Synthesis of the bulky phosphanide $[P(Si^{i}Pr_{3})_{2}]^{-}$ and its stabilization of low-coordinate Group 12 complexes.

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Abstract

Here, we report the first practical synthesis of the bulky phosphanide anion $[P(Si'Pr_3)_2]^-$ in synthetically useful yields, and its complexation to Group 12 metals. The ligand is obtained as the sodium salt NaP(Si'Pr_3)_2 **1** in a 42% isolated yield and a single step from red phosphorus and sodium. This is a significant improvement on the previously reported synthesis of this ligand, and we have thus applied **1** to the synthesis of the two-coordinate complexes M[P(Si'Pr_3)_2]_2 (M = Zn, Cd, Hg). These Group 12 complexes are all monomeric and with non-linear P–M–P angles in the solid state, with DFT calculations suggesting that this bending is due to the steric demands of the ligand. Multinuclear NMR spectroscopy revealed complex 2nd order splitting patterns due to strong PP' coupling. This work demonstrates that the synthesis of **1** is viable and provides a springboard for the synthesis of lowcoordinate d-block complexes featuring this unusual bulky ligand.

Introduction

The use of sterically demanding ligands to enforce low-coordination geometries upon d- and f-block metal centres remains an area of interest for inorganic chemists.^{1–5} Such complexes are typically highly reactive and thus capable of acting as a catalyst or activating small molecules.^{3,6–15} These complexes can also display unusual physical properties, such as single molecule magnet (SMM) behaviour.^{16–25} The use of amides as sterically demanding ligands dates to the 1960s, with the use of the [N(SiMe₃)₂][–] ligand to isolate two-coordinate d-block complexes.^{26–28} Since then, a wide array of bulky silylamide ligands have been developed and utilized, such as [N(Dipp)(SiMe₃)][–].^{14,29–35} More recently, the exceedingly bulky [KN(Si[/]Pr₃)₂] has been applied to the synthesis of linear f-block species, which display large magnetic anisotropy and have the potential for extremely high U_{eff} values (U_{eff} = barrier to magnetization,^{36–38} as well as group 2 Lewis acidic cations.³⁹ Most recently, investigations of (^tBu₃Si)₂NH showed the amide to be resistant to deprotonation even by ⁿBuLi/KO^tBu superbase mixtures. However, coordination of (^tBu₃Si)₂N[–] to Cs was achieved through the reaction with Cs⁰/THP electride solution (THP = tetrahydropyran) and the resulting (^tBu₃Si)₂NCs complex was shown to undergo a metathesis reaction when reacted with Lil.⁴⁰

While bulky silylamides are relatively well established, the corresponding phosphorus analogues have received considerably less attention. Studies with $[P(SiMe_3)_2]^-$ ligands afforded dimeric, rather than monomeric, structures due to the larger size of the P atom.^{41–43} To the best of our knowledge, the only two-coordinate metal bis(silylphosphanido) complexes to date are M[P(SiPh_3)_2]₂ (M = Zn, Cd, Hg), prepared by Matchett *et al.*⁴⁴ Here, the higher steric demands of the –SiPh₃ group offset the larger P atom, allowing for isolation of monomeric species. Thus, we propose that the phosphorus analogue of the above-discussed [N(Si'Pr₃)₂]⁻ ligand is of considerable interest due to its steric bulk, which should allow the isolation of monomeric complexes. While the $[P(Si'Pr_3)_2]^-$ ligand is known, it has scarcely been studied due to difficulties in its preparation. Westerhausen *et al.* prepared the Li salt [(THF)LiP(Si'Pr₃)₂]₂ by first reacting "BuLi with PH₃ in the presence of DME (DME = 1,2-dimethoxyethane) to obtain (DME)LiPH₂ in an 82–91% yield.^{45,46} This was then reacted ⁱPr₃SiCl to afford P(Si'Pr₃)₃ (64%) and (ⁱPr₃Si)₂PH (13%).⁴⁷ Further reaction of the minor product (ⁱPr₃Si)₂PH with "BuLi in THF afforded [(THF)LiP(Si'Pr₃)₂]₂ in 83% yield,⁴⁸ giving an overall yield from PH₃ of at most 9.8%. Given the difficult and low-yielding synthesis, [(THF)LiP(Si'Pr₃)₂]₂ was used to prepare only one complex, [(THF)₄Li][(ⁱPr₃Si)₂PW(CO)₅].⁴⁸ As such, the potential of this ligand is largely unexplored.

Herein, we present a much-improved synthesis of an alkali metal complex of this ligand, the Na⁺ salt NaP(SiⁱPr₃)₂ (**1**), which has been obtained in a 42% isolated yield and in a single step. This has allowed us to prepare the family of Group 12 complexes $M[P(SiⁱPr_3)_2]_2$ (M = Zn (**2**), Cd (**3**), Hg (**4**)), demonstrating the synthetic utility of this ligand precursor in transmetallation reactions.

Results and discussion

$NaP(SiⁱPr_3)_2$ 1

To obtain a more direct route to the $[P(Si'Pr_3)_2]^-$ anion than previously reported,⁴⁸ we looked to the synthesis of $P(Si'Pr_3)_3$ published by von Hänisch. Here, red phosphorus was reacted with NaK in refluxing DME to generate $(Na/K)_3P$, which was subsequently reacted with ${}^{i}Pr_3SiCl.^{49}$ Since $P(SiMe_3)_3$ can be converted to $(Me_3Si)_2PH$ by hydrolysis or methanolysis,^{50,51} we postulated that it could be possible to obtain $({}^{i}Pr_3Si)_2PH$ in a similar manner. However, the use of highly pyrophoric NaK alloy was a safety concern. To mitigate this, we instead used Na with 10 mol% naphthalene as an electron transfer agent.⁵² This method has been used previously to generate Na_3P *in situ*,^{53,54} for the preparation of tris(trimethylsilyl)phosphine, $P(SiMe_3)_3$.⁵⁵

In our initial testing, we found that it was necessary to reflux the Na/naphthalene and red P for 24 hours in DME, otherwise the resultant product contained significant amounts of unreacted ^{*i*}Pr₃SiCl and (^{*i*}Pr₃Si)₂. This is believed to occur due to incomplete formation of Na₃P and the presence of unreacted Na. When monitoring the reaction by ³¹P{¹H} NMR spectroscopy, we found that a mixture of P containing species were formed, including (^{*i*}Pr₃Si)₃P and (^{*i*}Pr₃Si)₂PH, which were identified by comparison with the literature.⁵⁶ Another significant ³¹P NMR signal was observed at –378 ppm (compound **1**). By removing the DME *in vacuo*, then extracting the resulting residue in hexane or toluene, it was possible to precipitate **1** from the reaction mixture as a white pyrophoric solid, while P(Si^{*i*}Pr₃)₃, (^{*i*}Pr₃Si)₂PH, and other P-containing by-products remained in solution. ¹H, ¹³C{¹H}, ³¹P, and ³¹P{¹H} NMR spectroscopy of **1** suggested the complex contained an –P(Si^{*i*}Pr₃)₂ moiety with no minor residual solvent peaks (see Supporting Information Figures S2 and S3). While it was not possible to obtain crystals of **1** suitable for single crystal X-ray diffraction studies, crystals of [(THF)NaP(Si^{*i*}Pr₃)₂]₂ (**1a**) were obtained when a reaction mixture containing **1** was dissolved in C₆D₆ and THF (Figure 1) and left at room temperature for four weeks. Based on this structure and the NMR spectroscopic data, we

propose that **1** corresponds to NaP(SiⁱPr₃)₂. Due to the very high sensitivity of **1**, it was not possible to obtain high resolution mass spectrometric data on this compound.

Given that our aim had been to convert $P(Si'Pr_3)_3$ to the $[P(Si'Pr_3)_2]^-$ anion *via* a multi-step process, the observation of **1** was quite exciting. Here, we were directly forming a phosphanide anion in a single step and purifying it by precipitation and filtration. Thus, we focused on optimising the synthesis to maximise the yield of **1**, rather than $P(Si'Pr_3)_3$. This led to the development of the methodology shown in Scheme **1**. Na and 10 mol% naphthalene were refluxed in DME for 24 hours, after which ${}^{i}Pr_3SiCl$ was added and the reaction heated for a further 24 hours. After filtration to remove insoluble impurities, the DME was removed *in vacuo* and the resulting oil was extracted into toluene. This precipitated **1**, which was isolated by filtration in 42% yield and sufficient purity for further synthesis. The crude reaction mixture showed the formation of **1**, $({}^{i}Pr_3Si)_2PH$ and $P(Si'Pr_3)_3$ in an approximate 1:0.28:0.08 ratio (see Supporting Information Figure S6). As $({}^{i}Pr_3Si)_2PH$ has been previously shown to be readily converted to $[(THF)LiP(Si'Pr_3)_2]_2$,⁴⁸ which can also be used in transmetallation reactions, it is suggested that isolation of this by-product would further increase the yield of usable phosphanide precursors from this reaction. Note that, concurrent with our reported work, the Mills group has developed a similar (albeit lower yielding) synthesis of **1**.⁵⁷



Scheme 1. Optimised synthesis of NaP(SiⁱPr₃)₂ (1).



Figure 1. Single crystal XRD structure of $[(THF)NaP(Si'Pr_3)_2]_2$ **1a**. Coordinated THF represented as a wireframe, minor disorder components and hydrogen atoms omitted for clarity. Thermal ellipsoids are set to 50% probability. Atoms marked with ' are obtained using the following symmetry operation, 1-x, +y, $\frac{1}{2}z$. Selected bond lengths (Å) and angles (°): Na1–P1 2.8039(11), Na1–P1' 2.806(1), Na–O1A 2.200(6), Na–O1B 2.203(6), Na–O1C 2.309(3), Na1…Na1' 3.4586(18), P1–Si1 2.2207(8), P1–Si2 2.2163(7), P1–Na1–P1' 103.84(3) Na1–P1–Na1' 76.15(3).

Group 12 complexes 2-4

The two-coordinate Group 12 complexes **2–4** were prepared by the metathesis reaction of **1** with the appropriate metal halide (ZnCl₂, Cdl₂, HgBr₂) in diethyl ether (Scheme 2). The resulting complexes were

isolated as white crystalline solids in moderate to good yields (40–57%) after extraction and recrystallisation from *n*-hexane. For the formation of **3**, it was necessary to use Cdl_2 , as reactions between **1** and $CdCl_2$ in diethyl ether led to the precipitation of Cd(0). Complexes **2**–**4** are air and moisture sensitive and were characterized by single crystal X-ray diffraction and multinuclear NMR spectroscopy. Complex **2** was also characterized by HRMS and CHN microanalysis; the high toxicity of complexes **3** and **4** precluded their analysis by these methods.

NaP(SiⁱPr₃)₂ + MX₂ $\xrightarrow{Et_2O, RT, 16 h}$ -2 NaX $\stackrel{i}{\rightarrow} Pr_3Si \xrightarrow{P} M \xrightarrow{SiⁱPr_3}$ 1 2: M = Zn 3: M = Cd 4: M = Hg

Scheme 2: Synthesis of Group 12 bis(silylphosphanido) complexes 2-4. MX₂ = ZnCl₂, Cdl₂, HgBr₂.



Figure 2: View of the single crystal X-ray diffraction structures of a) **2**, b) **3** and c) **4**. Hydrogen atoms and minor disorder components of **3** and **4** omitted for clarity. Thermal ellipsoids shown at 50% probability.

	2	2a	3	4
M1-P1	2.2291(3)	2.2309(4)	2.4213(7)	2.3946(5)
M1–P2	2.2234(4)	2.2562(4)	2.4216(7)	2.3930(5)
P1–Si1	2.2532(4)	2.2629(4)	2.2571(7)	2.2614(7)
P1–Si2	2.2537(4)	2.2550(5)	2.2487(7)	2.2657(8)
P2–Si3	2.2456(4)	2.2598(5)	2.2557(8)	2.2644(7)
P2–Si4	2.2479(4)	2.2527(4)	2.2570(6)	2.2541(8)
P1-M1-P2	168.747(12)	163.593(18)	169.215(19)	170.086(16)
∑° around P1	334.141(18)	337.05(13)	330.52(3)	325.73(3)
∑° around P2	339.755(17)	322.26(13)	324.87(3)	331.16(3)

Table 1. Selected bond lengths (Å) and angles (°) for $M[P(Si^{i}Pr_{3})_{2}]_{2}$ (M = Zn (2), Cd (3), Hg (4)). Complexes 2, 3, and 4 were crystallised from *n*-hexane. 2a is a polymorph of 2 crystallised from diethyl ether.

Crystals of **2**–**4** suitable for single crystal X-ray diffraction were obtained from storage of saturated *n*-hexane solutions at –30 °C (Figure 2). A polymorph structure of **2** (**2a**) was also obtained by slow evaporation from diethyl ether (Figure S1. **2** and **2a** crystallise in the same space group ($P\overline{1}$) but with a differing unit cell (Table S1) and with significantly different P1–Zn1–P2 angles [168.747(12)° *vs* 163.593(18)°]. All structures show **2**–**4** to be monomeric and two-coordinate in the solid state. The M1–P1 and M1–P2 bond lengths (Table 1) are similar to those seen in the terminal silvl phosphanido groups in[M(P(SiMe_3)_2{\mu_2-P(SiMe_3)_2}]_2 (Zn–Pt 2.295(1) Å, Cd–Pt 2.459(1) Å and Hg–Pt 2.402(1) Å).⁴² The P–Si bond lengths differ slightly between complexes [2.2479(4)–2.2657(8) Å, Table 1] but are consistent with P–Si single bonds, with little evidence of P–Si double bond character [typical P=Si distances 2.062(1)-2.158(2) Å].⁵⁸ The sum of the angles around each phosphorus centre (Σ° , Table 1) is also consistent with an sp³ hybridized P atom (*i.e.* no P=Si bond character). All of the complexes exhibit a P–M–P unit, with this angle increasing from Zn > Cd > Hg (Table 1).

Closed-shell, two-coordinate metal complexes are frequently linear, 59-68 although non-linear species are known.^{66,69–71} Given that the only previous Group 12 bis(silylphosphanido) complex to be structurally characterized (Cd[P(SiPh₃)₂]₂) was linear,⁴⁴ DFT calculations were used to probe the reasons for the deviation from linearity for 2-4 in the solid state. Geometry optimizations were performed on 2-4 (PBE0/SARC-ZORA-TZVP for Cd and Hg, PBE0/ZORA-def2-TZVP for all other atoms).72-79 The optimized structures were in good agreement with those determined experimentally, and in all cases reproduced the non-linear P–M–P (M = Zn, Cd, Hg) bond angles (Table S2). Models of 2–4 were also optimized with a 180° P–M–P bond angle restraint, affording linear models (2', 3', 4'). These linear models were found to be significantly *less* thermodynamically stable than the bent structures (ΔG = 13.3 kcal mol⁻¹ for Zn; 10.7 kcal mol⁻¹ for Cd; 8.9 kcal mol⁻¹ for Hg). The linear structures show significant distortion about the P atoms, with asymmetry in the M-P-Si angles (Figure S31, Table S2). By contrast, the M–P–Si groups in the non-linear optimized structures were more symmetric (Figure S32, Table S2). This suggests that the bent P–M–P bond angles are a consequence of the steric demands of the $[P(Si'Pr_3)_2]^-$ ligands. To fit these ligands around the metal, it is necessary to distort at either the metal centre or the P atoms, with the distortion at the metal being more favourable. The solid state structure of Cd[P(SiPh₃)₂]₂ shows relatively symmetric Cd–P–Si angles (100.9(2)°, 98.2(1)°) and a linear P-Cd-P angle,⁴⁴ suggesting that a smaller ligand removes the need for distortion. Geometry optimization (without restraints) of the less sterically demanding $Cd[P(SiMe_3)_2]_2$, starting from linear and non-linear geometries, afforded both linear (P–Cd–P = 179.9°) and near-linear (P–Cd– P = 177.5°) molecules. These two geometries showed near-identical energies ($\Delta G = 0.1 \text{ kcal mol}^{-1}$), suggesting that there is little energetic difference between these two coordination environments for the less sterically demanding $[P(SiMe_3)_2]^-$ ligand.

NMR spectroscopic analysis

The ¹³C{¹H} NMR spectra of **2**–**4** (Figure 3) and the ²⁹Si NMR spectrum of **4** (Figure 4) show evidence of second order effects due to strong virtual coupling between the ³¹P nuclei (²J_{PP'}). Similar effects have been reported in the literature for analogous phosphorus-carbon ABX and AA'X systems.^{80–82} Despite the different appearances of the ¹³C{¹H} NMR signals, the ²J_{CP} and ³J_{CP} coupling constants are similar across the series [²J_{CP} = 10.7 Hz (**2**), 10.3 Hz (**3**), 10.2 Hz (**4**); ³J_{CP} = 3.6 Hz (**1**) 3.7 Hz (**2**), 3.5 Hz (**4**)]. This indicates that the differences between **2**–**4** are likely caused by the changing magnitude of ²J_{PP'} across the series.

While the ²⁹Si NMR spectra of **2** and **3** show apparent doublets, that of **4** is more complex, consistent with an AA'X spin system with virtual coupling. This spectrum was well simulated with parameters of ${}^{1}J_{\text{SiP}} = 50.6 \text{ Hz}$, ${}^{3}J_{\text{SiP}'} = 0.0 \text{ Hz}$, ${}^{2}J_{\text{PP}'} = 19.0 \text{ Hz}$ (Figure 4). This ${}^{2}J_{\text{PP}'}$ coupling of 19.0 Hz was also used to successfully simulate the ${}^{13}\text{C}{}^{1}\text{H}$ NMR signals of **4** (see Supporting Information Figures S25 and S26), further supporting this value for ${}^{2}J_{\text{PP}'}$.

Also of note are the ²⁹Si satellites in the ³¹P{¹H} NMR spectra of **2**–**4**. While **2** and **4** show apparent ²⁹Si satellites, the measured coupling from these satellite peaks does not match that found in the ²⁹Si NMR spectra. This is likely due to the presence of one spin-active ²⁹Si nucleus causing the two ³¹P nuclei to become magnetically inequivalent, such that the satellite signal is not a simple doublet. For **3**, the measured ²J_{SiP} from the satellites does match the ²⁹Si NMR spectrum, suggesting that the two P atoms are (closer to) magnetically equivalent in **3**. The ³¹P{¹H</sup> NMR signal for **4** ($\delta_P = -209$ ppm) occurs significantly downfield of the signals for **2** or **3** ($\delta_P = -288$ and -284 ppm, respectively), which is consistent with previously published Group 12 bis(silylphosphanido) complexes.⁴⁴ The ¹¹³Cd and ¹⁹⁹Hg NMR spectra of **3** and **4** both appear as triplets, with large couplings to phosphorus (¹J_{CdP} = 350 Hz, ¹J_{HgP} = 408 Hz).



Figure 3: ¹³C{¹H} NMR spectra of a) **2**, b) **3**, and c) **4** showing the extent of virtual coupling.



Figure 4: The experimental (red) and simulated (blue) ²⁹Si NMR spectrum of **4**, modelled using the parameters ${}^{1}J_{SiP} = 50.6$ Hz, ${}^{3}J_{SiP'} = 0.0$ Hz and ${}^{2}J_{PP'} = 19.0$ Hz.

Conclusions

We present the first one-step synthesis of a source of the phosphanide anion $[P(Si'Pr_3)_2]^-$, in the form of NaP(Si'Pr_3)₂ (**1**). Complex **1** was obtained in 42% isolated yield, far higher than the previously reported Li phosphanide $[(THF)LiP(Si'Pr_3)_2]_2$, thereby offering a significantly improved route to the practical use of this ligand in synthesis. $[(THF)NaP(Si'Pr_3)_2]$, **1a** obtained from the solvation of **1** in THF, was characterized by single crystal X-ray diffraction. With this synthetically useful methodology to **1**, we were able to complex this sterically demanding phosphanide ligand to Zn, Cd, and Hg, affording the novel two-coordinate complexes **2–4**. Single crystal X-ray diffraction revealed that complexes **2–4** all show significant deviations from linearity in the solid state, with DFT calculations suggesting this is due to the steric demands of the ligand. ¹³C{¹H} and ²⁹Si{¹H} NMR spectroscopy of these ligands revealed strong second-order effects, suggesting the presence of virtual coupling between the two ³¹P nuclei in these complexes. These studies show that $[P(Si'Pr_3)_2]^-$ is now an accessible bulky, monodentate, monoanionic ligand.

Acknowledgements

We acknowledge the EPSRC [grant number EP/R004064/1; grant number EP/S023909/1]; the Leverhulme Trust [grant number RPG-2021-183] and the University of Nottingham for financial support of this research. We thank Prof. David Mills and co-workers at the Department of Chemistry, University of Manchester, for invaluable chemical discussions regarding the synthesis of the $[P(Si'Pr_3)_2]^-$ complexes. We also thank the University of Nottingham Analytical Services Team for mass spectrometry, CHN microanalysis, and NMR spectroscopy measurements. We thank Dr Kevin Butler and Dr Huw Williams at the University of Nottingham for advice on simulating NMR spectra. We are also grateful for access to the University of Nottingham's Ada High Performance Computing Service.

Associated Content

Electronic Supplementary Information (ESI) available: full experimental details for the synthesis, characterization, crystallographic data, and CIF files. The CCDC (2372409–2372413) contains the supplementary crystallographic data for this paper. A data repository containing computational output files and spectroscopic data in their raw (NMR) and processed forms (IR, mass spectrometry, CHN) can be found via the following DOI: http://doi.org/10.17639/nott.7443.

Conflicts of interest

There are no conflicts to declare.

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