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Facile One-Step Synthesis of MPHMes from $MesPCl_2$ (M = Li, Na, K; Mes = 2,4,6-$Me_3C_6H_2$)

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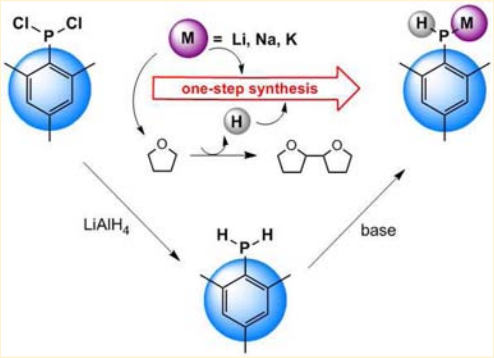
Supporting Information

ABSTRACT: Reaction of alkali metals (Li, Na, K) with mesityldichlorophosphane ($MesPCl_2$, Mes = 2,4,6-$Me_3C_6H_2$) in ethereal solvents leads to formation of the corresponding mesitylphosphanides MPHMes in good purity and yield. ^{31}P NMR spectroscopic studies in deuterated solvents strongly support a mechanism of the reaction that involves protonation/disproportionation steps in which the solvent is the only possible proton source. Li(thf)(tmeda)PHMes (**1**), $[Na(tmeda)(\mu\text{-}PHMes)]_\infty$ (**2**), and $[K(pmdeta)(\mu\text{-}PHMes)]_2$ (**3**) (tmeda = *N,N,N′,N′*-tetramethylethylenediamine, pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) were obtained; in the solid state, **2** forms zigzag chains while **3** is a dimeric compound.



INTRODUCTION

Alkali metal phosphanides are an important class of starting materials with intriguing structural chemistry.[1,2] In recent years the structural principles governing this class of compounds have been further unraveled. Thus, the motifs for alkali metal phosphanides in the solid state range from monomers, dimers, and trimers to polymeric and three-dimensional structures, and their reactivity is dependent on the nature of the substituents on the phosphorus atom, the solvating ligands, and the metal itself. These developments have opened up a rich area of transition metal[3] and main group metal coordination chemistry.[4]

Initially we were interested in finding more facile routes to alkali metal polyphosphanides.[5] Thus, we obtained $M_2(P_4Mes_4)$ (M = Na and K), albeit in moderate yields,[6] and employed them in the preparation of a wide variety of main group and transition metal complexes.[5a−c,7] However, as some of the target compounds were only obtained in low yield and many others were difficult to prepare using these highly reactive Na or K salts, lithium tetramesityltetraphosphane-1,4-diide seemed to be a more promising starting material. In our search for a facile synthesis of $Li_2(P_4Mes_4)$ we observed that, depending on the stoichiometry, solvent, and reaction conditions, formation of LiPHMes is favored, and we decided to explore the analogous reactions with Na and K.

To date, several procedures for preparation of alkali metal phosphanides have been described in the literature.[2b,8−10] The most common method is direct metalation of a primary or secondary phosphane with a strong deprotonating agent such as an alkyl lithium or alkali metal hydride.[8] Other methods include direct metalation of a primary or secondary phosphane with a heavier alkali metal[9] and P−C_{aryl} cleavage of an aryl-substituted tertiary phosphane with an alkali metal in a donor solvent or in liquid ammonia or with the help of a strong base such as *n*BuLi.[10] A common disadvantage of these procedures is the use of primary or secondary phosphanes, which are obtained mainly by reduction of the corresponding chlorophosphanes with $LiAlH_4$,[11] a reaction step that is not very convenient in practice. In this work, we report a facile method for preparation of alkali metal mesitylphosphanides MPHMes directly from the alkali metal and $MesPCl_2$[12] (M = Li, 10:4; M = Na, K, 6:2) in ethereal solvents. The previously known lithium salt Li(thf)(tmeda)PHMes (**1**), $[Na(tmeda)(\mu\text{-}PHMes)]_\infty$ (**2**), and $[K(pmdeta)(\mu\text{-}PHMes)]_2$ (**3**) were thus obtained, and **2** and **3** were fully characterized. While reaction of alkali metals with dichlorophosphanes is well investigated and leads to different phosphanes and phosphanides,[6,13,14] we show here that variation of the stoichiometry and reaction conditions leads in a clean, straightforward reaction to monophosphanides MPHMes in high yields.

RESULTS AND DISCUSSION

Reactions with Lithium. We recently reported that reaction of 4 equiv of $MesPCl_2$ with 10 equiv of alkali metal in refluxing THF (48 h for Na and 6 h for K) leads to $M_2(P_4Mes_4)$ (M = Na, K) in moderate yields.[6] We thus decided to explore the same reaction using lithium sand in order to synthesize $Li_2(P_4Mes_4)$. However, after 6 h formation of the $(PHMes)^-$ ion as the only P-containing product was confirmed by the appearance of a doublet at −157 ppm ($^1J_{PH}$ = 162 Hz) in the ^{31}P NMR spectrum.

Further experiments using different reaction times and temperatures showed that formation of cyclo-P_4Mes_4 and

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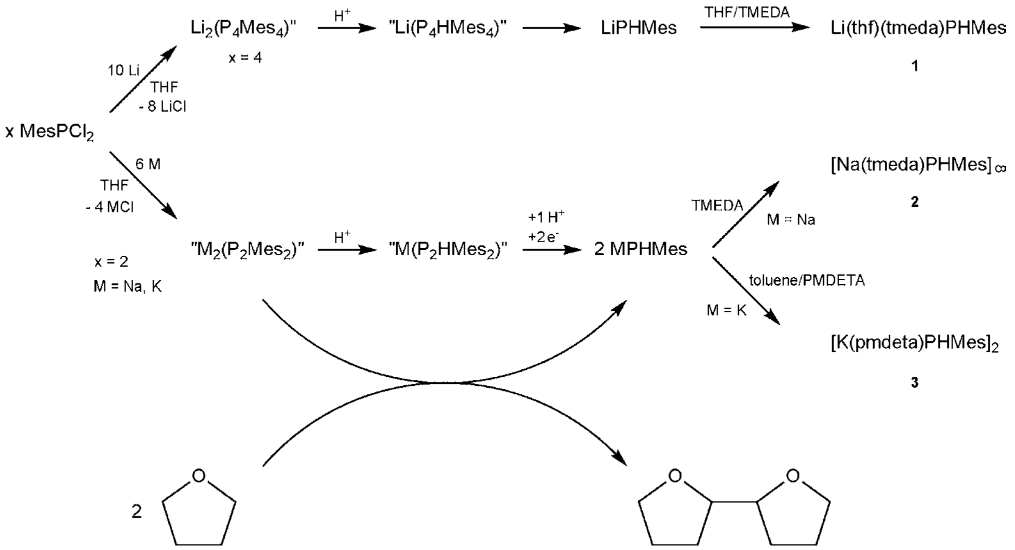
Scheme 1



cyclo-P_3Mes_3 occurred in just 5 min, while formation of $Li_2(P_4Mes_4)$ was observed after only 30 min at room temperature (characteristic AA′XX′ spin system in the $^{31}P\{^1H\}$ NMR spectrum at ca. −12 and −115 ppm).[15]

In view of these results, formation of LiPHMes was studied. We observed that reaction of 1 equiv of $MesPCl_2$ and 10 equiv of lithium in refluxing THF led to LiPHMes as the only P-containing compound in 3 h (according to the ^{31}P NMR spectrum). Assuming that $Li_2(P_4Mes_4)$ is formed first, subsequent protonation may occur to give $M(P_4HMes_4)$,[16] which is very unstable and disproportionates in solution to give a mixture of phosphanes and phosphanides which may react further with lithium to give LiPHMes as the final product. Evaporation of the solvent, successive extractions of the residue with Et_2O, filtration, and recrystallization from THF/TMEDA gave the previously known Li(thf)(tmeda)PHMes (**1**).[17] When the reaction was carried out in noncoordinating solvents such as toluene or *n*-hexane, only formation of small amounts of cyclo-P_3Mes_3 and cyclo-P_4Mes_4 was observed.

Reactions with Sodium and Potassium. Similar behavior was observed in reactions of $MesPCl_2$ with sodium and potassium. Thus, our attempts to synthesize the dianion $M_2(P_2Mes_2)$ by reaction of 2 equiv of $MesPCl_2$ and 6 equiv of sodium sand or elemental potassium in refluxing THF gave MPHMes in high yield. After addition of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) for the Na salt or PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine) for the K salt, products $[Na(tmeda)(\mu\text{-PHMes})]_\infty$ (**2**) and $[K(pmdeta)(\mu\text{-PHMes})]_2$ (**3**) were obtained. In solution ([D_8]THF) both compounds exhibit a doublet in the ^{31}P NMR spectrum at −142.3 (M = K, $^1J_{PH}$ = 169.5 Hz) and −161.0 ppm (M = Na, $^1J_{PH}$ = 162.7 Hz).

A proposal for formation of **2** and **3** is shown in Scheme 1. We assume with respect to the stoichiometry that 1,2-dimesityldiphosphane-1,2-diide $M_2P_2Mes_2$ is formed first and, subsequently, a protonation takes place, followed by formation of $M(P_2HMes_2)$ as an intermediate for this reaction.[18] This disproportionates further to form MPHMes as a final product. A possible explanation for the protonation and reduction step is that CH_2 groups in the ethereal solvents (in this case THF) which are located next to the oxygen atom can form a radical, while a proton and an electron are liberated. Most likely, a redox reaction occurs in which 1,2-dimesityldiphosphane-1,2-diide $M_2(P_2Mes_2)$ is reductively cleaved to form two molecules of MPHMes, while two THF molecules are oxidatively coupled to form a THF dimer.[19] The latter could be detected by ESI mass spectrometry (m/z = 143 $[M + H]^+$), but polymerization of THF could not be excluded.[20] Finally, reaction of 1 equiv of $MesPCl_2$ and 10 equiv of sodium or potassium in refluxing THF gave MPHMes and traces of $MesPH_2$ in 6 h for sodium and 3 h for potassium (according to the ^{31}P NMR spectrum). Furthermore, other dichlorophosphanes (tBuPCl_2 and $PhPCl_2$) also react with alkali metals in ethereal solvents in a 6:2 (M:$RPCl_2$) ratio with formation of the expected alkali metal phosphanides, MPH*t*Bu[21] and MPHPh,[22] indicating that this method is quite general and mostly independent of the substituents on the phosphorus atom.

^{31}P NMR Spectroscopic Studies in [*D*$_8$]THF. Further support for the suggested mechanism was provided by an NMR spectroscopic study of the reaction of elemental potassium with $MesPCl_2$ (6:2) in [D_8]THF, which showed that the solvent is the only proton (deuterium) source in this reaction. The proton-coupled ^{31}P NMR spectrum of the reaction mixture obtained after 3 h of reflux showed two major species: A broad singlet for KPDMes at −142 ppm, and a broad singlet for $MesPD_2$ at −158 ppm. As expected, no phosphorus−proton coupling was observed, but both singlets are broadened due to the coupling between phosphorus and deuterium.[23] This result confirms the assumptions stated above and shows the importance of the solvent in the outcome of this reaction.

Molecular Structures of $[Na(tmeda)(\mu\text{-PHMes})]_\infty$ (2) and $[K(pmdeta)(\mu\text{-PHMes})]_2$ (3). Yellow crystals of **2** were obtained from a concentrated TMEDA solution at room temperature. The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell, Figure 1. In the solid state, **2** is polymeric and forms infinite zigzag chains along the *c* axis, Figure 2. Each phosphorus atom bridges two sodium atoms with a Na−P−Na angle of 114.9(1)°, which is significantly smaller than the essentially linear Li−P−Li angle (176.9(1)°) found in the zigzag structure of $[Li(DME)(\mu\text{-PH}_2)]_\infty$[24] but comparable with the infinite chain of alternating Li and P atoms in $[Li(diglyme)(\mu\text{-PHMe})]_\infty$[25] (Li−P−Li 132.1(1)°, diglyme = 1-methoxy-2-(2-methoxyethoxy)ethane).

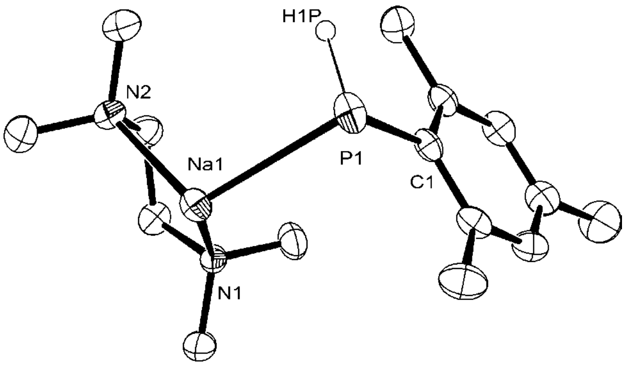


Figure 1. Asymmetric unit of [Na(tmeda)(μ-PHMes)]$_\infty$ (**2**). H atoms (except at P1) were omitted for clarity. Thermal ellipsoids are at the 50% level.

Table 1. Selected Bond Lengths (picometers) and Angles (degrees) for [Na(tmeda)(μ-PHMes)]$_\infty$ (2)

P(1)−Na(1)	286.4(5)	P(1)−Na(1)−P(1)′	128.5(2)
P(1)′−Na(1)	284.6(5)	Na(1)−P(1)−H(1P)	95.7(4)
P(1)−H(1P)	149.0(1)	N(1)−Na(1)−N(2)	75.7(3)
Na(1)−N(1)	245.3(1)	N(1)−Na(1)−P(1)	112.0(2)
Na(1)−N(2)	247.8(1)	N(2)−Na(1)−P(1)	110.9(3)
		P(1)−Na(1)−P(1)′	114.9(1)

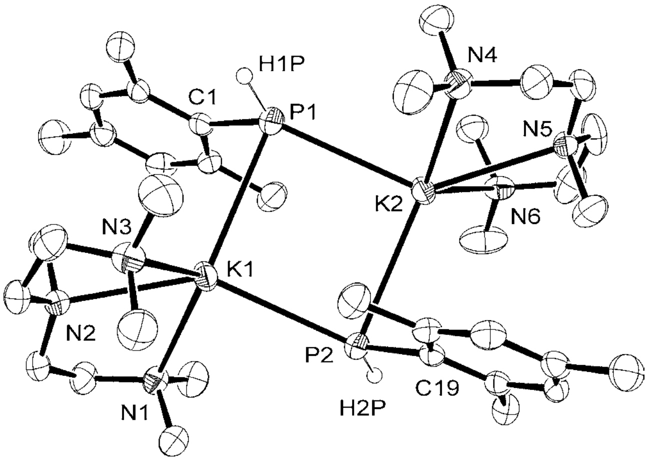


Figure 3. Molecular structure of [K(pmdeta)(μ-PHMes)]$_2$ (**3**). H atoms (except at P1 and P2) were omitted for clarity. Thermal ellipsoids are at the 50% level.

Table 2. Selected Bond Lengths (picometers) and Angles (degrees) for [K(pmdeta)(μ-PHMes)]$_2$ (3)

P(1)−H(1P)	139.8(9)	K(1)−P(2)	330.0(5)
P(2)−H(2P)	139.0(1)	K(2)−N(6)	282.8(1)
K(1)−N(1)	281.2(1)	K(2)−N(4)	286.5(1)
K(1)−N(2)	287.1(1)	K(2)−N(5)	288.8(1)
K(1)−N(3)	288.3(1)	K(2)−P(1)	325.1(6)
K(1)−P(1)	330.0(6)	K(2)−P(2)	329.9(5)
P(1)−K(1)−P(2)	90.7(1)	K(2)−P(1)−H(1P)	125.6(9)
P(1)−K(2)−P(2)	91.6(1)	K(1)−P(1)−H(1P)	106.0(8)
K(2)−P(1)−K(1)	88.4(1)	K(2)−P(2)−H(2P)	111.0(1)
K(2)−P(2)−K(1)	87.6(1)	K(1)−P(2)−H(2P)	127.0(2)

Na−P distances [286.4(5) and 284.6(5) pm] are comparable to those found in other structurally characterized sodium phosphanides, e.g., [Na(thf)$_2$(PMes)(SiF*t*Bu$_2$)] (289.0(1) pm)[26] and [Na(pmdeta)(μ-PHCy)]$_2$ (291.0(8) pm).[27] The coordination sphere of sodium is completed by two nitrogen atoms from a bidentate TMEDA ligand, and an unusual coordination number of four is achieved by each sodium atom.[7e,h28] The average Na−N distance of 246.6(1) pm is slightly shorter than the values of 254.0(2) pm in [Na(pmdeta)(μ-PHCy)]$_2$[23] and 265.6(3) pm in [Na(pmdeta)(μ-Ph)]$_2$,[29] Table 1.

Large red crystals of [K(pmdeta)(μ-PHMes)]$_2$ (**3**) were obtained from a PMDETA/*n*-hexane solution at room temperature. Compound **3** crystallizes in the triclinic space group $P\overline{1}$ with two formula units in the unit cell and forms dimers in which two (MesPH)$^-$ anions bridge two PMDETA-solvated potassium cations, Figure 3. Mesityl substituents at phosphorus have a trans arrangement. The central P$_2$M$_2$ ring is nearly planar (torsion angle P(1)−K(1)−P(2)−K(2) 9.5(1)°), Table 2. Both K$^+$ ions achieve a coordination number of 6 via M···C interaction with the *ipso*-carbon atom at phosphorus [K(1)−C(1) 340.1(1), K(2)−C(19) 331.2(1) pm]. K−P distances [325.1(6)−330.0(6) pm] are in the range of structurally characterized potassium phosphanides.[2c,22,29,30] K−N distances of the NMe$_2$ group opposite the mesityl group [K(1)−N(1) 281.2(1) pm, K(2)−N(6) 282.8(1) pm] are shorter than the other K−N distances (range 286.5(1)−288.8(1) pm), but all lie within the range of typical K−N distances for compounds in which potassium is coordinated by tertiary amines. For example, K−N distances are 285.3(3), 281.6(3), and 279.9(3) pm for the monomeric naphthyl-substituted phosphanide K(pmdeta){P(C$_{10}$H$_6$-8-NMe$_2$)(CH-(SiMe$_3$)$_2$)},[31] 285.7(2), 286.0(2), and 287.3(2) pm for the amino-functionalized mononuclear adduct K(pmdeta){P-(C$_6$H$_4$-2-NMe$_2$)(CH(SiMe$_3$)$_2$)},[32] and 293.6(6), 286.5(6), and 289.4(7) pm for the dimeric [K(pmdeta){μ-P*t*BuP(H)*t*Bu)}]$_2$.[33]

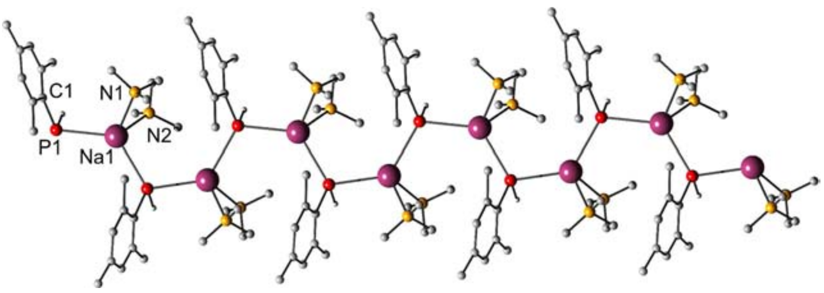


Figure 2. Polymeric zigzag chain of [Na(tmeda)(μ-PHMes)]$_\infty$ (**2**) along the *c* axis. H atoms (except at P1) were omitted for clarity.

■ CONCLUSIONS

Alkali metal mesitylphosphanides are readily obtained in a one-step synthesis from alkali metal and $MesPCl_2$ in ethereal solvents. ^{31}P NMR studies in $[D_8]$THF corroborate the assumption that this reaction occurs by initial protonation of oligophosphanediides by the solvent followed by disproportionation to give MPHMes as the final product. This new synthetic route is an interesting alternative to alkali metal phosphanides compared to those in the literature and offers much potential for further exploration of the solid-state structures of alkali metal mesitylphosphanides. Furthermore, analogous reactions using alternative precursors, such as *t*$BuPCl_2$ and $PhPCl_2$, also gave the corresponding alkali metal phosphanide, indicating the generality of this method. In addition, while the known procedures usually include reduction of chlorophosphanes to the corresponding primary or secondary phosphanes, the newly developed method described here omits this unpleasant reaction step.

■ EXPERIMENTAL SECTION

General Remarks. All experiments were carried out under dry nitrogen. Solvents were dried and freshly distilled under nitrogen and kept over a potassium mirror. TMEDA and PMDETA were acquired commercially, dried over Na, and stored under argon. $MesPCl_2$ was synthesized according to a literature procedure.[12]

NMR spectra were recorded at 25 °C with a Bruker AVANCE DRX 400 spectrometer (^1H NMR 400.13 MHz, internal standard TMS; ^{13}C NMR 100.16 MHz, internal standard TMS; ^{31}P NMR 161.97 MHz, external standard 85% H_3PO_4). IR spectra were recorded with a Perkin-Elmer Spektrum 2000 FT-IR spectrometer between 4000 and 400 cm^{-1} (as KBr pellets). Melting points (Gallenkamp) were determined in sealed capillaries under argon and are uncorrected.

Table 3. Crystallographic Data of [Na(tmeda)(*μ*-PHMes)]$_\infty$ (2) and [K(pmdeta)(*μ*-PHMes)]$_2$ (3)

	[Na(tmeda)(*μ*-PHMes)]$_\infty$ (**2**)	[K(pmdeta)(*μ*-PHMes)]$_2$ (**3**)
empirical formula	$C_{15}H_{28}N_2NaP$	$C_{36}H_{70}K_2N_6O_{0.22}P_2$[a]
M	290.35	730.64
T (K)	130(2)	130(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (pm)	844.88(2)	922.34(3)
b (pm)	2459.77(5)	1365.03(5)
c (pm)	868.42(2)	1818.38(6)
α (deg)	90	96.795(3)
β (deg)	90.522(2)	93.756(3)
γ (deg)	90	103.777(3)
V (nm^3)	1.80468(7)	2.1975(1)
Z	4	2
ρ_{calcd} ($Mg\ m^{-3}$)	1.069	1.104
$\theta_{min}-\theta_{max}$ (deg)	2.87–30.51	2.65–30.51
total data	19 675	24 110
unique data (R_{int})	5499 (0.0258)	13404 (0.0329)
params, restraints	284, 6	528, 4
GOF on F^2	0.918	0.794
R_1, wR_2 [$I > 2\sigma(I)$]	0.0325, 0.0794	0.0407, 0.0723
R_1, wR_2 (all data)	0.0539, 0.0834	0.0938, 0.0793
residual electron density (e $Å^{-3}$)	0.352 and −0.139	0.531 and −0.379

[a] Apparently, partial oxidation occurred during mounting of the crystals, while all NMR spectra showed only the unoxidized product.

Synthesis of Li(thf)(tmeda)PHMes (1). $MesPCl_2$ (6.6 g, 30.0 mmol) was dissolved in 150 mL of THF and added to freshly prepared lithium sand (2.08 g, 300.0 mmol, prepared using a Heidolph SilentCrusher M dispersant machine). The mixture was heated to reflux for 6 h and stirred for an additional 16 h at room temperature. The red suspension was then analyzed by ^{31}P NMR spectroscopy (THF/C_6D_6): $\delta = -157$ ppm ($^1J_{PH} = 162$ Hz). The solvent of the mixture was removed in vacuo, and the deep red solid residue was extracted with Et_2O (3 × 200 mL) and filtered (to remove LiCl and unconsumed Li). Solvent was evaporated, the oily residue dissolved in THF (30 mL), and then 3 mL of TMEDA added. The mixture was stored at −28 °C to give crystals of Li(thf)(tmeda)PHMes (**1**) over 1 week. Yield: 2.53 g, 37%. Spectroscopic data of **1** are in agreement with those reported previously.[17]

Synthesis of [Na(tmeda)(*μ*-PHMes)]$_\infty$ (2). $MesPCl_2$ (1.6 g, 7.2 mmol) was dissolved in 50 mL of THF and added to freshly prepared sodium sand (0.5 g, 21.7 mmol, prepared from Na in boiling toluene). The mixture was heated to reflux for 4 h and stirred for an additional 16 h at room temperature. A red suspension formed and was filtered. The solvent of the filtrate was completely removed in vacuum. The remaining yellow solid was washed with 3 × 10 mL of *n*-hexane and dissolved in 10 mL of TMEDA, and the orange solution was layered with 30 mL of *n*-hexane. Yellow crystals of [Na(tmeda)(*μ*-PHMes)]$_\infty$ (**2**) formed at room temperature within a few days. Yield: 1.7 g (82%). Mp: 139−142 °C, 230 °C decomposition to dark red oil. ^1H NMR ($[D_8]$THF): δ 2.15 (br s, 4H, CH_2CH_2 in TMEDA), 2.25 (s, 3H, *p*-Me in 2,4,6-$Me_3C_6H_2$), 2.35 (s, 12H, NMe_2 in TMEDA), 2.37 (s, 6H, *o*-Me in 2,4,6-$Me_3C_6H_2$), 6.61 (s, 2H, 2,4,6-$Me_3C_6H_2$). $^{13}C\{^1H\}$ NMR ($[D_8]$THF): $\delta = 20.19$ (s, *p*-CH_3 in 2,4,6-$Me_3C_6H_2$), 25.03 (s, *o*-CH_3 in 2,4,6-$Me_3C_6H_2$), 45.39 (s, $N(CH_3)_2$ in TMEDA), 58.11 (s, CH_2N), 122.53 (s, *p*-C in 2,4,6-$Me_3C_6H_2$), 126.11 (s, *m*-C in 2,4,6-$Me_3C_6H_2$), 134.13 (d, *o*-C in 2,4,6-$Me_3C_6H_2$, $^2J_{PC}$ 9.6 Hz), 153.67 (d, *ipso*-C in 2,4,6-$Me_3C_6H_2$, $^1J_{PC}$ 54.7 Hz). ^{31}P NMR ($[D_8]$THF): δ −161.0 (d, $^1J_{PH}$ 162.7 Hz). IR (KBr) cm^{-1}: 2359−2293 m, br (P−H). Anal. Calcd for $C_{15}H_{28}N_2NaP$ (290.35): C, 62.05; H, 9.72; N, 9.65. Found: C, 60.72; H, 9.67; N, 9.45.

Synthesis of [K(pmdeta)(*μ*-PHMes)]$_2$ (3). Small pieces (ca. 5 × 5 × 5 mm) of potassium (0.5 g, 12.7 mmol) were added to a solution of $MesPCl_2$ (0.94 g, 4.3 mmol) in 50 mL of THF. The mixture was heated to reflux for 3 h. The resulting dark red suspension was filtered, and the solvent was evaporated. The remaining red solid was washed three times with 10−20 mL of *n*-hexane. The solid was then dissolved in 10 mL of toluene, 2 mL of PMDETA was added, and the dark red solution was layered with 30 mL of *n*-hexane. Red crystals of [K(pmdeta)(*μ*-PHMes)]$_2$ (**3**) formed in 1 week at room temperature. Yield: 2.3 g (76%). Mp: 330−332 °C, decomposition to dark brown oil. ^1H NMR (C_6D_6): δ 1.96 (s, 3H, NMe in pmdeta), 2.04 (s, 12H, NMe_2 in pmdeta), 2.15 (m, 8H, CH_2CH_2 in pmdeta), 2.20 (s, 3H, *p*-Me in 2,4,6-$Me_3C_6H_2$), 2.65 (s, 6H, *o*-Me in 2,4,6-$Me_3C_6H_2$), 6.85 (s, 2H, 2,4,6-$Me_3C_6H_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.70 (s, *p*-CH_3 in 2,4,6-$Me_3C_6H_2$), 25.34 (d, *o*-CH_3 in 2,4,6-$Me_3C_6H_2$, $^2J_{PC}$ 12.7 Hz), 41.66 (s, NCH_3 in pmdeta), 45.18 (s, $N(CH_3)_2$ in pmdeta), 56.00 (s, CH_2N), 57.35 (s, CH_2N), 125.34 (s, *p*-C in 2,4,6-$Me_3C_6H_2$), 128.97 (s, *m*-C in 2,4,6-$Me_3C_6H_2$), 134.12 (d, *o*-C in 2,4,6-$Me_3C_6H_2$, $^2J_{PC}$ 9.0 Hz), 152.62 (d, *ipso*-C in 2,4,6-$Me_3C_6H_2$, $^1J_{PC}$ 50.3 Hz). ^{31}P NMR (C_6D_6): δ −142.3 (d, $^1J_{PH}$ 169.5 Hz). IR (KBr) cm^{-1}: 2355−2296 m, br (P−H). Anal. Calcd for $C_{36}H_{70}K_2N_6P_2$ (727.12): C, 59.47; H, 9.70; N, 11.56. Found: C, 58.25; H, 9.66; N, 11.79.

Test Reaction in $[D_8]$THF. Potassium sand (0.04 g, 1.02 mmol, prepared from K in boiling THF) was added to a solution of $MesPCl_2$ (0.07 g, 0.34 mmol) in 2 mL of $[D_8]$THF. The mixture was heated to reflux for 3 h. A dark red suspension formed, which was filtered. Filtrate was concentrated to 0.6 mL and transferred into an NMR tube, which was sealed under vacuum for measurement. ^{31}P NMR ($[D_8]$THF, 25 °C): δ −142 (br s, KPDMes), −158 (br s, $MesPD_2$).

Data Collection and Structure Determination of [Na(tmeda)(*μ*-PHMes)]$_\infty$ (2) and [K(pmdeta)(*μ*-PHMes)]$_2$ (3). Data for **2** and **3** were collected with an Oxford GEMINI CCD diffractometer (λ(Mo Kα) = 71.073 pm). Semiempirical absorption corrections from equivalents were carried out with SCALE3 ABSPACK.[34] Structures were solved by direct methods using SHELXS-97.[35] Structure refinement was carried out using full-matrix least-squares routines against F^2 with SHELXL-97.[35] All non-hydrogen atoms were refined anisotropically; hydrogen atoms of the methyl substituents and hydrogen atoms bonded to the partially oxidized phosphorus atoms in structure **3** are calculated on idealized positions; for all other hydrogen atoms a difference-density Fourier map was used to locate them. Table 3 summarizes the crystallographic data of **2** and **3**. Structure figures were generated with DIAMOND-3.[36] CCDC 914064 (**2**) and 914065 (**3**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Notes

The authors declare no competing financial interest.

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(15) Our efforts to isolate $Li_2(P_4Mes_4)$ were always unsuccessful. Isolation of $Li_2(P_4Mes_4)$ was attempted using short reaction times. However, after evaporation of the solvent, extraction of the residue with Et_2O, filtration and recrystallization from Et_2O/TMEDA or THF/TMEDA, only very small amounts of $[\{Li(tmeda)\}_2P_4Mes_4]\cdot Li(tmeda)Cl\cdot LiCl$ crystallized which were always contaminated with cyclo-P_4Mes_4 and cyclo-P_3Mes_3 (see Supporting Information).

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(22) ^{31}P NMR (MPHR, M = Na, R = Ph, in THF): −114.5 ppm, $^1J_{PH}$ = 173.8 Hz. Surprisingly, a singlet at $\delta = -108.0$ ppm confirms the formation of the 1,2-diphenyldiphosphane-1,2-diide, $Na_2P_2Ph_2$, which is relatively stable in solution and apparently more stable than its protonated species.

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