Synthesis and Structures of Lithium and Potassium Complexes of Phosphanyl-Substituted Bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriates

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The metathesis reaction of $[(THF)_4Li][Cp''_2Li]$ (**1**) ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$) with yttrium trichloride yields bis(tetrahydrofuran)lithium bis[1,3-bis(trimethylsilyl)cyclopentadienyl]-dichloroyttriate (**2**). The metathesis reaction of **2** with potassium (triisopropylsilyl)-phosphanide in toluene gives a stepwise exchange of the chloride ligands with the phosphanide substituents. In contrast to bis(tetrahydrofuran)lithium bis[1,3-bis(trimethylsilyl)cyclopentadienyl][(triisopropylsilyl)phosphanyl]chloroyttriate (**3**), which appears as an intermediate observable by NMR spectroscopy, (tetrahydrofuran)lithium bis[1,3-bis(trimethylsilyl)cyclopentadienyl][bis(triisopropylsilyl)phosphanyl]yttriate (**4**) is isolated as a colorless crystalline material with a YP_2Li cycle and Y−P bond lengths of 2.840 Å. In solution a dissociation is observed into lithium (triisopropylsilyl)phosphanide and the THF complex of bis[1,3-bis(trimethylsilyl)cyclopentadienyl][(triisopropylsilyl)phosphanyl]yttrium (**5**). The reaction of either **2** or **4** with potassium (triisopropylsilyl)phosphanide in benzene yields (η^6-benzene)potassium bis[1,3-bis(trimethylsilyl)cyclopentadienyl][bis(triisopropylsilyl)-phosphanyl]yttriate (**6**) with a YP_2K cycle and Y−P distances of 2.846 Å. The metathesis reaction of **2** with $(DME)LiPH_2$ gives (1,2-dimethoxyethane)lithium bis[1,3-bis(trimethylsilyl)-cyclopentadienyl]bis(phosphanyl)yttriate, which reacts with TMEDA to give colorless bis-[(TMEDA)lithium] bis[1,3-bis(trimethylsilyl)cyclopentadienyl]bis(phosphanyl)yttriate chloride (**7**). The central YP_2Li_2Cl cycle is nearly planar with Y−P bond lengths of 2.849 Å.

Introduction

The alkali-metal dihydrogenphosphanides are easily accessible PH_2 transfer reagents and valuable synthons for a wide variety of organophosphorus compounds.[1] The NMR spectroscopic characterization[2] of MPH_2 species with M = Li, Na, K, Rb, Cs as well as their structural characterization[3] has given detailed insight into the physical properties of these compounds. Due to the instability of $LiPH_2$ at room temperature[3] base adducts of this compound have been prepared which are soluble in ethers and can be handled at room temperature.[4] Depending on the number of 1,2-dimethoxyethane (DME) ligands, monomeric $(DME)_2LiPH_2$[5] and polymeric $[(DME)LiPH_2]_x$[6,7] have been structurally investigated. A representative of an alkaline-earth-metal bis(phosphanide) was already investigated 60 years ago: namely, the ammonia adduct of $Ca(PH_2)_2$.[8] However, there have been no structural reports of dihydrogenphosphanides bonded to alkaline-earth metals but, rather, of their trialkylsilyl-substituted derivatives.[9] Milder phosphanyl transfer reagents such as $Na[B(PH_2)_4]$[10] and $Na[Al(PH_2)_4]$[11] have been well-known for three decades. Tetraphosphanylsilane, $Si(PH_2)_4$, which is isoelectronic with the tetraphosphanylaluminate anion, as well as the homologous germane $Ge(PH_2)_4$ were reported recently.[12]

In contrast to this rich phosphanide chemistry of the electropositive main-group elements, there have been only a few examples of phosphanides of yttrium, namely $Y\{P[2\text{-}(MeO)C_6H_4]_2\}_3$,[13] $(THF)_2Y[PtBu_2]_3$,[14] $[(PhCO)_2$-

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$CH]_2YPPh_2$,[15] $Y[N(SiMe_3)_2]_2(PPh_2)(OPPh_3)$,[16] $(C_4Me_4P)_2Y(\mu\text{-}Cl)_2Li(dme)_2$,[17] $\{Y[P(SiMe_3)_2]_3\}_2$,[18,19] and $Cp''_2Y(THF)P(H)Si\mathit{t}Bu_3$[19] ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$), which were poorly characterized, with the exception of the last two compounds. The homoleptic $Y[P(SiMe_3)_2]_3$[18,19] crystallized as a dimer with two bridging bis(trimethylsilyl)phosphanide ligands, whereas the sterically shielded $Cp''_2Y(THF)P(H)Si\mathit{t}Bu_3$ is monomeric in the solid state and in solution.[19] In addition, several phosphane complexes of yttrium compounds are known; however, the phosphane base has to be incorporated into a multidentate ligand to prevent dissociation of the Y−P bond.[20−22] Thus far, phosphanyl-substituted alkali-metal yttriates are unknown; here, we report an example of an extremely reactive yttrocene bis(dihydrogenphosphanide) anion without shielding of the Y−P bonds by demanding P-bonded trialkylsilyl substituents. Furthermore, yttriates with (trialkylsilyl)phosphanide ligands are presented.

Results and Discussion

Synthesis. The synthesis of $Cp''_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (**2**; $Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$)[23] succeeded via the metathesis reaction of tetrakis(tetrahydrofuran)lithium bis[bis(trimethylsilyl)cyclopentadienyl]lithiate (**1**; $[(THF)_4Li^+][(Cp''_2Li^-])$ with yttrium trichloride. According to the proposed structure of **1** two ^7Li NMR signals were observed at δ 1.0 and −6.8. At −30 °C this compound precipitated as colorless crystals, and a crystal structure determination confirmed this structure also for the solid state. The lithocene anion is bent, due to the intramolecular repulsion of the trimethylsilyl groups; the angle $Cp''_{cent}-Li-Cp''_{cent}$ shows a value of 166.1°. This structural type is quite unusual for lithium cyclopentadienides,[24] and therefore, the molecular structure of the anion of **1** is presented in Figure 1. Another example of this structural type of a lithocene anion was published by Harder and Prosenc[25] for $[Ph_4P]^+[Cp_2Li]^-$ with a linear $Cp_{cent}-Li-Cp_{cent}$ fragment; this sandwich structure was enforced by the large tetraphenylphosphonium cations, and another example has been given by Zägel et al.[26]

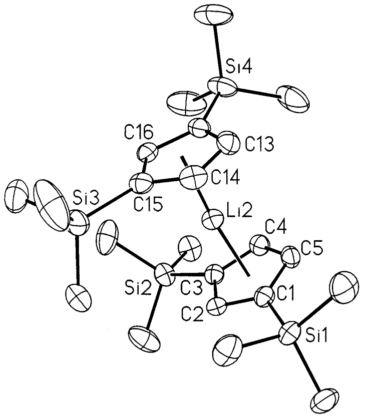
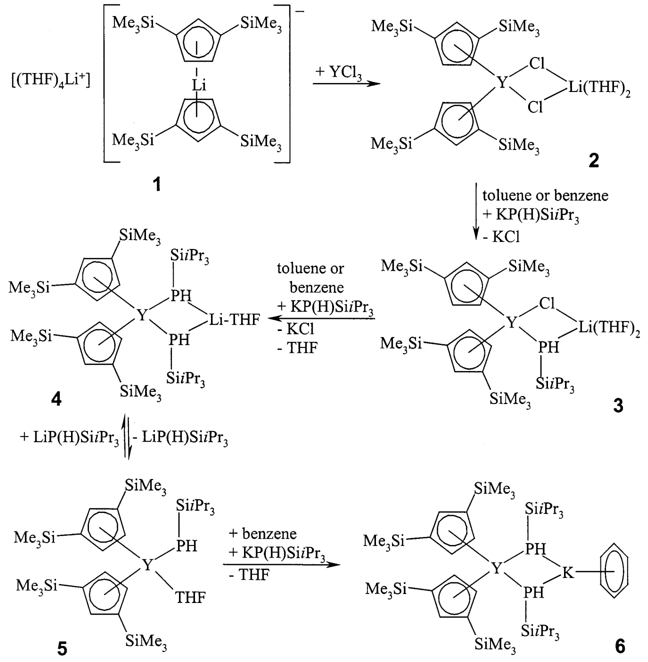


Figure 1. Perspectivic representation of the 1,1′,3,3′-tetrakis(trimethylsilyl)lithocene anion of **1**. The ellipsoids represent a probability of 40%. All hydrogen atoms are omitted for clarity reasons. Selected bond lengths (Å): Li2−C1 = 2.300(5), Li2−C2 = 2.306(5), Li2−C3 = 2.349(5), Li2−C4 = 2.332(6), Li2−C5 = 2.302(6), Li2−C12 = 2.301(5), Li2−C13 = 2.301(5), Li2−C14 = 2.340(6), Li2−C15 = 2.375(6), Li2−C16 = 2.317(5).

The structure of bis(tetrahydrofuran)lithium bis(μ-chloro)bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (**2**) was already proposed earlier;[17,27−30] however, for comparison purposes an X-ray structure determination was performed and the structural data are included in the discussion below.

The NMR spectroscopic pursuance of the reaction of **2** with potassium (triisopropylsilyl)phosphanide in toluene shows in the first step compound **3** with one bridging chloride and another bridging phosphanide ligand according to eq 1. The chemical shifts are $\delta(^{31}P)$ −256.2 and $\delta(^7Li)$ 3.25 with characteristic coupling



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constants (^1J(Y,P) = 97.5 Hz, ^1J(P,Li) = 42.5 Hz). We were not able to isolate this intermediate, but the second reaction step led to a substitution of the second chloride anion by the (triisopropylsilyl)phosphanide ligand, thus giving (tetrahydrofuran)lithium bis[μ-(triisopropylsilyl)-phosphanyl]bis[1,3-bis(trimethylsilyl)cyclopentadienyl]-yttriate (**4**). This complex was identified from the NMR data by a triplet in the ^{7}Li NMR spectrum at δ 4.25 with a ^1J(P,Li) coupling constant of 38.6 Hz. The ^1J(P,Y) value of 91.0 Hz was slightly smaller, also, than observed for **3**. Compound **4** partly dissociated into lithium (triisopropylsilyl)phosphanide and Cp″Y(THF)-PHSi*i*Pr$_3$ (**5**), which was identified by NMR spectroscopy. Compound **5** was extremely sensitive toward moisture and air, and an isolation failed. Therefore, a mixture of **4** and **5** was obtained; however, after cooling only **4** crystallized. Dissolving of crystalline **4** in toluene again resulted in a mixture of **4** and **5**. The change of the solvent to benzene and the further addition of KP(H)Si*i*Pr$_3$ yielded the potassium yttriate **6**, according to eq 1. Stirring of **2** with an excess of potassium (triisopropylsilyl)phosphanide in benzene gave a metathesis reaction and a metal−metal exchange, and thereafter, (η^6-benzene)potassium bis[μ-(triisopropylsilyl)phosphanyl]bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (**6**) was isolated without observing the product **4** as an intermediate. The potassium complex **6** shows a ^1J(P,Y) coupling constant of 96.4 Hz.

The different products starting from **2** depend on the solvent. In toluene **4** can be isolated and **5** has been detected, whereas in benzene **4** was not detected by NMR spectroscopy. This observation could be explained by LiCl elimination from **3** in benzene. Still present potassium (triisopropylsilyl)phosphanide could immediately add to the thus formed yttrocene phosphanide **5** to give complex **6**.

Reduced steric strain should enhance the reactivity of the phosphanyl-substituted yttriates. The metathesis reaction of bis(tetrahydrofuran)lithium bis(μ-chloro)bis-[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (**2**) and (1,2-dimethoxyethane)lithium phosphanide in toluene yields lithium bis(phosphanyl)bis[1,3-bis(trimethylsilyl)-cyclopentadienyl]yttriate (**7**). Figure 2 shows the ^{31}P NMR spectrum of an AA′M$_2$M′$_2$X spin system as well as its simulation. The interpretation of the ^{31}P NMR spectrum gives a ^1J(Y,P) coupling constant of −57.3 Hz and a ^2J(P,P) value of 40.3 Hz. A coupling between the phosphorus and the lithium atoms was not observed. Attempts to isolate this complex led to decomposition reactions. The ^1J(Y,P) coupling constant is a characteristic value for a bridging phosphanide, as deduced from {Y[P(SiMe$_3$)$_2$]$_3$}$_2$;[18] however, this value is a great deal smaller than is observed for the trialkylsilyl-substituted derivatives. The ^2J(P,P) value of 40.3 Hz is 8 times larger than in {Y[P(SiMe$_3$)$_2$]$_3$}$_2$.[18] In phosphanediides with heterocubane structures such as (η^6-toluene)BaSn$_3$-(PSi*t*Bu$_3$)$_4$[31] and [(THF)$_3$Ca]$_2$Sn$_2$(PSiMe$_3$)$_4$[32] values of 26 and 66 Hz, respectively, were observed and show the variation of those coupling constants. An extremely large ^2J(P,P) coupling constant of 135 Hz was elucidated for [(Me$_3$Si)$_2$N−Ca(DME)(μ-PHSi*i*Pr$_3$)]$_2$.[33]

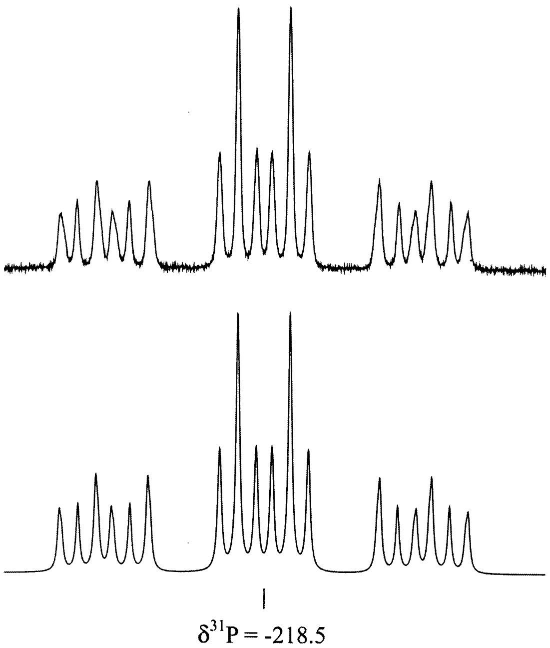
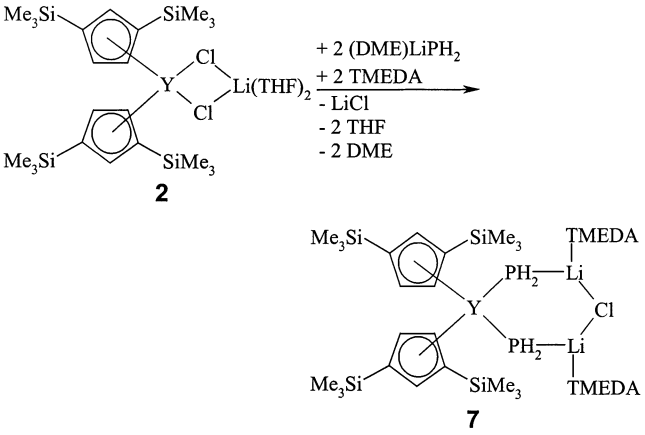


Figure 2. ^{31}P NMR spectrum of the metathesis reaction of (DME)LiPH$_2$ and Cp″$_2$Y(μ-Cl)$_2$Li(THF)$_2$ in toluene in the absence of TMEDA (solvent [D$_8$]toluene, 25 °C).

To obtain single crystals suitable for an X-ray structure determination, TMEDA was added and the TMEDA complex **7** formed according to eq 2. The yield is rather poor, due to a competing reaction in which lithium 1,3-bis(trimethylsilyl)cyclopentadienide instead of LiCl is formed. Cooling of the benzene solution gave crystalline **6**, which was NMR spectroscopically pure and contained also 1 equiv of LiCl. This complex can be described by its components as [Cp″YPH$_2$·(TMEDA)-LiPH$_2$·(TMEDA)LiCl].



Compound **7** is extremely sensitive toward moisture and air and decomposes at room temperature even under an argon atmosphere. Isolating this compound and redissolving in toluene leads to decomposition within a few days accompanied by the formation of

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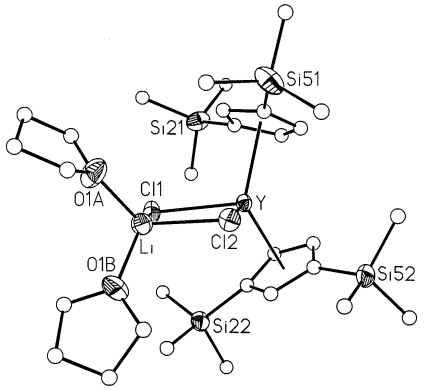

Figure 3. Molecular structure of **2**. The ellipsoids represent a probability of 40%. The carbon atoms are drawn with arbitrary radii. All hydrogen atoms are omitted for clarity reasons. Selected bond lengths (Å): Y−Cl1 = 2.6307(9), Y−Cl2 = 2.6260(9), Li−Cl1 = 2.362(6), Li−Cl2 = 2.365(6), Li−O1A = 1.915(6), Li−O1B = 1.908(6). Selected bond angles (deg): Cl1−Y−Cl2 = 84.94(3), Cl1−Li−Cl2 = 97.3(2), O1A−Li−O1B = 105.4(3), Li−Cl1−Y = 88.8(2), Li−Cl2−Y = 88.8(2).

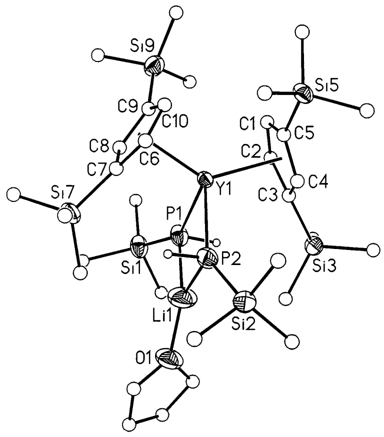

Figure 4. Perspectivic representation of the molecular structure of **4**. The ellipsoids represent a probability of 40%. Carbon atoms are drawn with arbitrary radii, and hydrogen atoms (with the exception of those bonded to P1 and P2) and the methyl groups of the isopropyl substituents are neglected for reasons of clarity. Selected bond lengths (Å): Y1−P1 = 2.8388(9), Y1−P2 = 2.8406(9), Li1−P1 = 2.556(8), Li1−P2 = 2.540(7), P1−Si1 = 2.239(1), P2−Si2 = 2.236(1), Li1−O1 = 1.903(7). Selected bond angles (deg): P1−Y1−P2 = 90.32(3), P1−Li1−P2 = 104.4(2), Li1−P1−Y1 = 82.5(2), Li1−P1−Si1 = 117.7(2), Y1−P1−Si1 = 149.97(5), Li1−P2−Y1 = 82.7(2), Li1−P2−Si2 = 119.3(2), Y1−P2−Si2 = 149.52(4), P1−Li1−O1 = 125.1(4), P2−Li1−O1 = 130.5(4).

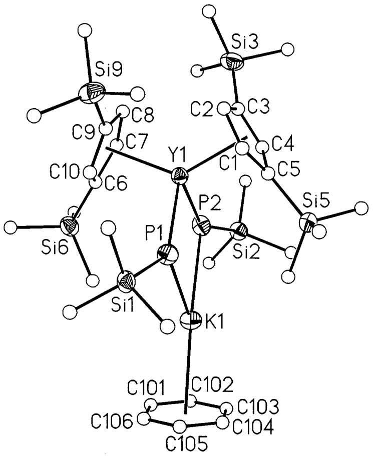

Figure 5. Molecular structure and numbering scheme of **6**. The ellipsoids represent a probability of 40%. The methyl groups of the isopropyl substituents as well as the hydrogen atoms are omitted for reasons of clarity. The carbon atoms are shown with arbitrary radii. Selected bond lengths (Å): Y1−P1 = 2.851(3), Y1−P2 = 2.841(3), P1−Si1 = 2.237(4), P2−Si2 = 2.237(4), K1−P1 = 3.241(4), K1−P2 = 3.312(4), K1−C101 = 3.26(1), K1−C102 = 3.23(1), K1−C103 = 3.19(1), K1−C104 = 3.25(1), K1−C105 = 3.29(1), K1−C106 = 3.34(1). Selected bond angles (deg): P1−Y1−P2 = 94.48(9), P1−K1−P2 = 79.22(9), K1−P1−Y1 = 93.80(9), K1−P1−Si1 = 119.6(1), Y1−P1−Si1 = 141.4(2), K1−P2−Y1 = 92.49(9), K1−P2−Si2 = 112.1(1), Y1−P2−Si2 = 148.4(2).

phosphane, PH_3, as well as a small amount of (trimethylsilyl)phosphane, H_2PSiMe_3.

Molecular Structures. Figure 3 shows the molecular structure of **2** and the numbering scheme. Both metal atoms are coordinated in a distorted-tetrahedral manner by four ligands. The central moiety is a nearly planar $LiCl_2Y$ cycle with mean Li−Cl and Y−Cl bond lengths of 2.36 and 2.63 Å, respectively. The distance between the yttrium atom and the cyclopentadienyl centers $\text{Cp}''_{\text{cent}}$ lies at 2.38 Å. The Cp″ ligands show a staggered orientation with an $\text{Cp}''_{\text{cent}}-\text{Y}-\text{Cp}''_{\text{cent}}$ angle of 127.4°. The Li−O distances to the THF molecules of 1.91 Å lie in the characteristic region and also show no sterical strain. The Cl−M−Cl bond angles at Li and Y amount to 97.3 and 84.9°, respectively.

The molecular structure of **4** and the numbering scheme are displayed in Figure 4. The yttrium atom is coordinated by two Cp″ ligands and two bridging phosphanide substituents. The $\text{Cp}''_{\text{cent}}-\text{Y}-\text{Cp}''_{\text{cent}}$ angle of 130.9° is larger than observed for **2**. The lithium center is in a distorted-trigonal-planar environment with mean Li−P distances of 2.55 Å. The mean Y−P bond length amounts to 2.84 Å, and both of the M−P distances are larger than the corresponding M−Cl values of **2**. The intramolecular steric strain between the Cp″ ligands and the triisopropylsilyl groups leads to a widening of the $\text{Cp}''_{\text{cent}}-\text{Y}-\text{Cp}''_{\text{cent}}$ angle in **4**. On the other hand, the P-bonded triisopropylsilyl groups are bent toward the lithium atom, thus reducing the number of the coordinated THF molecules at the alkali metal. The four-membered LiP_2Y cycle is nearly planar and shows PYP and PLiP bond angles of 90.3 and 104.4°, respectively, which are approximately 6° larger than observed for the corresponding Cl−M−Cl values of compound **2**, a consequence of the larger size of the phosphorus atoms.

The exchange of the (THF)Li moiety with a (η^6-benzene)K fragment leads to characteristic structural changes. Figure 5 shows the molecular structure of **6** and the numbering scheme. The larger radius of the alkali metal leads to a widening of the P−Y−P bond angle of approximately 4°. Due to the large K−P distances of 3.24 and 3.31 Å a narrow P−K−P angle of 79.2° is observed. The potassium atom is coordinated in a distorted-trigonal-planar manner by two phosphorus atoms and a benzene molecule. However, agostic interactions between the alkali metal and the trimethylsilyl substituents of the Cp″ ligand enhance the

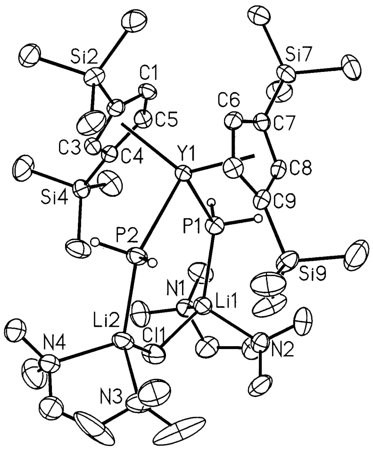

Figure 6. Molecular structure of **7**. The ellipsoids represent a probability of 40%. The C-bonded hydrogen atoms are omitted for clarity reasons. The P-bonded H atoms are shown with arbitrary radii. Selected bond lengths (Å): Y1−P1 = 2.842(2), Y1−P2 = 2.856(2), Li1−P1 = 2.571(7), Li2−P2 = 2.606(8), Li1−Cl1 = 2.293(6), Li2−Cl1 = 2.275(8), Li1−N1 = 2.098(8), Li1−N2 = 2.141(8), Li2−N3 = 2.118(8), Li2−N4 = 2.125(8). Selected bond angles (deg): P1−Y1−P2 = 91.75(4), Y1−P1−Li1 = 132.6(2), Y1−P2−Li2 = 133.4(2), P1−Li1−Cl1 = 120.1(3), P2−Li2−Cl1 = 118.3(3), Li1−Cl1−Li2 = 122.4(3).

coordinative shielding, with K···H distances of 2.82 and 2.93 Å.

The steric intramolecular repulsion leads to a large widening of the Y−P−Si angles of **4** and **6**. In both compounds values of approximately 150° are observed. The flattening of the coordination sphere of the phosphorus atoms, neglecting the hydrogen atoms, and the formation of nearly planar MPYSi fragments are also a consequence of the extremely bulky P-bonded trialkylsilyl substituents. The large Y−P−Si angles increase the shielding of the alkali metals, and therefore, only one additional neutral coligand is bonded to lithium in **4** (THF molecule) and potassium in **6** (η^6-bonded benzene).

The molecular structure of **7** is represented in Figure 6. The main fragment is the nearly planar six-membered YP_2Li_2Cl cycle. The P-bonded hydrogen atoms were found and refined isotropically; the H−P(n)−H bond angles amount to 91° ($n = 1$) and 86° ($n = 2$). These values account for the fact that the binding situation is not in agreement with sp^3 hydridization at the phosphorus atom, which is in agreement with the observations at $[(DME)LiPH_2]_x$.[6,7] Due to this fact, the Li(n)−P(n)−Y1 angles with values of 132.6 and 133.4° are larger than tetrahedral angles and, therefore, the binding situation can be considered as Li−P−Y three-center two-electron bonds with a p orbital at the phosphorus atom. The Y−P bond lengths of approximately 2.85 Å are large and lie in the characteristic region for bridging phosphanides. The Li−P distances of 2.57 and 2.61 Å are comparable to those of polymeric $[(DME)LiPH_2]_x$[6,7] and organyl-substituted lithium phosphanides.[34]

The reduced intramolecular strain allows the lithium cations to adopt the characteristic coordination number of 4 and a distorted-tetrahedral coordination sphere. Whereas the six-membered YP_2Li_2Cl cycle is unique within the chemistry of the lanthanides and the scandium group, the four-membered YP_2Li fragment was already known for some lanthanide phosphanides such as, for example, in $Eu[(\mu\text{-}PtBu_2)_2Li(thf)]_2$[35] and the isotypic samarium[36] as well as ytterbium complexes.[37]

Table 1. Selected NMR Data of the PH Fragments of Compounds 3−7 and Selected Bond Lengths and Angles Deduced from X-ray Crystal Structure Determinations

	3	**4**	**5**	**6**	**7**
$\delta(^{31}P)$	−256.2	−251.6	−188.0	−241	−218.5
$^1J(Y,P)$/Hz	97.5	91.0	139.5	96.4	−57.3
$^1J(P,H)$/Hz	206.0	*a*	207.3	183.1	+174.0
$^1J(P,Li)$/Hz	42.5	38.6			*b*
$^2J(P,P)$/Hz		*a*		57.1	+40.3
$\delta(^7Li)$	3.25	4.25			4.20
$\delta(^{29}Si\textit{i}Pr_3)$	26.1	26.8	25.3	26.4	
$\lvert ^1J(P,Si) + {}^3J(P,Si) \rvert$	14.4	15.1	15.6	25.0	
$^2J(Y,Si)$	4.0	3.2	6.9	3.8	
$\delta(^{29}SiMe_3)$	−10.1	−9.2	−8.9	−9.2	−9.3
d(Y−P)/Å		2.84		2.85	2.85
P−Y−P/deg		90.3		94.5	91.8
Y−P−M/deg		82.6		93.1	133.0
Cp″−Y−Cp″/deg		130.9		129.6	130.3

[a] The calculation of these coupling constants was impossible due to the broadness of the signals. [b] In neither the ^{31}P NMR nor the ^7Li NMR spectrum was a $^1J(P,Li)$ coupling observed.

NMR Spectroscopy. Selected NMR parameters are summarized in Table 1 together with selected mean structural parameters. The $^1J(Y,P)$ coupling constants for the bridging (triisopropylsilyl)phosphanide ligands show values of approximately 95 Hz, which lies in the characteristic region for yttrium phosphanides.[3,4] In **5** with a terminally bonded phosphanide substituent, the $^1J(Y,P)$ value is approximately 45 Hz larger than observed for bridging phosphanide ligands. The different coordination mode also leads to a low-field shift of the ^{31}P NMR resonance.

The coupling between the phosphorus and the lithium nuclei with $^1J(P,Li)$ values of 42.5 Hz for **3** and 38.6 Hz for **4** clearly proves that these complexes retain as a contact ion pair in solution. The ^{31}P NMR spectrum of **3** shows double doublet fine structure, due to the coupling with the ^1H and ^{89}Y nuclei. Furthermore, each line is split into a 1:1:1:1 quartet due to the coupling with a ^7Li nucleus. The $^1J(P,Li)$ coupling constants listed in Table 1 are in the same order of magnitude as observed for other lithium phosphanides.[1b,38] In the $^{29}Si\{^1H\}$ NMR spectra of **4** and **6** an AA′MX spectrum type is observed; the $^2J(Si,Li)$ coupling of **4** is smaller than the spectral resolution. The simulation of the ^{31}P NMR spectrum of **6** with an AA′MM′X coupling pattern allows the calculation of the $^2J(P,P)$ coupling of 57.1 Hz. As mentioned earlier, this is a characteristic value for a $^2J(P,P)$ coupling constant.

The $^1J(Y,P)$ constant of −57 Hz observed for **7** is remarkably small. This fact can possibly be explained

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Table 2. Crystallographic Data for Compounds 1, 2, 4, 6, and 7

	1	**2**	**4**	**6**	**7**
empirical formula	$C_{38}H_{74}Li_2O_4Si_4$	$C_{30}H_{58}Cl_2LiO_2Si_4Y$	$C_{44}H_{94}LiOP_2Si_6Y$	$C_{46}H_{92}KP_2Si_6Y$	$C_{34}H_{78}ClLi_2N_4P_2Si_4Y$
fw	721.21	729.87	965.52	1003.68	855.54
temp, T (K)	183(2)	200(3)	193(2)	193(2)	193(2)
space group[45]	$Pca2_1$ (No. 29)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	20.956(3)	16.669(1)	12.8669(8)	11.887(4)	19.239(14)
b (Å)	11.525(2)	19.850(1)	19.028(1)	12.150(4)	12.763(9)
c (Å)	19.688(3)	12.5717(9)	23.898(2)	21.941(7)	20.684(15)
α (deg)	90	90	90	91.731(6)	90
β (deg)	90	93.367(9)	92.138(1)	92.095(5)	95.22(1)
γ (deg)	90	90	90	109.239(6)	90
V (Å^3)	4754(1)	4152.6(5)	5847.0(7)	2987(2)	5058(6)
Z	4	4	4	2	4
ρ_{calcd} (g cm^3)	1.008	1.167	1.097	1.116	1.124
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	0.156	1.671	1.203	1.247	1.389
no. of indep rflns	9668	6269	11190	9357	10048
no. of obsd rflns ($I > 2\sigma(I)$)	7247	4246	7314	3164	5933
abs cor	SADABS	numerical	SADABS	SADABS	SADABS
min/max transmission	0.955/0.969	0.666/0.761	0.762/1.000	0.825/1.000	0.701/1.000
wR2[a] (on F^2)	0.1540	0.0727	0.0971	0.2079	0.1230
R1[a] ($I > 2\sigma(I)$)	0.0578	0.0343	0.0413	0.0880	0.0548
goodness of fit s[b] on F^2	1.039	0.864	0.944	0.908	0.950

[a] Definition of the R indices: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = - \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

by the ring geometry and the binding situation. Whereas the compounds **4** (M = Li) and **6** (M = K) crystallize with four-membered MP_2Y cycles, a six-membered $ClLi_2P_2Y$ ring is observed for **7**. This leads to a widening of the M−P−Y bond angles and therefore to an enhancement of the p orbital participation as mentioned above. The geometry of the PH_2 substituent is best explained by a YPLi three-center two-electron bond with a p orbital at the phosphorus atom. A similar postulate was used to explain the zigzag chain structure of (DME)-$LiPH_2$.[6,7]

Experimental Section

General Considerations. All experiments and manipulations were carried out under purified argon. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting $[(THF)_4Li][Cp''_2Li]$ (**1**),[39] KP(H)Si*i*Pr$_3$,[40] (DME)$LiPH_2$,[41] and $Cp''_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (**2**)[25,42] were prepared by literature procedures. NMR spectra were recorded on JEOL GSX270 and EX400 spectrometers. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra. All phosphanyl-substituted yttriates were extremely sensitive toward moisture and air, and even single-crystal material decomposed after isolation under an argon atmosphere. Therefore, only the alkali-metal-to-yttrium ratios of the crystalline compounds were investigated by ICP after a workup with nitric acid and were in agreement with the proposed structures and NMR parameters. Due to the fact that these compounds decomposed even at room temperature, no melting points are given. All NMR spectra were recorded at room temperature as [D$_6$]benzene solutions. The ^{7}Li, ^{29}Si, and ^{31}P NMR parameters are summarized in Table 1.

(Tetrahydrofuran)lithium Bis[*μ*-(triisopropylsilyl)phosphanyl]bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (4). To a suspension of 187 mg of **2** (0.26 mmol) in 5 mL of toluene was added at once 140 mg of potassium (triisopropylsilyl)phosphanide (0.52 mmol). The solution was stirred at room temperature for 1 day. A precipitate formed. The solution was decanted and the residue washed with 5 mL of toluene. Cooling of the mother liquor to −30 °C yielded colorless crystals of **4**. The solution contained **5**, which was identified by NMR spectroscopy (Table 1). The yields of 63% and 25% for **4** and **5** were determined by integration of the ^{31}P NMR spectrum. ^{1}H NMR: δ 0.47 (s, SiMe$_3$), 1.27 (br, CH *i*Pr), 1.31 (d, CH$_3$ *i*Pr, ^3J(H,H) = 2.6 Hz), 1.33 and 3.63 (m, THF), 6.75 (t, Cp), 6.82 (d, Cp, ^4J(H,H) = 1.9 Hz); the assignment of PH was not possible. ^{13}C{^{1}H} NMR: δ 1.2 (SiMe$_3$), 15.4 (CH *i*Pr), 19.4 (CH$_3$ *i*Pr, ^3J(P,C) = 2.8 Hz), 25.0 and 69.0 (THF), 121.0, 123.5, and 130.5 (Cp).

(η^6-Benzene)potassium Bis[*μ*-(triisopropylsilyl)phosphanyl]bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (6). A suspension was prepared by adding 407 mg of **2** to 10 mL of benzene. A 241 mg portion of potassium (triisopropylsilyl)phosphanide was added and the solution stirred at room temperature for 2 days. A gray precipitate formed. The solution was decanted and its volume reduced to a few milliliters. At −30 °C 0.32 g of yellow crystals precipitated (0.32 mmol, 78%), which decomposed quickly after isolation. ^{1}H NMR: δ 0.38 (s, SiMe$_3$), 1.18 (br, CH *i*Pr), 1.31 (br, CH$_3$ *i*Pr), 6.77 (d, Cp), 7.33 (t, Cp, ^4J(H,H) = 2.2 Hz); the assignment of the PH group was not possible. ^{13}C{^{1}H} NMR: δ 1.1 (SiMe$_3$), 15.6 (CH *i*Pr), 18.8 (CH$_3$ *i*Pr, ^3J(P,C) = 3.3 Hz), 127.2, 129.1, and 130.4 (Cp), 128.3 (benzene).

Bis[(TMEDA)lithium] Bis(phosphanyl)bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate Chloride (7). To a solution of 333 mg of bis(tetrahydrofuran)lithium bis(*μ*-chloro)-bis[1,3-bis(trimethylsilyl)cyclopentadienyl]yttriate (0.46 mmol) in 5 mL of toluene was added 119 mg of (DME)$LiPH_2$ (0.92 mmol) at room temperature. The solution was stirred for 12 h. After approximately 8 h a pale yellow precipitate formed. The solution was decanted and the volume reduced. After addition of 0.14 g of TMEDA (0.92 mmol) and subsequent cooling to −30 °C colorless crystals of **7** precipitated. These crystals decomposed after isolation, and therefore, the yield of 68% was determined spectroscopically. ^{1}H NMR: δ 0.49 (s, 36H, Si*Me*$_3$), 0.44 (m, P*H*, ^1J(P,H) = 174.0 Hz, ^2J(Y,H) = 1.0 Hz), 1.93 and 2.13 (br, TMEDA), 6.69 (d, Cp, ^4J(H,H) = 1.8 Hz), 6.83 (t, Cp, ^4J(H,H) = 1.8 Hz). ^{13}C{^{1}H} NMR: δ 1.4 (Si*Me*$_3$), 46.3 and 56.8 (TMEDA), 119.0, 122.2, 129.1 (Cp). IR (Nujol): 2287 cm^{-1} (br, ν(P−H)).

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Structure Determination of 1. Data were collected on a STOE-IPDS (**2**) and a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**1**, **4**, **6**, and **7**) with graphite-monochromated Mo Kα radiation ($\lambda = 71.073$ pm) using oil-coated,[43,44] rapidly cooled single crystals. Crystallographic parameters and details of the data collection and refinement procedures are summarized in Table 2.

All structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[46] Neutral scattering factors were taken from Cromer and Mann[47] and, for the hydrogen atoms, from Stewart et al.[48] The non-hydrogen atoms were refined anisotropically. Most of the H atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atoms; however, the P-bonded hydrogen atoms of **4** and **7** and those of the cyclopentadienyl substituents were refined isotropically. The data of **6** were weak, and therefore, rather high *R* values were obtained.

Supporting Information Available: Listings of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of non-hydrogen atoms for **1**, **2**, **4,** and **6**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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