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Synthesis and crystal structures of novel silylsubstituted diphosphanes

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ABSTRACT

Reaction of two equivalents of lithium hypersilylphosphanide (hypersilyl, Hyp = tris(trimethylsilyl)silyl) with dichlorotetramethyldisilane at low temperatures gives $[HypPH–SiMe_2–]_2$ **1**, a compound with high steric protection on both phosphane functionalities. Dehydrogenation reaction of **1** with *n*-butyl lithium yields the dilithiated [2.1.1] bicyclic phosphanide salt $[HypPLi–SiMe_2–]_2$ **2**. The bicyclic structure is confirmed by NMR spectroscopy and X-ray diffraction analysis. As a major byproduct during the synthesis of **1** as well as *via* reaction of **2** with dichlorotetramethyldisilane, 1,4-diphospha-cyclosilahexane $[HypP–(SiMe_2)_2–]_2$ **3** is obtained. X-Ray diffraction analysis shows exclusive formation of the *trans*-conformer **3a** in the solid state, which is supported by calculations at the level of density functional theory (DFT).

1. Introduction

Compounds featuring two σ^3-P atoms, e.g. diphosphanes, have been known in literature for many years. Similar to their monophosphane counterparts [1,2], diphosphanes are frequently used as ligands to transition metals. As a result of the electron donating properties of phosphorus, complexes of the general type $(R_2P–CH_2–)_2M$ (Fig. 1, Type **A**, with R = Me, Ph, and larger substituents; M = Ru, W, Mo) as well as coordination compounds with various group 14 metal halides have been synthesized [3,4]. In all those compounds, the ligands are providing stabilization through interaction of the lone pairs located on the phosphorus atom [5,6]. In contrast to those diphosphane ligands, diphosphanide-based (Type **B**) complexes with a covalent P–M bond are not that common, though known for some 30 years [7].

All compounds mentioned so far feature a carbon moiety as a backbone (chains or parts of aromatic ring systems) connecting the phosphorus atoms; corresponding silicon derivatives $(R_2P–SiMe_2–)_2$ (Type **C**) and $(RP–SiMe_2–)_2M$ (Type **D**) are comparatively unexplored.

For effective ligand design and synthesis, small building blocks as precursors are advantageous. $[H_2P–SiMe_2–]_2$ and its methyl derivative $[MePH–SiMe_2–]_2$ [8] are ideal starting points for synthesis, providing a hydrogen functionality which could easily be used for either introduction of a bulky substituent or formation of a covalent metal–P bond *via* the corresponding lithiated compounds $[HPLi–SiMe_2–]_2$ and $[MePLi–SiMe_2–]_2$, or similar dianionic intermediates. Aside from similar compounds with a larger aliphatic moiety ($[iPrPH–SiMe_2–]_2$ [9]) aromatic systems such as the type **D** derivative of $[PhPH–SiMe_2–]_2$ are also known [10,11]. Abstraction of the hydrogen is not obligatory; the molybdenum complex $[PhPHSiMe_2–]_2Mo(CO)_4$ [12] shows a donor–acceptor interaction pattern similar to its methyl-substituted derivate $[Me_2P–SiMe_2–]_2Mo(CO)_4$ [13]. Tetraphenylated $[Ph_2P–SiMe_2–]_2$ has been synthesized by Hassler [14] but has not found any application thus far.

Further variations of P-substituents have been achieved through introduction of boron based moieties. $\{[(iPr_2N)_2B]PH–SiMe_2–\}_2$ [15] has been proven to be a suitable type **C** ligand for the molybdenum tetracarbonyl complex $\{[(iPr_2N)_2B]PH–SiMe_2–\}_2Mo(CO)_4$ [16]. The corresponding [2.1.1] bicyclic derivative, $\{[(iPr_2N)_2B]PSiMe_2–\}_2$, has also shown the ability to form complexes with iron pentacarbonyl [17].

While all these compounds feature a $(SiMe_2-)_2$ backbone, corresponding derivatives with a silicon-based terminal P-substituent, that could provide kinetic stabilization, have not been reported to date. In group 14 chemistry, $SiMe_3$ groups have been used as sterically demanding, stabilizing substituents for several years [18–20]. In 2006, Hassler et al. reported on several phosphanes and diphosphanes featuring a bulky $–Si(SiMe_3)_3$ group, most interestingly simple hypersilylphosphane $[(SiMe_3)_3Si–PH_2]$ [21]. Linkage of those monophosphane building blocks opens the way to a new type of diphosphane system. In this work we present the synthesis and full characterization of such type **C** and **D** compounds.

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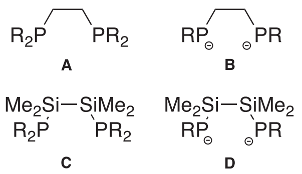

Fig. 1. Diphosphane and diphosphanide structure motifs.

2. Experimental

2.1. General procedures

All reactions, unless otherwise stated, were carried out using standard Schlenk line techniques or in a glovebox under nitrogen atmosphere. All dried and deoxygenated solvents were obtained from a solvent drying system (Innovative Technology, Inc.). C_6D_6 was distilled over sodium and stored under nitrogen atmosphere. *n*-Butyl lithium and potassium *tert*-butylate were purchased from Aldrich and used as received. Dichlorotetramethyldisilane was prepared following standard procedures [22]. $HypPH_2$, HypPHLi, $HypP(SiMe_3)_2$ $HypP(SiMe_3)K$ were prepared following procedures previously published [21]. After successful synthesis, all compounds were stored under inert conditions at room temperature and were stable for several months.

2.2. NMR

^1H (300.2 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz) and ^{31}P (121.5 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25 °C. Chemical shifts are given in parts per million (ppm) relative to TMS ($\delta = 0$ ppm) regarding ^1H, ^{13}C and ^{31}Si and relative to 85% H_3PO_4 for ^{31}P. Coupling constants (J) are reported in Hertz (Hz). All NMR spectra were measured in C_6D_6. Reactions were monitored using a D_2O capillary as external lock signal.

2.3. X-ray diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk under inert conditions and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by an Oxford Cryosystems cryometer. Single crystal data collection was performed on a BRUKER APEX II diffractometer with use of Mo Kα radiation ($\lambda = 0.71073$ Å) and a CCD area detector. Empirical absorption corrections were applied using SADABS [23,24]. The structures were solved with use of either direct methods or the Patterson option in SHELXS and refined by the full-matrix least-squares procedures in SHELXL [25,26]. The space group assignments and structural solutions were evaluated using PLATON [27,28]. Disorder, as observed for compound **2** was handled by modeling the occupancies of the individual orientations using free variables to refine the respective occupancy of the affected fragments [26]. Disordered positions for the coordinated solvent diethyl ether were refined using 70/30 split positions. Disorder in the terminal $SiMe_3$ groups was refined using 50/50 split positions. Table 1 contains crystallographic data and details of measurements and refinements for compounds **1**–**3a**. CCDC 986633, 986634 and 986635 contain the Supplementary crystallographic data for compounds **1**–**3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. Computational details

All calculations have been carried out using the Gaussian09 program package [29] on a computing cluster with blade architecture. For all calculations except calculations of NMR shieldings the mPW1PW91 hybrid functional [30] was used. NMR shieldings were calculated using the M06L [31] pure functional as implemented in Gaussian09. For optimizations and calculation of frequencies the Stuttgart/Dresden basis set denoted by SDD as implemented in Gaussian09 was used, consisting of the D95 basis set [32] for elements up to Argon and Stuttgart/Dresden ECPs for heavier elements [33,34]. For calculation of NMR shieldings the all electron IGLO-II [35] basis set was used.

2.5. Synthesis

2.5.1. Synthesis of $[HypPH–SiMe_2–]_2$ **1**

A solution of HypPHLi (1.17 g, 4.10 mmol) in 6 mL of diethyl ether was cooled to −78 °C and slowly added to a cooled (−78 °C) solution of $Me_4Si_2Cl_2$ in 10 mL of toluene *via* cannula under vigorous stirring. The reaction was allowed to warm up to room temperature and was vigorously stirred for 16 h. After removal of solvents under reduced pressure the residue was dissolved in pentane and filtered from salts. Crystals suitable for X-ray diffraction analysis were obtained from pentane at −30 °C. ^1H NMR (C_6D_6, 293 K): δ 0.31 ppm (54H, d, $(Me_3Si)_3Si$, $^4J_{PH} = 2.4$ Hz), 0.55 ppm (12H, d, Me_2Si, $^3J_{PH} = 4.2$ Hz), 1.06 ppm (2H, d, PH, $^1J_{PH} = 193.8$ Hz). ^{13}C NMR (C_6D_6, 293 K): δ 1.3 ppm (18C, s, $(Me_3Si)_3Si$), 1.6 ppm (6C, s, Me_3Si). ^{29}Si NMR (C_6D_6, 293 K): δ −99.4 ppm (2Si, dd, $^1J_{SiP} = 74.0$ Hz, $^4J_{SiP} = 2.4$ Hz, $(Me_3Si)_3Si$), −16.3 ppm (2Si, dd, $^1J_{SiP} = 57.9$ Hz, $^2J_{SiP} = 23.9$ Hz), −10.7 ppm (6Si, "t", $^2J_{SiP}$ 5.1 Hz, $(Me_3Si)_3Si$). ^{31}P NMR (C_6D_6, 293 K): δ −263.8 ppm (2P, d, $^1J_{PH} = 193.8$ Hz). Yield: 1.01 g, 73%.

2.5.2. Synthesis of $[HypPLi–SiMe_2–]_2$ **2**

$[HypPH–SiMe_2–]_2$ (2.04 g, 3.02 mmol) was dissolved in 10 mL of diethyl ether and cooled to −78 °C. 4.13 mL (6.60 mmol) of 1.6 M *n*-butyl lithium in hexanes were added drop-wise *via* syringe to the solution through a septum. After removal of cooling the reaction was stirred for 2 h. Solvents were removed under reduced pressure and replaced with toluene. Crystals suitable for X-ray diffraction analysis were obtained from toluene at −30 °C. ^1H NMR (C_6D_6, 293 K): δ 0.40 ppm (54H, s, $(Me_3Si)_3Si$), 0.62 ppm (12H, broad s, Me_2Si). ^{13}C NMR (C_6D_6, 293 K): δ 1.9 ppm (18C, s, $(Me_3Si)_3$-Si), 2.0 ppm (6C, s, Me_3Si). ^{29}Si NMR (C_6D_6, 293 K): δ −97.8 ppm (2Si, "t", $^1J_{SiP} = 36.9$ Hz, (Me_3Si) $_3Si$), −25.7 ppm (2Si, "t", $^1J_{SiP} = {}^3J_{SiP} = 21.1$ Hz), −15.2 ppm (6Si, "t", $^2J_{SiP} = 4.0$ Hz, $(Me_3Si)_3Si$). ^{31}P NMR (C_6D_6, 293 K): δ −337.9 ppm (2P, sep, $^1J_{PLi} = 55.5$ Hz). Yield: 1.83 g, 88%.

2.5.3. Synthesis of $[HypP–(SiMe_2)_2–]_2$ **3a**

A solution of $[HypPLi–SiMe_2–]_2$ (0.80 g, 1.16 mmol) in diethyl ether was added to a cooled (−78 °C), vigorously stirred solution of dichlorotetramethyldisilane *via* cannula. After letting the reaction solution warm up to room temperature, the solvent was removed under reduced pressure and replaced by pentane. Crystals suitable for X-ray diffraction analysis were obtained from pentane at −30 °C. ^1H NMR (C_6D_6, 293 K): δ 0.57 ppm (12H, d, $^3J_{HP} = 5.4$ Hz, $SiMe_2$), 0.36 ppm (54H, s, $SiMe_3$). ^{13}C NMR (C_6D_6, 293 K): δ 2.84 ppm (4C, "t", $^2J_{CP} = 4.3$ Hz, $SiMe_2$), 3.19 ppm (18C, "t", AMM′, $^3J_{CP} = 1.0$ Hz, $SiMe_3$). ^{29}Si NMR (C_6D_6, 293 K): δ −94.3 ppm (2Si, dd, $^1J_{PSi} = 106.1$ Hz, $^3J_{PSi} = 98.6$ Hz, $Si(SiMe_3)_3$), −14.9 ppm (dd, $^1J_{SiP} = 83.5$ Hz, $^2J_{SiP} = 34.5$ Hz, $SiMe_2$), −10.7 ppm (6Si, "t", $^2J_{PSi} = 8.7$ Hz, $SiMe_3$). ^{31}P NMR (C_6D_6, 293 K): δ −269.4 ppm (2P, s). Yield: 0.84 g, 92%.