



Silver tetrakis(hexafluoroisopropoxy)aluminate as hexafluoroisopropyl transfer reagent for the chlorine/hexafluoroisopropyl exchange in imino phosphanes

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ABSTRACT

Treating 1,3-dichloro-2,4-bis[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane, [HypNPCl]₂ ((Me₃Si)₃Si = Hyp), or *N*-(2,4,6-tri-*tert*-butylphenyl)imino(chloro)phosphane, Mes⁺-N=P-Cl (Mes⁺ = 2,4,6-tri-*tert*-butylphenyl), with Ag[Al(OCH(CF₃)₂)₄] leads to the abstraction of [OCH(CF₃)₂]⁻ from the counter ion [Al(OCH(CF₃)₂)₄]⁻ in a formal Lewis acid/Lewis base reaction. The final products Hyp₂N₂P₂(Cl)-(OCH(CF₃)₂), Mes⁺-N=P-OCH(CF₃)₂ and the dimeric Lewis acid [Al(OCH(CF₃)₂)₂]₂ have been characterized by means of X-ray analysis.

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1. Introduction

In the last two decades 1,3-dichloro-*cyclo*-diphosphadiazanes [RNPCl]₂ with several groups R have been intensively studied, as they are used as potential starting materials for e.g., ring-opening and transformation reactions, oligomerization and polymerization [1–4] or the preparation of macrocycles, polymers, main-group complexes and the generation of cyclic binary PN cations [5,6]. Only little is known of 1-chloro-*cyclo*-diphosphadiazanium salts of the type [R₂N₂P₂Cl]⁺ [6a]. These cyclic phosphorus–nitrogen cations have been synthesized by chloride abstraction from kinetically stabilized 1,3-dichloro-*cyclo*-diphosphadiazanes. The monochlorodiphosphadiazanium cation ([R₂N₂P₂Cl]⁺, R = ^tBu) was first observed by Cowley et al. [7] in the reaction of the corresponding *cyclo*-diphosphadiazane with AlCl₃. Burford et al. [8] assumed 1-halo-2,4-di(aryl)-*cyclo*-1,3-dipnicta-2,4-diazanium cations as reactive intermediate species in the reaction of [RNPX]₂ (R = 2,6-dimethylphenyl, 2,6-diisopropylphenyl; X = Cl, Br) with GaX₃, which led to trimeric species [RNPX]₃ via GaX₃ induced heterocycle expansion [9]. The supermesityl substituted iminophosphonium

cation as tetrachloridoaluminate salt [Mes⁺-N=P][AlCl₄] was first prepared by Niecke et al. by means of chloride abstraction from Mes⁺-N=P-Cl with AlCl₃ as Lewis acid [15].

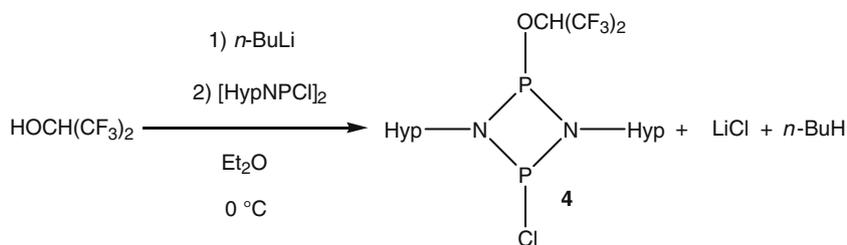
Recent work in our group [10] has focused on a new strategy for the generation and stabilization of cyclic and acyclic P(III)–N cations utilizing bulky groups such as the hypersilyl ((Me₃Si)₃Si = hyp) [11,12] and the supermesityl group (Mes⁺ = 2,4,6-tri-*tert*-butylphenyl). For this reason we have studied a number of differently substituted 1,3-dichloro-*cyclo*-diphosphadiazanes [RNPCl]₂. Moreover, since Michaelis and Schroeter [13] discovered the first example of a *cyclo*-diphosphadiazane, it is known, that there is a formal monomer–dimer equilibrium depending on the organic group R: 2 RNPCl ⇌ [RNPCl]₂. Burford et al. assumed that dependent upon steric strain in derivatives of [RPNR]₂ the dimer can be destabilized with respect to the monomer [8,9,14]. The intriguing equilibrium is best illustrated by the fact, that Mes⁺-N=P-Cl is observed as an iminophosphane monomer in the solid state [15], while slightly smaller substituents such as 2,6-diisopropylphenyl or the *m*-terphenyl allow dimerization [6,14].

To be able to isolate reactive PN⁺ ions two things need to be considered: (i) A bulky group should be used to kinetically protect the cation as well as (ii) a weakly coordinating anion, which should be chemically robust [16]. Here we report on attempts to isolate [Mes⁺-N=P]⁺ and [Hyp₂N₂P₂Cl]⁺ ions as tetrakis(hexafluoroisopropoxy)aluminate salts, which led unintentionally to the

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Scheme 4. Attempted direct synthesis of 1-chloro-3-(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphane-2,4-bis[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane (**4**).

the $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ ion finally undergoing a similar Lewis acid/Lewis base reaction as discussed before.

Again, several attempts were made to generate **4** in a direct synthetic route. Firstly, a solution of $\text{Li}[\text{OCH}(\text{CF}_3)_2]$ was treated with a solution of $[\text{HypNPCI}]_2$ in diethyl ether (**Scheme 4**). No reaction occurred, which nicely demonstrates the kinetic protection of the two hypersilyl groups in the dimer in contrast to the insufficient protection of the Mes^+ group in monomeric $\text{Mes}^+-\text{N}=\text{P}-\text{Cl}$. Secondly, the reactivity of $\text{Li}[\text{OCH}(\text{CF}_3)_2]$ was increased by addition of ethylenediamine, which however resulted in an ethylenediamine bridged *cyclo*-diphosphadiazane (see supporting information).

Separation of **3** and **4** obtained from the decomposition of the red oil (see above) is possible when $\text{Li}[\text{OCH}(\text{CF}_3)_2]$ was directly added to a mixture of **3** and **4** in *n*-hexane. A rapid reaction was observed leading to the precipitation of $\text{Li}[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]$ and unreacted **3** which remains dissolved in *n*-hexane.

Compounds **2**, **3** and **4** are thermally stable, moisture sensitive but stable under argon atmosphere over a long period as solid and in polar solvents at ambient temperature. Compound **2** is easily prepared in bulk and stable for a long time when stored in a sealed tube.

2.3. X-ray crystallography

The solid-state structures of compounds **1**, **2**, **3** and **4** are shown in **Figs. 1–4**. Crystallographic details are given in **Table 1**. More details are found in the supporting information file. X-ray quality crystals of $\text{Mes}^+-\text{N}=\text{P}-\text{Cl}$ (**1**), $\text{Mes}^+-\text{N}=\text{P}-\text{OCH}(\text{CF}_3)_2$ (**2**), $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_3]_2$ (**3**), and $\text{Hyp}_2\text{N}_2\text{P}_2(\text{Cl})\text{OCH}(\text{CF}_3)_2$ (**4**) were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperatures. All samples were cooled to 173(2) K during measurement. It should be mentioned, that a solid-state structure of compound **1**

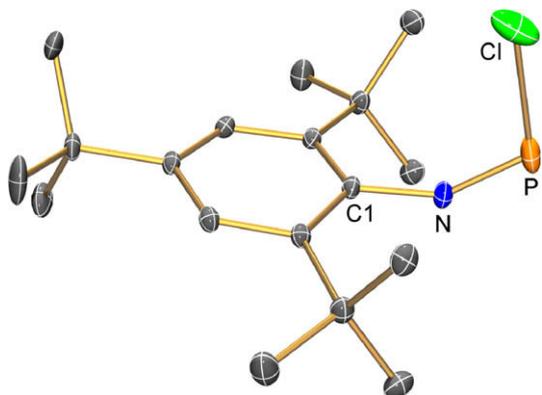


Fig. 1. ORTEP drawing of the molecular structure of **1** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity. Selected bond lengths in Å, angles in °: N–C1 1.413(3), N–P 1.506(2), P–Cl 2.118(1); C1–N–P 146.7(2), N–P–Cl 111.30(9), C1–N–P–Cl 0.3(3).

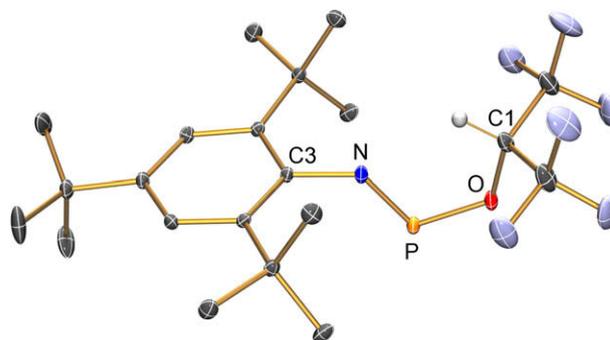


Fig. 2. ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms of the *tert*-Bu groups are omitted for clarity. Selected bond lengths in Å, angles in °: P–N 1.540(2), P–O 1.642(2), N–C3 1.429(2), O–C1 1.405(3); N–P–O 105.17(9), C3–N–P 127.0(1), C1–O–P 125.1(1).

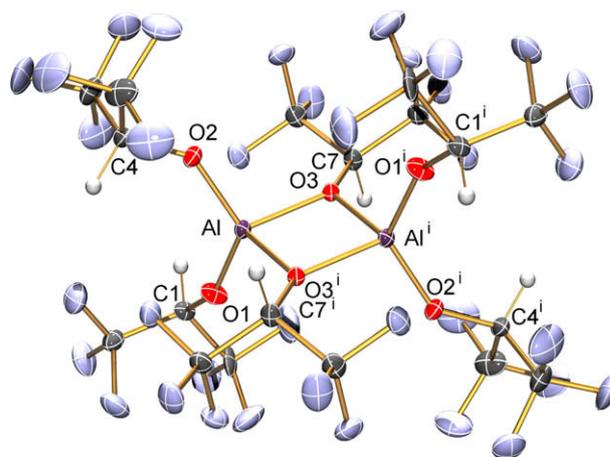


Fig. 3. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Selected bond lengths in Å, angles in °: Al–O2 1.666(2), Al–O1 1.685(2), Al–O3ⁱ 1.843(2), Al–O3 1.854(2), Al–Alⁱ 2.818(2), O1–C1 1.371(3); O2–Al–O1 124.9(1), O2–Al–O3ⁱ 114.5(1), O1–Al–O3ⁱ 108.11(9), O2–Al–O3 109.14(9), O1–Al–O3 110.77(8), O3ⁱ–Al–O3 80.68(8), O2–Al–Alⁱ 119.12(9), O1–Al–Alⁱ 115.89(7), C1–O1–Al 142.1(2).

has been reported [15], but in the present structure redetermination, a different modification was found with significantly different structural data (see below).

$\text{Mes}^+-\text{N}=\text{P}-\text{Cl}$ (**1**) crystallizes in the monoclinic space group $P2_1/n$ with four formula units per cell. One of the *t*-Bu groups is found to be disordered and was split in two parts. The structure consists of $\text{Mes}^+-\text{N}=\text{P}-\text{Cl}$ (Fig. 1) molecules arranged in parallel layers allowing π stacking. $\text{Mes}^+-\text{N}=\text{P}-\text{Cl}$ adopts a *cis* configuration with respect to the position of the C1-atom and chlorine ($\angle(\text{C1}-\text{N}-\text{P}-\text{Cl}) = 0.3(3)^\circ$). A fairly short P–N bond lengths of N–P 1.506(2) Å is

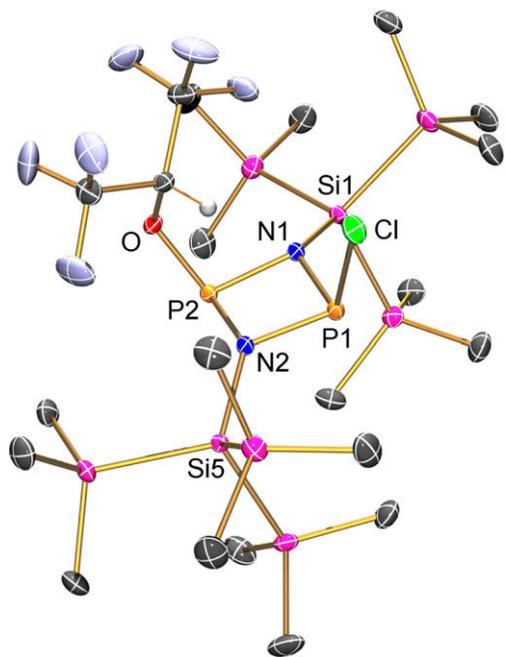


Fig. 4. ORTEP drawing of the molecular structure of **4** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms of the Me_3Si groups are omitted for clarity. Selected bond lengths in Å, angles in $^\circ$: P1–N1 1.697(2), P1–N2 1.711(1), P1–Cl1 2.139(1), P1–P2 2.521(1), P2–O1 1.658(1), P2–N1 1.721(1), P2–N2 1.725(2), N1–Si1 1.801(2), N2–Si5 1.806(1); O1–C1 1.409(2), N1–P1–N2 85.50(7), N1–P1–Cl1 104.58(5), N2–P1–Cl1 102.46(5), N1–P1–P2 42.83(4), N2–P1–P2 43.01(5), Cl1–P1–P2 112.80(4), O1–P2–N1 106.05(7), O1–P2–N2 104.91(6), N1–P2–N2 84.36(6), O1–P2–P1 115.26(5), N1–P2–P1 42.11(5), N2–P2–P1 42.58(4), P1–N1–P2 95.07(7), P1–N1–Si1 127.88(8), P2–N1–Si1 127.14(7), P1–N2–P2 94.41(7), P1–N2–Si5 125.44(7), P2–N2–Si5 132.49(7), C1–O1–P2 125.82(9).

observed, which indicates a bond order larger than two due to hyperconjugation [20] (cf. $\sum r_{\text{cov}}(\text{N}=\text{P}) = 1.8$, $\sum r_{\text{cov}}(\text{N}=\text{P}) = 1.6$ Å) [21]. As expected, a large C1–N–P angle of $146.7(2)^\circ$ is found for the imino nitrogen atom, while the N–P–Cl angle amounts to

$111.30(9)^\circ$. Interestingly, Niecke et al. published a modification of **1** which crystallized in the space group $Pnma$ and shows significantly different structural data (cf. $d(\text{P}=\text{N})$ 1.495(4) Å, $\angle(\text{P}=\text{N}=\text{C}1)$ $154.8(4)^\circ$, and $\text{N}=\text{P}=\text{Cl}$ $112.4(2)^\circ$), nicely displaying the influence and magnitude of lattice effects in the solid state [15].

$\text{Mes}^-\text{N}=\text{P}=\text{OCH}(\text{CF}_3)_2$ (**2**) crystallizes in the monoclinic space group $P2_1/m$ with two formula units per cell. One of the *t*-Bu groups is found to be disordered and was split in two parts. As depicted in Fig. 2, the structure consists of $\text{Mes}^-\text{N}=\text{P}=\text{OCH}(\text{CF}_3)_2$ molecules also arranged in parallel layers in the unit cell. $\text{Mes}^-\text{N}=\text{P}=\text{OCH}(\text{CF}_3)_2$ adopts a *cis* configuration with respect to the position of the C3-atom and the oxygen atom ($\angle(\text{O}=\text{P}=\text{N}=\text{C}3) = 180.0^\circ$), while a *trans* arrangement is found along the C1–O–P–N moiety (0.0° C). Compared to **1** the P–N distance is slightly increased with 1.540(2) Å (cf. **1**: 1.506(2) Å) and the P–O bond length of 1.642(2) Å is slightly shorter than a typical P–O single bond ($\sum r_{\text{cov}}(\text{O}=\text{P}) = 1.76$ Å) [21]. A short non-classical intramolecular C–H...N hydrogen bond is found with a donor–acceptor distance of 2.872(3) Å.

$[\text{Al}(\text{OCH}(\text{CF}_3)_2)_3]_2$ (**3**) crystallizes in the monoclinic space group $P2_1/n$ with two formula units per cell. One of the $\text{OCH}(\text{CF}_3)_2$ groups in **3** is found to be disordered and was split in two parts. The occupancy of each part was refined freely (0.672(3)/0.328(3)) and the group with larger occupancy is displayed in Fig. 3. As depicted in Fig. 3, the Al_2O_2 ring is planar, but slightly distorted with two longer Al–O bond lengths ($d(\text{Al}=\text{O}3) = 1.854(2)$ Å) and two slightly shorter Al–O bond lengths ($d(\text{Al}=\text{O}3^1) = 1.843(2)$ Å; cf. $\sum r_{\text{cov}}(\text{O}=\text{Al}) = 1.81$ Å, Fig. 3). These Al–O bond lengths are again substantially longer than those of the exocyclic Al–O bonds ($d(\text{Al}=\text{O}2) = 1.666(2)$, $d(\text{Al}=\text{O}1) = 1.685(2)$ Å). The Al...Al distance is rather short with 2.818(2) Å and compares to the Al...Al distance in aluminium metal ($d_{\text{metal}}(\text{Al}=\text{Al}) = 2.864$ Å) [21].

$\text{Hyp}_2\text{N}_2\text{P}_2(\text{Cl})\text{OCH}(\text{CF}_3)_2$ (**4**) crystallizes in the triclinic space group $P\bar{1}$ with four formula units per cell. The crystallographic asymmetric unit contains two crystallographically independent molecules, which are arranged in the unit cell in such a manner that stacked chains of alternating polar “NPCL-units” and non-polar “hyp-units” are formed as already observed for Hyp–N(H)–PCL₂

Table 1
Crystallographic details of **1–4**.

	1	2	3	4
Chemical formula	$\text{C}_{18}\text{H}_{29}\text{ClNP}$	$\text{C}_{21}\text{H}_{30}\text{F}_6\text{NOP}$	$\text{C}_{18}\text{H}_6\text{Al}_2\text{F}_{36}\text{O}_6$	$\text{C}_{21}\text{H}_{55}\text{ClF}_6\text{N}_2\text{OP}_2\text{Si}_8$
Formula weight (g mol ⁻¹)	325.84	457.43	1056.19	787.78
Colour	Red	Orange	Colourless	Colourless
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/m$	$P2_1/n$	$P\bar{1}$
<i>a</i> (Å)	5.8515(12)	5.930(2)	10.394(8)	14.748(7)
<i>b</i> (Å)	33.661(7)	14.828(6)	10.206(9)	16.885(9)
<i>c</i> (Å)	9.6883(19)	13.051(5)	16.211(15)	18.920(9)
α ($^\circ$)	90.00	90.00	90.00	86.82(2)
β ($^\circ$)	98.72(3)	91.064(11)	91.439(18)	69.247(16)
γ ($^\circ$)	90.00	90.00	90.00	71.949(10)
<i>V</i> (Å ³)	1886.2(7)	1147.4(7)	1719(3)	4181(4)
<i>Z</i>	4	2	2	4
ρ_{calc} (g cm ⁻³)	1.147	1.324	2.040	1.251
μ (mm ⁻¹)	0.283	0.180	0.316	0.443
$\lambda_{\text{MoK}\alpha}$ (Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	173(2)	173(2)	173(2)	173(2)
Measured reflections	16 368	11 716	14 477	98 586
Independent reflections	4322	3128	3922	24 279
Reflections with $I > 2\sigma(I)$	3157	2329	2490	18 042
R_{int}	0.0412	0.0355	0.0353	0.0411
$F(0\ 0\ 0)$	704	480	1024	1664
R_1 ($R[F^2 > 2\sigma(F^2)]$)	0.0590	0.0470	0.0504	0.0397
wR_2 (F^2)	0.1346	0.1310	0.1406	0.1033
Goodness-of-fit (GOF)	1.071	1.045	1.020	1.047
Parameters	212	160	344	775
CCDC #	753943	753944	753946	753945

[6b]. Only very weak intermolecular contacts are observed. As depicted in Fig. 4, the P_2N_2 ring is almost planar (deviation from planarity: $\langle(N-P1-N-P2) = 7.7^\circ$), but slightly distorted with two longer P–N bond lengths ($d(P2-N1) = 1.721(1)$, $d(P2-N2) = 1.725(2)$ Å) and two slightly shorter P–N bond lengths ($d(P1-N1) = 1.697(2)$, $d(P1-N2) = 1.711(1)$). These P–N bond lengths are again substantially shorter than the sum of the covalent radii (see above). The P–O bond length is rather short with $1.658(1)$ Å, and the P–Cl bond length amounts to $2.139(1)$ Å. A difference of ca. 10° is found between the N–P–N and P–N–P angles ($85.5/84.4^\circ$ vs. $95.1/94.4^\circ$), in accord with that found e.g. in $[(C_6H_5)_2NPCI]_2$ (80.1° vs. 99.7°) [3]. A short non-classical intramolecular C–H...Cl hydrogen bond is found for both molecules in the asymmetric unit with donor–acceptor distances of $3.482(2)$ and $3.555(3)$ Å.

3. Conclusion

In conclusion, we present here highly reactive hypersilylated *cyclo*-diphosphadiazanium $[Hyp_2N_2P_2Cl]^+$ and supermesityl substituted iminophosphonium $[Mes^--N=P]^+$ cations, which are capable of abstracting $[OCH(CF_3)_2]^-$ from the $[Al(OCH(CF_3)_2)_4]^-$ counter ion in formal Lewis acid/Lewis base reactions. By this approach the hitherto unknown $Mes^--N=P-OCH(CF_3)_2$ and $Hyp_2N_2P_2(Cl)OCH(CF_3)_2$ as well as the dimer of the free Lewis acid $[Al(OCH(CF_3)_2)_3]_2$ have been obtained and fully characterized.

4. Experimental details

4.1. General Information

All manipulations were carried out under oxygen- and moisture-free conditions in an argon atmosphere using standard Schlenk or dry box techniques.

Dichloromethane was dried over P_4O_{10} and freshly distilled prior to use. Diethyl ether was dried over Na/benzophenone, *n*-hexane was dried over Na/benzophenone/tetraglyme and freshly distilled prior to use. *N*-BuLi (2.5 M, Acros) was used as received. Silver tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate $Ag[Al(OCH(CF_3)_2)_4]$, *N*-(2,4,6-tri-*tert*-butylphenyl)imino-(chloro)phosphane Mes^--NPCl (**1**), and 1,2-dichloro-2,4-bis[tris(trimethylsilyl)silyl]-*cyclo*-diphosphadiazane $[HypNPCl]_2$, were prepared as previously reported [6b,15,17,19].

NMR: ^{29}Si INEPT, $^{19}F\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, and 1H NMR spectra were obtained on a Bruker AVANCE 250, or 300 spectrometer and were referenced internally to the deuterated solvent (^{13}C , CD_2Cl_2 : $\delta_{reference} = 54$ ppm) or to protic impurities in the deuterated solvent (1H , $CDHCl_2$: $\delta_{reference} = 5.31$ ppm). CD_2Cl_2 was dried over P_4O_{10} and freshly distilled prior to use.

IR: Nicolet 6700 FT-IR spectrometer with a Smart Endurance ATR device was used. Raman: Bruker VERTEX 70 FT-IR with RAM II FT-Raman module, equipped with a Nd:YAG laser (1064 nm) was used. CHN analyses: C/H/N/S-Mikronalysator TruSpec-932 from Leco was used. Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate $20^\circ C/min$ (clearing-points are reported).

4.2. Reaction of *N*-(2,4,6-tri-*tert*-butylphenyl)imino(chloro)phosphane (**1**) with silver tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate

To a stirred solution of *N*-(2,4,6-tri-*tert*-butylphenyl)imino-(chloro)phosphane Mes^--NPCl (**1**) (0.326 g, 1.0 mmol) in dichloromethane (10 mL), silver tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate $Ag[Al(OCH(CF_3)_2)_4]$ (0.883 g, 1.1 mmol) in dichloromethane (5 mL) is added dropwise at $-30^\circ C$ over a period

of 10 min. The resulting orange suspension is warmed to ambient temperatures over a period of 30 min, and filtered (F4). The resulting clear orange solution is concentrated to an approximate volume of 3 mL *in vacuo* and is stored at $-25^\circ C$ for 10 h, which results in the deposition of colourless crystals. The crystals were identified as bis[tris(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminium] (**3**), the only phosphorous containing product was identified as *N*-2,4,6-tri-*tert*-butylphenyl)imino-(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphane (**2**) by ^{31}P NMR.

4.3. Reaction of 1,3-dichloro-2,4-bis[tris(trimethylsilyl)silyl]-*cyclo*-diphosphadiazane with silver tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate

To a stirred solution of 1,3-dichloro-2,4-bis-[tris(trimethylsilyl)silyl]-*cyclo*-diphosphadiazane $[HypNPCl]_2$ (0.656 g, 1.0 mmol) in dichloromethane (10 mL), silver tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate $Ag[Al(OCH(CF_3)_2)_4]$ (0.883 g, 1.1 mmol) in dichloromethane (5 mL) is added dropwise at $-30^\circ C$ over a period of 10 min. The resulting dark red suspension is warmed to ambient temperatures over a period of 30 min, and filtered (F4). Removal of solvent *in vacuo* at ambient temperature yields a red oil, which is characterized as 2-chloro-3,4-bis[tris(trimethylsilyl)silyl]-*cyclo*-diphosphadiazanium tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate $[Hyp_2N_2P_2Cl][Al(OCH(CF_3)_2)_4]$ by NMR. Storage at ambient temperatures for 10 h, results in the deposition of colourless crystals. The crystals were identified as 1-chloro-3-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,4-bis-[tris(trimethylsilyl)silyl]-*cyclo*-diphosphadiazane $Hyp_2N_2P_2(Cl)OCH(CF_3)_2$ (**4**).

$[Hyp_2N_2P_2Cl][Al(OCH(CF_3)_2)_4]$: 1H NMR (25 $^\circ C$, CD_2Cl_2 , 300.13 MHz): $\delta = 0.36$ (s, 54 H, Si(CH₃)₃), 4.50 (sept, 4H, CH(CF₃)₂), $^3J(^{19}F-^1H) = 6.0$ Hz. $^{13}C\{^1H\}$ NMR (25 $^\circ C$, CD_2Cl_2 , 75.5 MHz): $\delta = 0.95$ (s, Si(CH₃)₃), 71.5 (sept, CH(CF₃)₂), $^2J(^{19}F-^{13}C) = 32.9$ Hz, 123.7 (q, CF₃), $^1J(^{19}F-^{13}C) = 283.3$ Hz. ^{29}Si NMR (25 $^\circ C$, CD_2Cl_2 , 59.6 MHz): $\delta = -26.0$ (m, Si(CH₃)₃), -12.8 (m, Si(CH₃)₃). $^{19}F\{^1H\}$ NMR (25 $^\circ C$, CD_2Cl_2 , 282.4 MHz): $\delta = -77.3$ (s, CF₃).

4.4. Synthesis of *N*-(2,4,6-tri-*tert*-butylphenyl)imino-(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphane (**2**)

To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol HOCH(CF₃)₂ (0.252 g, 1.5 mmol) in diethyl ether (10 mL), *n*-BuLi (2.5 M, 0.6 mL, 1.5 mmol) is added dropwise at $0^\circ C$ over a period of 5 min. The resulting colourless, clear solution is stirred for 10 min at this temperature, and is then added dropwise to a stirred solution of *N*-(2,4,6-tri-*tert*-butylphenyl)imino(chloro)phosphane Mes^--NPCl (**1**) (0.489 g, 1.5 mmol) in diethyl ether (8 mL) over a period of 5 min at $0^\circ C$. The resulting orange suspension is stirred at this temperature for 30 min and is then slowly warmed to ambient temperatures. The solvent is removed *in vacuo*, resulting in an orange residue which is extracted with *n*-hexane (15 mL), and filtered (F4). The resulting clear orange solution is concentrated to an approximate volume of 3 mL *in vacuo* and is stored at $-25^\circ C$ for 10 h, which results in the deposition of orange needlelike crystals. The supernatant is removed by syringe and the crystalline residue is dried *in vacuo*, which yields 0.652 g (1.43 mmol, 95%) of **2** as an orange crystalline solid. M.p. $102^\circ C$ (dec.). Anal. Calc.: C, 55.14; H, 6.61; N, 3.06. Found: C, 54.91; H, 6.59; N, 3.30%. 1H NMR (25 $^\circ C$, CD_2Cl_2 , 300.13 MHz): $\delta = 1.33$ (s, 9H, *p*-C(CH₃)₃), 1.47 (s, 18H, *o*-C(CH₃)₃), 5.18 (m, 1H, CH(CF₃)₂), $^4J(^{31}P-^{19}F) = 5.9$ Hz, 7.35 (d, 2H, *m*-CH, $^5J(^{31}P-^1H) = 1.4$ Hz). $^{13}C\{^1H\}$ NMR (25 $^\circ C$, CD_2Cl_2 , 75.5 MHz): $\delta = 30.8$ (d, *o*-C(CH₃)₃), $^5J(^{13}C-^{31}P) = 2.4$ Hz, 31.8 (s, *p*-C(CH₃)₃), 35.4 (s, *p*-C(CH₃)₃), 36.2 (d, *o*-C(CH₃)₃), $^4J(^{13}C-^{31}P) = 0.9$ Hz, 68.4 (m, CH(CF₃)₂), $^2J(^{19}F-^{13}C) = 34.7$ Hz, $^2J(^{31}P-^{13}C) = 10.4$ Hz, 121.5 (m, CF₃), $^1J(^{19}F-^{13}C) = 283.2$ Hz, $^3J(^{31}P-^{13}C) = 3$ Hz),

122.5 (d, *m*-CH, $^4J(^{31}\text{P}-^{13}\text{C}) = 2.3$ Hz), 137.7 (d, *p*-C, $^5J(^{31}\text{P}-^{13}\text{C}) = 31.4$ Hz), 140.9 (d, *o*-C, $^3J(^{31}\text{P}-^{13}\text{C}) = 9.1$ Hz), 146.6 (d, *ipso*-C, $^2J(^{31}\text{P}-^{13}\text{C}) = 4.2$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 282.4 MHz): $\delta = -74.4$ (m, CF_3 , $^3J(^{19}\text{F}-^1\text{H}) = 5.9$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5 MHz): $\delta = 138.4$. IR (ATR, 16 scans): 3100 (w), 2962 (m), 2935 (m), 2911 (m), 2872 (m), 2744 (w), 1506 (w), 1477 (w), 1471 (w), 1464 (w), 1456 (w), 1451 (w), 1421 (m), 1390 (w), 1382 (m), 1362 (m), 1337 (m), 1310 (w), 1278 (m), 1260 (m), 1229 (s), 1219 (s), 1188 (s), 1145 (w), 1134 (w), 1106 (s), 1083 (s), 1020 (w), 979 (w), 925 (w), 901 (m), 878 (m), 868 (s), 811 (s), 786 (m), 764 (m), 730 (w), 710 (w), 686 (s), 669 (w), 644 (m), 567 (m), 552 (w), 535 (m). Raman (200 mW, 25 °C, 219 scans, cm^{-1}): = 3101 (1), 2965 (10), 2933 (9), 2910 (9), 2880 (5), 2776 (1), 2710 (2), 1598 (4), 1470 (2), 1449 (3), 1423 (4), 1390 (2), 1364 (2), 1336 (3), 1310 (8), 1199 (3), 1153 (1), 1081 (1), 1055 (1), 1026 (1), 927 (2), 868 (1), 823 (3), 784 (1), 731 (2), 687 (1), 568 (2), 537 (1), 509 (1), 475 (1), 421 (1), 389 (1), 338 (1), 299 (1), 256 (1), 126 (5). MS (Cl^+ , isobutane): 458 $[\text{M}+\text{H}]^+$, 402 $[\text{M}-t\text{Bu}+2\text{H}]^+$.

Crystals suitable for X-ray crystallographic analysis were obtained directly from the above reaction solution.

4.5. Attempted synthesis of 1-chloro-3-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,4-bis-[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane (4)

To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol HOCH(CF_3)₂ (0.168 g, 1.0 mmol) in diethylether (10 mL), *n*-BuLi (2.5 M, 0.4 mL, 1.0 mmol) is added dropwise at 0 °C over a period of 5 min. The resulting colourless, clear solution is stirred for 10 min at this temperature, and is then added dropwise to a stirred solution of 1,3-dichloro-2,4-bis-[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane [HypNPCI_2] (0.656 g, 1.0 mmol) in diethyl ether (8 mL) over a period of 5 min at 0 °C. The resulting colourless solution is then slowly warmed to ambient temperatures. Even after several hours at ambient temperatures, no reaction is observed as shown by ^{31}P NMR. The solvent is removed *in vacuo*, resulting in a colourless residue which is extracted with *n*-hexane (15 mL), and filtered (F4). The resulting clear colourless solution is concentrated to an approximate volume of 3 mL *in vacuo* and is stored at -25 °C for 10 h, which results in the deposition of colourless crystals of the starting material 1,3-dichloro-2,4-bis[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane [HypNPCI_2] almost quantitatively.

4.6. Synthesis of 1-chloro-3-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,4-bis[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazane (4)

The mixture of **3** and **4** (from the decomposition reaction of 2-chloro-3,4-bis[tris(trimethylsilyl)silyl]-cyclo-diphosphadiazanium tetrakis(1,1,1,3,3,3-hexafluoro-2-propoxy)aluminate [$\text{Hyp}_2\text{N}_2\text{P}_2\text{-Cl}]^+[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$) is dissolved in *n*-hexane (10 mL) resulting in a yellowish suspension, which is added dropwise to a colourless suspension of $\text{Li}[\text{OCH}(\text{CF}_3)_2]$ (prepared from 1,1,1,3,3,3-hexafluoro-2-propanol HOCH(CF_3)₂ (0.168 g, 1.0 mmol) and *n*-BuLi (2.5 M, 0.4 mL, 1.0 mmol) in *n*-hexane (5 mL) at ambient temperatures over a period of 10 min. The resulting colourless suspension is stirred for 1 h at ambient temperatures and filtered (F4). The resulting colourless solution is concentrated to an approximate volume of 5 mL *in vacuo* and is stored at -25 °C for 10 h which leads to the deposition of colourless crystals. Removal of supernatant by syringe and drying *in vacuo* yields 0.190 g (0.24 mmol, 24%) of **4** as colourless crystalline solid. Mp 127 °C; T_{dec} 186 °C. Anal. Calc.: C, 32.02; H, 7.04; N, 3.56. Found: C, 31.72; H, 7.03; N, 3.46%. ^1H NMR (25 °C, CD_2Cl_2 , 300.13 MHz): $\delta = 0.27$ (s, 54 H, Si($\text{Si}(\text{CH}_3)_3$)), 5.38 (m, 1H, CH(CF_3)), $^3J(^{19}\text{F}-^1\text{H}) = 3.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 °C,

CD_2Cl_2 , 75.5 MHz): $\delta = 1.6$ (s, Si($\text{Si}(\text{CH}_3)_3$)). 71.4 (sept, CH(CF_3)), $^2J(^{19}\text{F}-^{13}\text{C}) = 33.4$ Hz). ^{29}Si NMR (25 °C, CD_2Cl_2 , 59.6 MHz): $\delta = -33.3$ (m, Si($\text{Si}(\text{CH}_3)_3$)), -13.5 (m, Si($\text{Si}(\text{CH}_3)_3$)). $^{19}\text{F}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 282.4 MHz): $\delta = -72.0$ (d, CF_3 , $^4J(^{19}\text{F}-^{31}\text{P}) = 4.3$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2 , 121.5 MHz): $\delta = 199.8$ (d, $^2J(^{31}\text{P}-^{31}\text{P}) = 100$ Hz), 233.1 (d, $^2J(^{31}\text{P}-^{31}\text{P}) = 100$ Hz). IR (ATR, 16 scans): 2949 (w), 2894 (w), 1371 (w), 1290 (m), 1258 (m), 1244 (m), 1220 (m), 1192 (s), 1162 (m), 1105 (m), 1075 (m), 1012 (w), 1000 (w), 953 (w), 898 (w), 890 (m), 875 (m), 820 (vs), 787 (s), 748 (m), 740 (m), 685 (s), 623 (s), 561 (m). MS (Cl^+ , isobutane): 787 $[\text{M}+\text{H}]^+$, 771 $[\text{M}-\text{Me}]^+$, 751 $[\text{M}-\text{Cl}]^+$, 713 $[\text{M}-\text{SiMe}_3]^+$, 678 $[\text{M}-\text{SiMe}_3-\text{Cl}]^+$, 619 $[\text{M}-\text{OCH}(\text{CF}_3)_2]^+$.

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Appendix A. Supplementary material

CCDC 753943, 753944, 753946 and 753945 contains 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.11.014](https://doi.org/10.1016/j.jorganchem.2009.11.014).

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