectroscopy scale reactions, we observed the same formation of a grey precipitate as seen in the large-scale reactions. We isolated this solid from a 3:1 InCl_3 : $\text{Ph}_2\text{PSiMe}_3$ reaction in THF through cannula filtration and dried it *in vacuo*. A powder X-ray diffraction pattern revealed a good agreement with the formation of indium metal, along with some unreacted InCl_3 (Figure

2).

metallic piece of pure indium (ESI Figure S3.3).

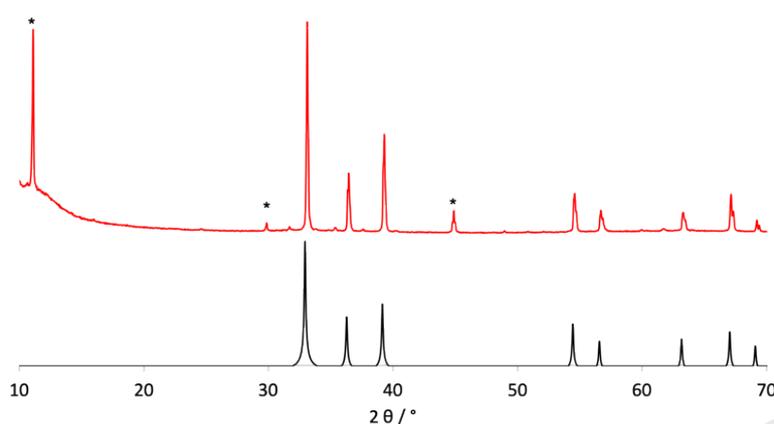


Figure 2. Powder X-ray diffraction pattern of a 3:1 reaction of InCl_3 and $\text{Ph}_2\text{PSiMe}_3$ in THF (red) with that of In metal (black).²³ Residual InCl_3 is present and labelled with a *.

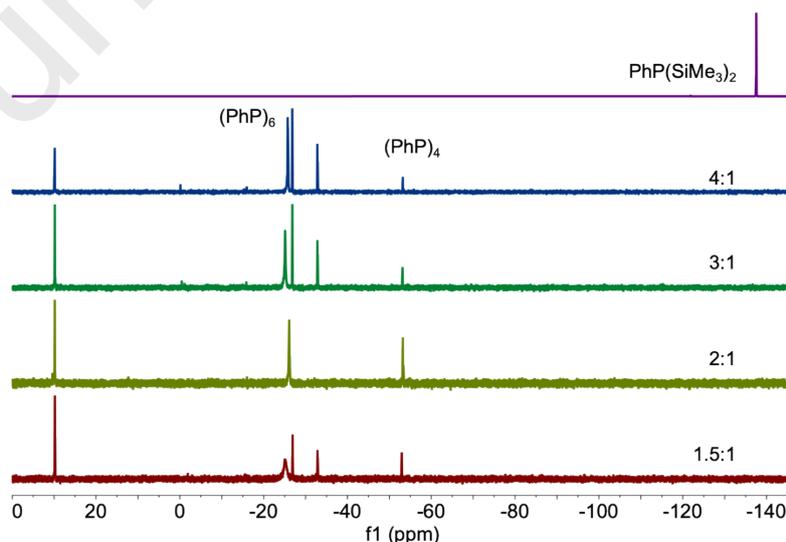
To rule out any involvement of Ph_2PH , we performed test reactions of $\text{In}(\text{OAc})_3$ and diphenylphosphine and observed no formation of $(\text{Ph}_2\text{P})_2$ (ESI Figure S2.7). This indicates that the lability of the P-Si bond is key, with the formation of the Si-X bond providing a driving force. This is analogous to behaviour previously seen in palladium catalysed cross-couplings.²⁴

From these results we proposed a hypothesis that InX_3 salts were mediating a one-electron oxidative coupling of diphenyltrimethylsilylphosphine. Further evidence for the reduction of the indium(III) salts came from the evolution of a purple precipitate during InI_3 reactions (ESI Figure 3.2), which would then disappear upon further heating to form the usual grey precipitate. This purple colour is diagnostic for the formation of indium(I) iodide.²⁵ Reactions with InCl_3 passed through a yellow colour prior to the formation of the grey precipitate, which corresponds to the transient formation of indium(I) chloride. Interestingly, in the InI_3 reactions that were not subject to further heat treatment, we observed the appearance of a new signal at $\delta^{31}\text{P} = -17.5$ (q, $J = 7.0$ Hz), $\delta^{31}\text{P}\{^1\text{H}\} = -17.5$ (s). Heating the reaction mixture resulted in the loss of the purple colour and corresponds to a reduction in intensity of the peak at -17.5 ppm and an increase in the amount of $(\text{Ph}_2\text{P})_2$. We also observed this signal when using InI to probe the reaction mechanism. This signal disappeared when InI is treated with excess amounts of $\text{Ph}_2\text{PSiMe}_3$ (ESI Figure S2.8), and so we cautiously assign it to an adduct of $\text{InI}\cdot\text{Ph}_2\text{PSiMe}_3$. We monitored a reaction utilising InCl_3 over time, where we see broad signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at -23.0 ppm and -31.1 ppm reduce over the course of 2 hours, which is accompanied by an increase in intensity of a pair of doublets centred at $\delta^{31}\text{P}\{^1\text{H}\} = -10.8$ ppm and $\delta^{31}\text{P}\{^1\text{H}\} = -30.9$ ppm ($J = 195$ Hz, ESI Figure S2.10). The broad signals at -23.0 ppm and -31.1 ppm are not present with indium triiodide, thereby suggesting the involvement of indium trichloride. Their short lifetime, coupled with the short lifetime of InCl , suggest that they might be comparable to the adduct of $\text{InI}\cdot\text{Ph}_2\text{PSiMe}_3$ identified at $\delta^{31}\text{P} = -17.5$ ppm. On the other hand, the doublets at $\delta^{31}\text{P}\{^1\text{H}\} = -10.8$ ppm and $\delta^{31}\text{P}\{^1\text{H}\} = -30.9$ ppm are independent of

the oxidation by-product such as the mixed valence P(III)-P(V) species $\text{Ph}_2\text{P}(\text{O})\text{PPh}_2$ when compared to the literature,²⁶ but may relate to tetraphenyldiphosphine coordinated to In(0).

We therefore tentatively propose a reaction scheme (ESI Figure S4.1) where Lewis basic $\text{Ph}_2\text{PSiMe}_3$ forms an adduct with Lewis acidic InX_3 (**1**), before releasing Me_3SiX through the expected desilylation to form **2**. Further examples of $\text{Ph}_2\text{PSiMe}_3$ react to form a doubly phosphinated indium (**3**) before releasing $(\text{Ph}_2\text{P})_2$ and an indium(I) salt. This indium(I) salt can undergo further reduction when subjected to excess silylphosphine. Alternatively, the In(I) salt is relatively unstable and undergoes disproportionation to In(0) and In(III).²⁷ This perhaps explains why elemental indium was only isolated in high yields (95% conversion) when 10-fold excess of the phosphine was used. If In(I) disproportionated, the resultant In(III) could be once more reduced until it was all used up.

Inspired by this reductive coupling, we decided to see if this system could be extended to form larger structures by the use of bis(trimethylsilyl)phenylphosphine [$\text{PhP}(\text{SiMe}_3)_2$]. This species should be able to form catenanted species or rings *via* a two-electron oxidation of phosphorus. This method presents an opportunity to trial a different synthetic route to oligophosphanes or cyclooligophosphanes than the more common dehydrochlorination, reduction, catalytic dehydrogenation or preparation from P_4 . For two excellent recent reviews on the area, see refs. 28 and 29.^{28,29} Test reactions on an NMR scale of $\text{PhP}(\text{SiMe}_3)_2$ and InI_3 , the cleanest oxidising agent for the mono-silylated phosphines, gave rise to a mixture of different species, amongst which could be seen $(\text{PhP})_6$ ($\delta^{31\text{P}} = -22.7$)^{17,30} and $(\text{PhP})_4$ ($\delta^{31\text{P}} = -48.3$),³¹ with no residual starting material left (Figure 3). There are also a number of other peaks that are singlets in both the $^{31\text{P}}$ and $^{31\text{P}}\{^1\text{H}\}$ NMR spectra, indicating that they are either single P units, or symmetrical P dimers. There is no evidence for $(\text{PhP})_5$ ($\delta^{31\text{P}} = -8.27$),^{30,32} $(\text{PhP})_3$ ($\delta^{31\text{P}} = -131 \text{ ppm}$)³¹ or the one-electron reduction species $[\text{Ph}(\text{Me}_3\text{Si})\text{P}]_2$ ($\delta^{31\text{P}} = -108 \text{ ppm}$),³³ and nor are there the expected oxidised P products such as phenylphosphonic acid ($\delta^{31\text{P}} = 20 \text{ ppm}$) or phenylphosphinic acid ($\delta^{31\text{P}} = 47 \text{ ppm}$). We were unable to perform GC-MS, or MS analysis on the products from $\text{Ph}_2\text{PSiMe}_3$, owing to the strong stench and rapid onset of visible decomposition when aliquots were transferred to GC-MS sample vials.



right hand side, with $\text{PhP}(\text{SiMe}_3)_2$ overlaid on top.

The use of indium halide salts as oxidation reagents to catalyse the formation of P-P bonds expands the toolkit available to the synthetic inorganic chemist to make suitable cyclooligophosphanes. There are clear selectivity issues to be overcome with the $\text{PhP}(\text{SiMe}_3)_2$ system, which will be the scope of future work – to selectively form rings of certain sizes. The oxidative capability of indium salts towards silylphosphines should also not be overlooked by materials chemists seeking to make InP quantum dots, as there may be unexpected side reactions taking place.

Conclusions

In conclusion, we have demonstrated that indium(III) and indium(I) salts are non-innocent in terms of redox reactivity with silylphosphines. This has resulted in the observation of one- and two-electron reductive P-P coupling for $\text{Ph}_2\text{PSiMe}_3$ and $\text{PhP}(\text{SiMe}_3)_2$ respectively, with the formation of new P-P bonds resulting in the preparation of $(\text{Ph}_2\text{P})_2$ and the all phosphorus cyclic compounds $(\text{PhP})_4$ and $(\text{PhP})_6$.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Royal Society (research grant) and the UK Government and European Union as contributors to the Smart Energy Network Demonstrator, ERDF project number 32R16P00706) for funding.

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1. General Experimental & Synthetic Procedures
2. NMR Spectra
3. Reaction Pictures
4. References

Journal Pre-proofs

Standard Schlenk line and glovebox techniques were followed for all manipulations in an atmosphere of N₂. THF was distilled from Na/benzophenone and d8-THF distilled from NaK. All chemicals were purchased from Sigma Aldrich Ltd, with the exception of InCl₃ which was purchased from Fluorochem Ltd. InCl₃ was dried by heating to 110 °C under a dynamic vacuum for 8 hours. Ph₂PSiMe₃¹⁸ and PhP(SiMe₃)₂³⁴⁻⁴ were prepared according to the literature procedure.

1.1 General NMR scale reaction procedure

In a glovebox, the In salt was dissolved in d8-THF in a J Youngs NMR tube before the trimethylsilyl phosphine was added and the tube sealed. For heated reactions the tube was heated using an aluminium heating block.

1.2 Full scale reaction

In a glovebox, InCl₃ (295 mg, 1.33 mmol) was dissolved in THF (10 mL) and Ph₂PSiMe₃ (1.03 g, 1 mL, 4.0 mmol) was added. The reaction vessel was transferred to a Schlenk line and heated to reflux overnight. After cooling to RT, the solution was filtered through Celite and concentrated in vacuo to leave (Ph₂P)₂ as a white solid (620 mg, 84% yield). Crystals suitable for X-ray diffraction were obtained from concentrated THF solutions stored at -20°C. ³¹P{¹H} NMR (400 MHz, C₆D₆) δ (ppm) = -14.8 (s).

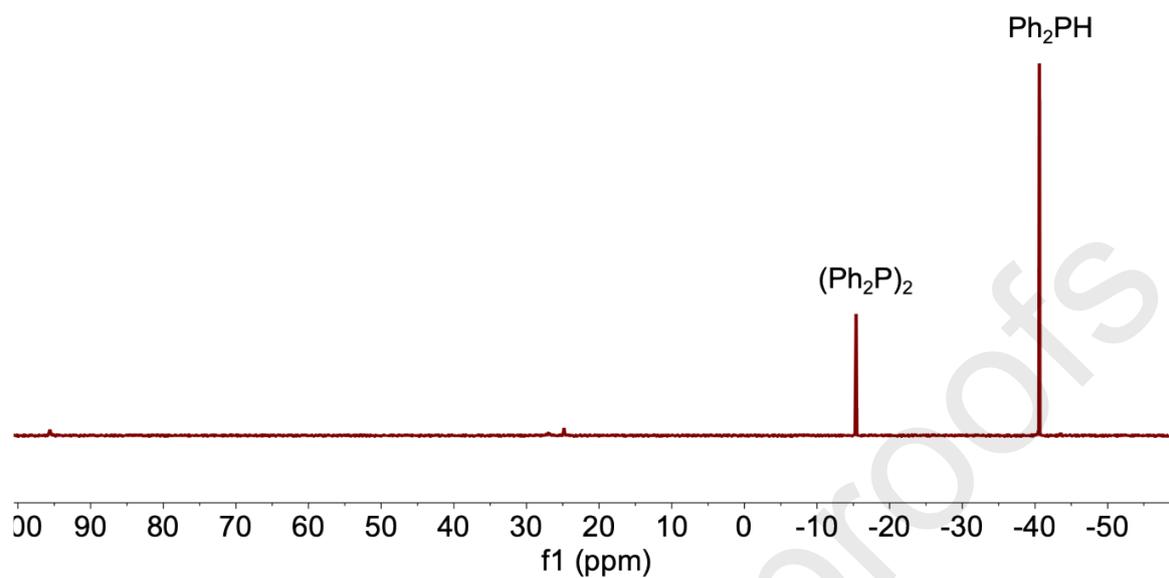


Figure S2.1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{InF}_3$ reaction after heating to reflux for 16 hours.

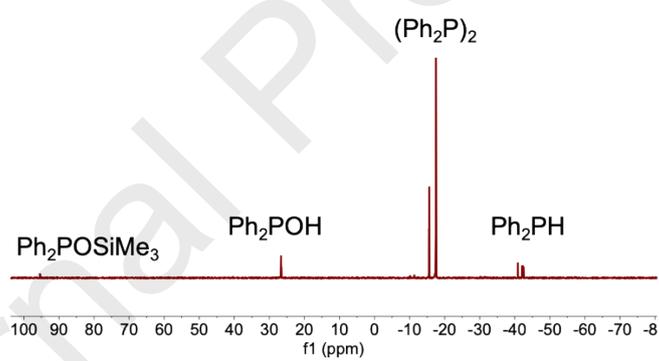


Figure S2.2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{InI}_3$ reaction.

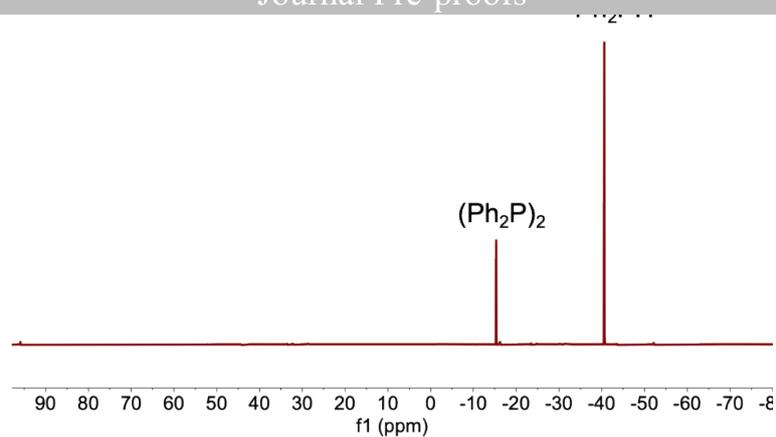


Figure S2.3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{In}(\text{OAc})_3$ reaction after heating to reflux for 16 hours.

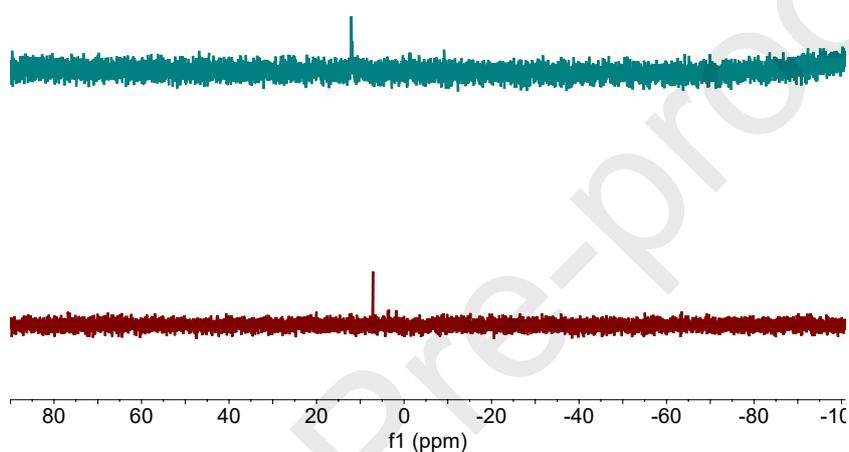


Figure S2.6. ^{29}Si NMR spectra of 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{InF}_3$ (top) and 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{InI}_3$ (bottom) reaction after heating to reflux for 16 hours indicating the presence of Me_3SiF and Me_3SiI respectively.

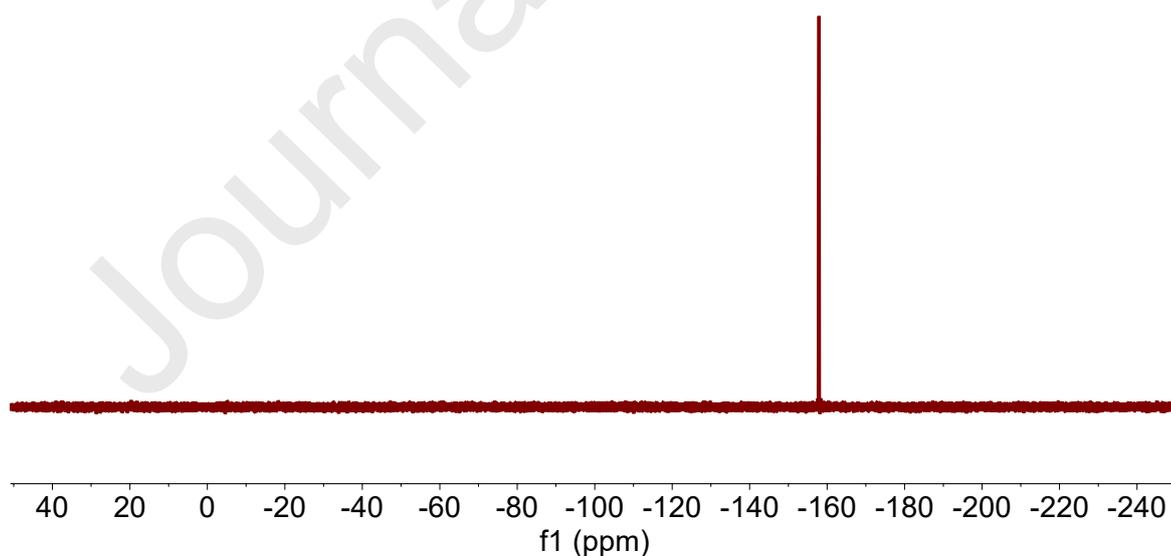


Figure S2.5. ^{19}F NMR spectra of 1:1 $\text{Ph}_2\text{PSiMe}_3:\text{InF}_3$ reaction after heating to reflux for 16 hours.

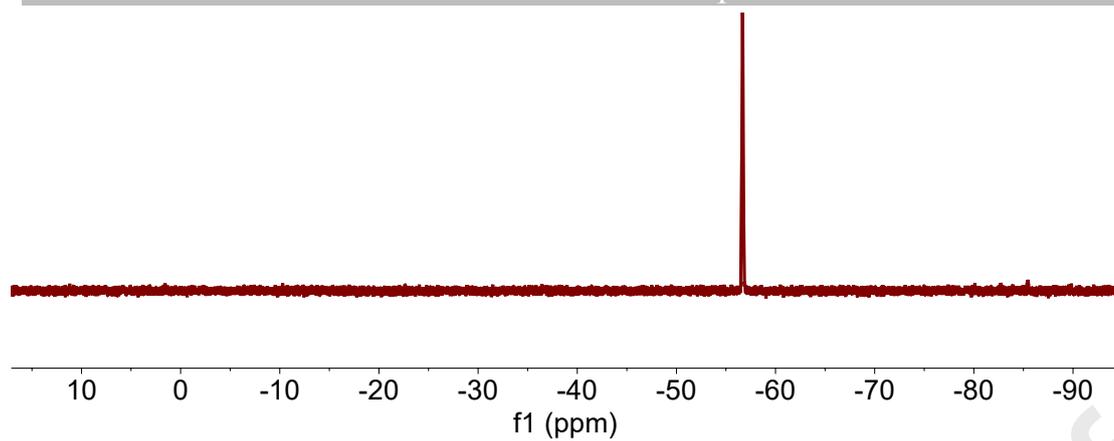


Figure S2.6. ^{31}P NMR spectra of $\text{Ph}_2\text{PSiMe}_3$ showing no hydrolysis.

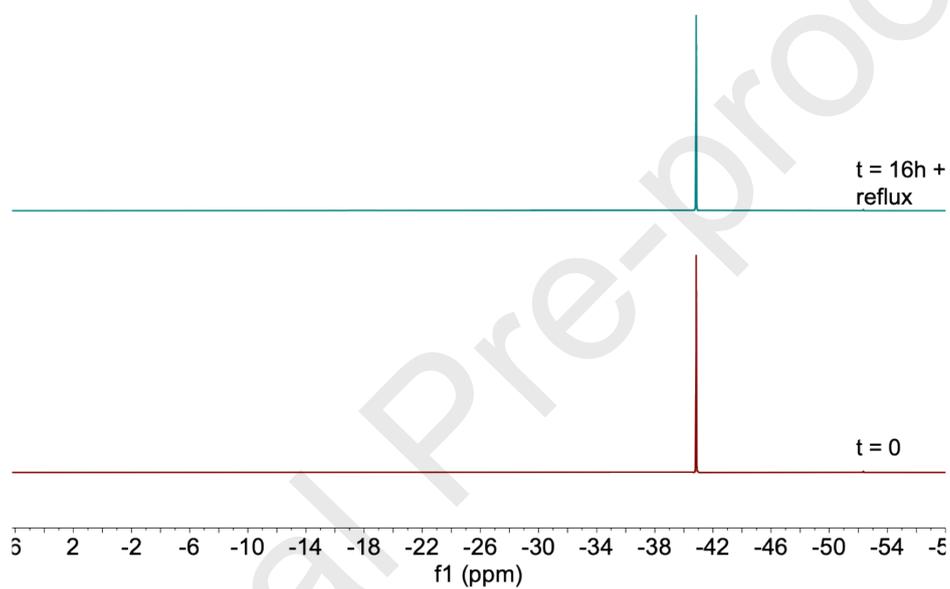


Figure S2.7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction between Ph_2PH_2 and $\text{In}(\text{OAc})_3$ at $t = 0$ h and after heating to reflux overnight indicates no reaction between the two.

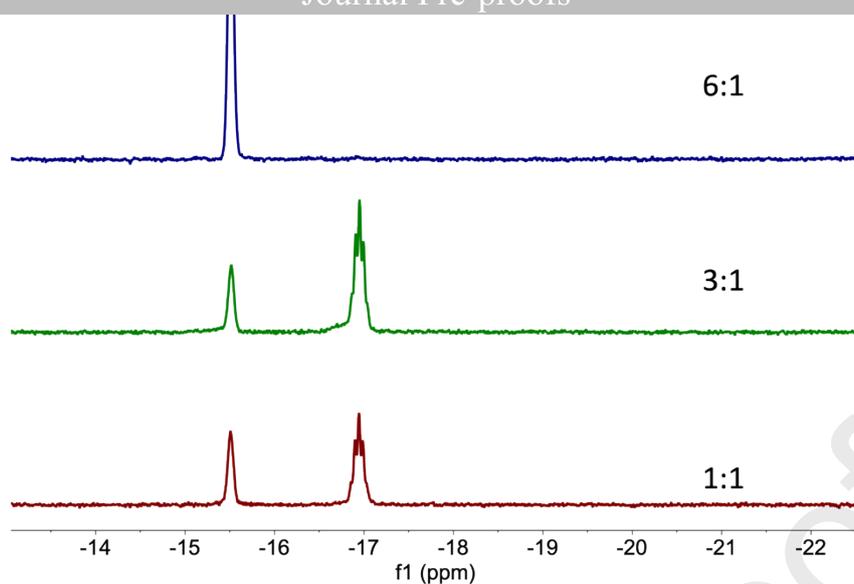


Figure S2.8. ^{31}P NMR spectra of the reaction between $\text{Ph}_2\text{PSiMe}_3$ and InI at ratios of 1:1, 3:1 and 6:1.

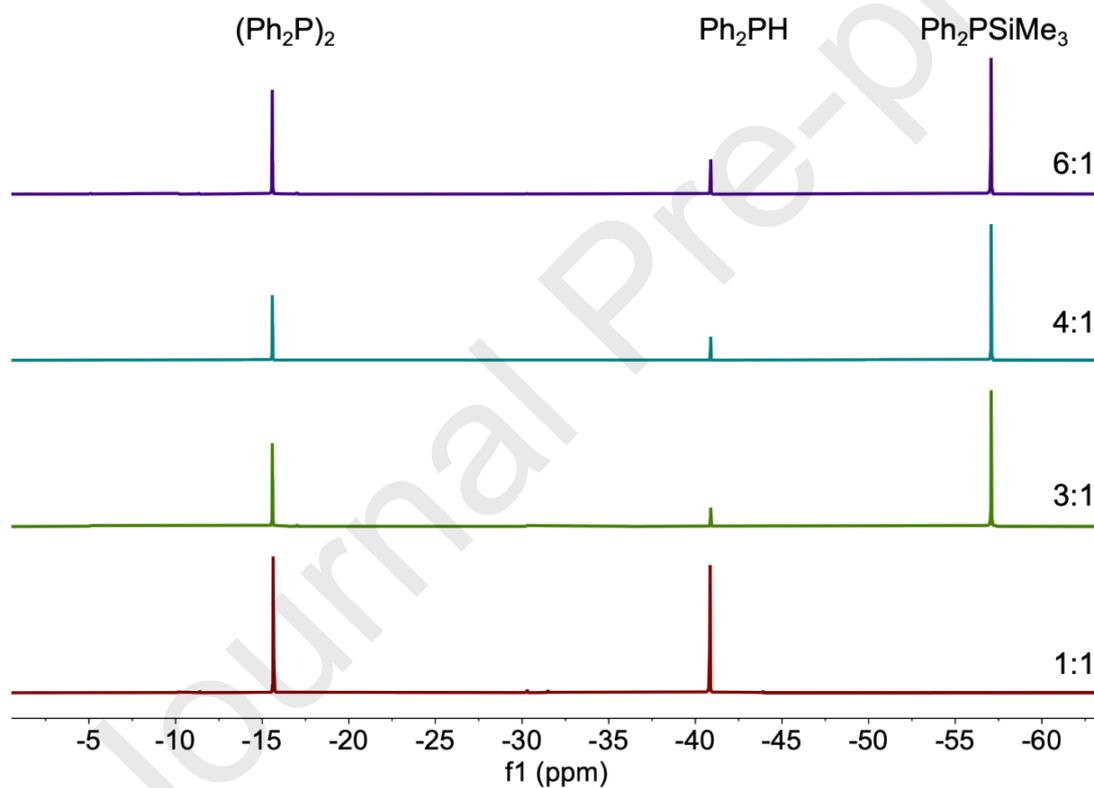


Figure S2.9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reactions between $\text{Ph}_2\text{PSiMe}_3$ and undried InCl_3 at different ratios in d_8 -THF, labelled as P:In on the right-hand side, showing the presence of a large amount of hydrolysis product Ph_2PH .

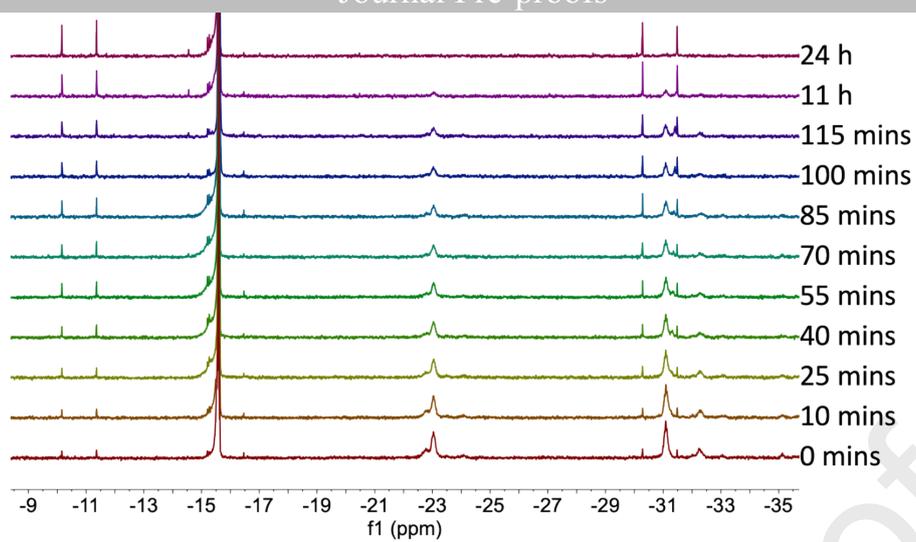


Figure S2.10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a reaction between $\text{Ph}_2\text{PSiMe}_3$ and InCl_3 (3:1) over time in $\text{d}_8\text{-THF}$.

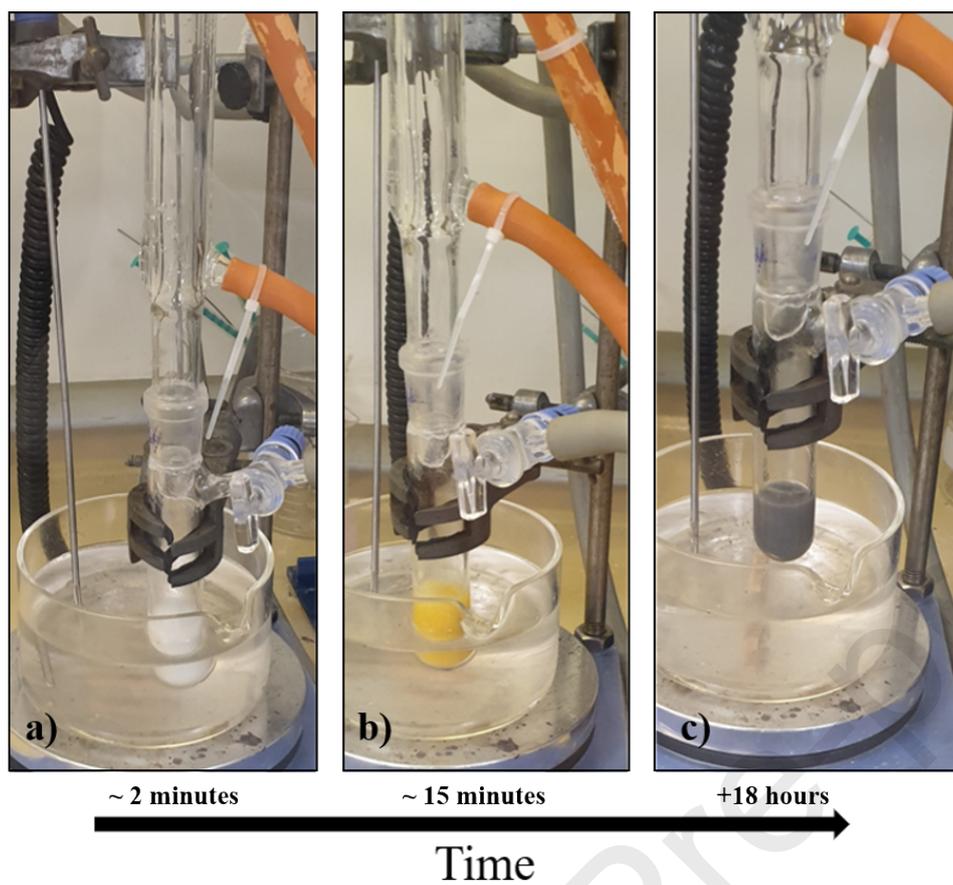


Figure S3.1. Colour progression of a typical $\text{In}(\text{OAc})_3 + \text{Ph}_2\text{PSiMe}_3$ reaction in THF showing the transient formation of .

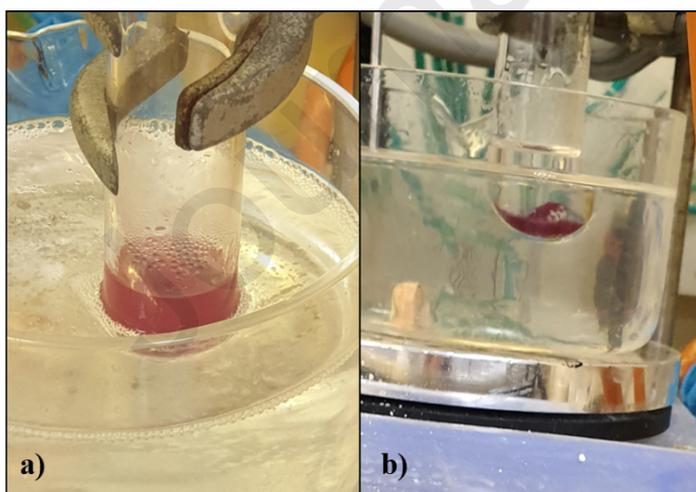


Figure S3.2. Colour change of a typical $\text{InI}_3 + \text{Ph}_2\text{PSiMe}_3$ reaction in THF showing the formation of purple indium(I) iodide.

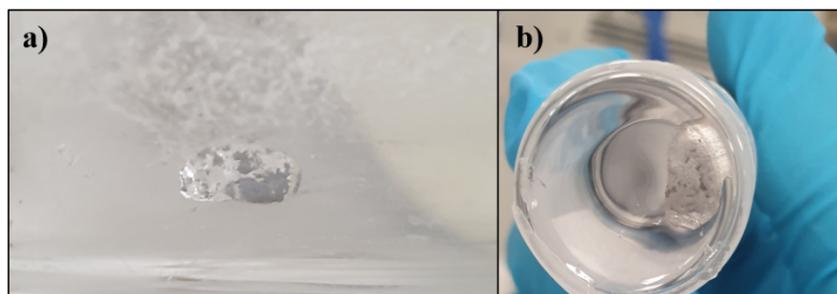


Figure S3.3. Image of indium metal isolated from a reaction of InCl_3 + 10 equivalents of $\text{Ph}_2\text{PSiMe}_3$ in THF.

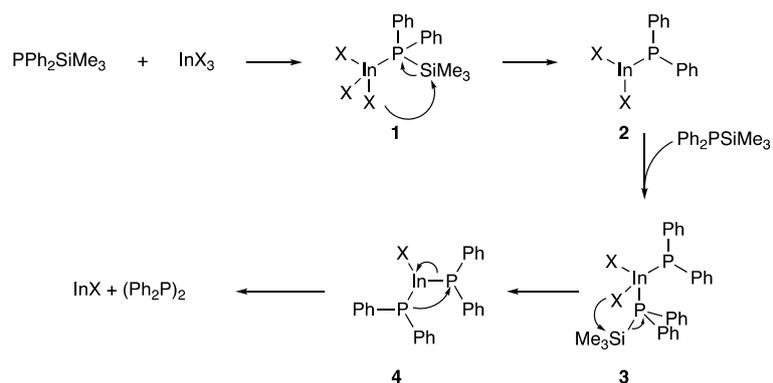


Figure S4.1. Proposed reaction scheme for the formation of tetraphenyldiphosphine.

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Ashleigh J Cartlidge

Methodology

Peter D Matthews

Conceptualization, Methodology, Writing, Project administration

Highlights

- P-P bond formation
- Redox coupling
- Silylphosphines
- Indium(III) reduction
- Phosphorus oxidative coupling

