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Synthesis and Structure of Potassium and Samarium Phosphine(phosphinimino)methanides

Michael T. Gamer and Peter W. Roesky*

Institut für Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany

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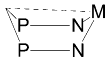
The monoanionic phosphine(phosphinimino)methanide ligand $(Ph_2PCHPPh_2NSiMe_3)^-$ is introduced in organometallic chemistry. Starting from the established compound $Ph_2PCH_2PPh_2NSiMe_3$ (**1**) the potassium salt $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ (**2**) was prepared. The solid state structure of **2** shows a η^3-N−P−C heteroallyl coordination of the ligand as well as a π-coordination of the phenyl rings to the potassium atoms. These coordination modes lead to an infinite chain in the solid state. Compound **2** was further reacted to the samarium complex $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$, in which the $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand coordinates in η^3-heteroallylic fashion via the N atom and the methine group to the center metal.

Introduction

Phosphinimines and phosphinimides have been used as popular ligands in main group and transition metal chemistry in recent years. Lately, the deprotonated derivatives of the well-known bis(phosphinimine) $CH_2(PPh_2NSiMe_3)_2$[1] have drawn the attention by a number of research groups. It was shown that a monoanionic[2−5] and a dianionic species[6,7] ($\{CH(PPh_2NSiMe_3)_2\}^-$ and $\{C(PPh_2NSiMe_3)_2\}^{2-}$, respectively) can be generated by deprotonation of the precursor $CH_2(PPh_2NSiMe_3)_2$. The monoanionic species was used as a ligand in main group and transition metal chemistry,[8−13] whereas the dianionic ligand was reported by Cavell and co-workers to form carbene-like complexes with a series of transition metals.[9,14] $\{CH(PPh_2NSiMe_3)_2\}^-$ tends to show an uncommon coordination mode. In most of the solid state structures the methine carbon atom coordinates via a long interaction onto the metal atom.[8−13] Thus, the six-membered metallacycle (N1−P1−C1−P2−N2−M), which is formed by chelation of the two trimethlysilylimine groups to the metal center, adopts a pseudo-boat conformation (Scheme 1). Motivated by these results we were interested to get some insight into the coordination chemistry of the deprotonated derivate of the related phosphine-phosphinimine $Ph_2PCH_2PPh_2NSiMe_3$ (**1**).[15] In the heterodifunctional compound **1** one of the phosphorus atoms is in oxidation state +3 whereas the other one is in +5. **1** is available via a Staudinger reaction from bis(diphenylphosphino)methane (dppm) and trimethylsilyl azide (Scheme 2).[15] Previously **1** was used either as a ligand in late transition metal chemistry[16] or as a precursor for the formation of phoshoranimine complexes ($Ph_2PCH_2PPh_2N$−M).[17] The latter compounds were obtained via the cleavage of the N−$SiMe_3$ bond. To the best of our knowledge no anionic derivative of

Scheme 1



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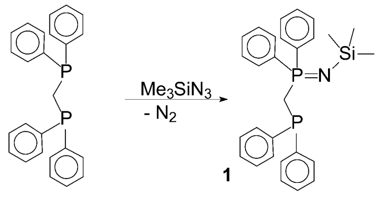
Scheme 2



composition $(Ph_2PCHPPh_2NSiMe_3)^-$ has been reported. On the other hand the coordination chemistry of some main group metals of the somewhat related ligand $(Me_3SiCHPPh_2NSiMe_3)^-$ was reported by Lappert et al.[18] Herein we describe the synthesis of the potassium compound $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ and a further reaction to the samarium complex $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$.

Experimental Section

General Procedures. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. Ether solvents (THF and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) as well as benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥ 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a Bruker AC 250 or JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively.

$Ph_2PCH_2PPh_2NSiMe_3$ (1). To a suspension of 5.0 g (13.0 mmol) of bis(diphenylphosphino)methane in 15 mL of toluene was added 2 mL (1.72 g, 14.9 mmol) of trimethylsilyl azide. The mixture was refluxed for 12 h. Then, the solvent and unreacted trimethylsilyl azide were removed in vacuo at 100 °C. The remaining oily residue was treated with 20 mL of pentane and dried in vacuo. Then, the resulting suspension was filtered and the solvent removed. The remaining solid was washed with *n*-pentane (2 × 10 mL) and dried in vacuo. Usually the resulting raw product can be used for subsequent reactions without further purification. A pure product is obtained by crystallization from hot toluene (in this case the yield decreases by about 30%). Yield: 5.37 g (88%), colorless powder. ^1H NMR (C_6D_6, 250 MHz, 25 °C): δ 0.14 (s, 9H, $SiMe_3$), 2.95 (dd, 1H, CH_2, $^2J(H,P) = 11.85$ Hz, $^2J(H,P) = 11.86$ Hz), 7.00−7.05 (m, 12H, Ph), 7.38−7.45 (m, 4H, Ph), 7.60−7.69 (m, 4H, Ph). ^{29}Si NMR (C_6D_6, 49.7 MHz, 25°C): δ −11.8. $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz, 25 °C): δ −26.7 (d, $^2J(P,P) = 56.4$ Hz), −2.1 (d, $^2J(P,P) = 56.4$ Hz). Anal. Calcd for $C_{28}H_{31}NP_2Si$ (471.59): C 71.31, H 6.63, N 2.97. Found: C 71.22, H 6.55, N 2.89. EI/MS (70 eV) *m/z* (%): 471 ($[M]^+$, rel int 90), 456 ($[M-Me]^+$, 100), 394 ($[C_{22}H_{26}NP_2Si]^+$, 93), 272 ($[C_{15}H_{19}NPSi]^+$, 72), 199 ($[C_{13}H_{12}P]^+$, 64).

Table 1. Crystallographic Details of $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ (2) and $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$ (3)[a]

	2·(toluene)	2 **3**·(toluene)
formula	$C_{63}H_{68}K_2N_2P_4Si_2$	$C_{103}H_{128}N_2P_4Si_2Sm_2$
fw	1111.45	1874.84
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	12.087(2)	22.4232(8)
b, Å	12.676(3)	14.8800(8)
c, Å	20.777(4)	14.846(2)
α, deg	77.86(3)	
β, deg	86.31(3)	109.289(8)
γ, deg	85.86(3)	
V, Å^3	3100.2(11)	4675.4(6)
Z	2	4
density (g/cm^3)	1.191	1.332
radiation	Ag Kα (λ = 0.56086 Å)	Ag Kα (λ = 0.56086 Å)
μ, mm^{-1}	0.176	0.743
absorp corr	none	none
no. of reflns collected	18 293	27 984
no. of unique reflns	10 479 [R_{int} = 0.1271]	12 919 [R_{int} = 0.0523]
no. of obsd reflns	4052	9135
GOF on F^2	0.873	1.036
R1[b]; wR2[c]	0.0824; 0.1890	0.0421; 0.1170

[a] All data collected at 203 K. [b] $R1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

$[K(Ph_2PCHPPh_2NSiMe_3)]_n$ (2). To a suspension of 0.69 g (17.2 mmol) of KH in THF was slowly added 5.37 g (11.4 mmol) of **1** dissolved in 40 mL of THF at room temperature. The mixture was refluxed for 6 h. Then, the unreacted KH was filtered off and the filtrate was concentrated in vacuo to dryness. The remaining residue was crystallized from toluene. Yield: 3.86 g (67%), colorless powder. ^1H NMR (d_8-THF, 400 MHz, 20 °C): δ −0.21 (s, 9H, $SiMe_3$), 1.59 (dd, 1H, P_2CH, $^2J(H,P^{III}) = 14.13$ Hz, $^2J(H,P^V) = 6.79$ Hz), 6.98−7.02 (m, 2H, Ph), 7.07−7.14 (m, 10H, Ph), 7.50−7.54 (m, 4H, Ph), 7.70−7.76 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (d_8-THF, 100.4 MHz, 20 °C): δ 4.3 (dd, $SiMe_3$, $^3J(C,P^V) = 4.0$ Hz, $^5J(C,P^{III}) = 0.9$ Hz), 21.2 (dd, PCP, $^1J(C,P^V) = 138.4$ Hz, $^1J(C,P^{III}) = 3.5$ Hz), 126.2 (s, *p*-PhP^{III}), 127.7 (d, *m*-PhP^V, $^3J(C,P^V) = 10.7$ Hz), 128.0 (d, *m*-PhP^{III}, $^3J(C,P^{III}) = 5.8$ Hz), 128.6 (d, *p*-PhP^V, $^4J(C,P^V) = 2.5$ Hz), 132.4 (d, *o*-PhP^{III}, $^2J(C,P^{III}) = 9.9$ Hz), 132.6 (d, *o*-PhP^V, $^2J(C,P^V) = 17.7$ Hz), 147.1 (dd, *i*-PhP^V, $^1J(C,P^V) = 90.7$ Hz, $^3J(C,P^{III}) = 3.6$ Hz), 151.4 (dd, *i*-PhP^{III}, $^1J(C,P^{III}) = 12.0$ Hz, $^3J(C,P^V) = 9.1$ Hz). ^{29}Si NMR (d_8-THF, 79.4 MHz, 20 °C): δ −15.6. $^{31}P\{^1H\}$ NMR (d_8-THF, 161.7 MHz, 20 °C): δ −15.2 (d, $^2J(P,P) = 136.3$ Hz), 21.7 (d, $^2J(P,P) = 136.3$ Hz). Anal. Calcd for $C_{28}H_{30}KNP_2Si$ (509.68): C 65.98, H 5.93, N 2.75. Found: C 65.77, H 6.12, N 2.78.

$[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$ (3). THF (20 mL) was condensed at −196 °C onto a mixture of 250 mg (1.0 mmol) of $SmCl_3$ and 500 mg (1.0 mmol) of **2**. The mixture was stirred for 18 h at room temperature. The solvent was then evaporated in a vacuum, and 349 mg (2.0 mmol) KC_5Me_5 was added to the remaining solid. Again, 20 mL of THF was condensed at −196 °C onto the mixture, and the suspension was stirred for 18 h at room temperature. The solvent was then evaporated in a vacuum and toluene (20 mL) condensed onto the mixture. Then, the solution was shortly heated under reflux and filtered, and the solvent was removed. The remaining solid was washed with *n*-pentane (10 mL) and dried in a vacuum. Finally, the product was crystallized from hot toluene. Yield: 72 mg (23%). Anal. Calcd for $C_{48}H_{60}NP_2SiSm$ (891.40): C 64.68, H 6.78, N 1.57. Found: C 64.39, H 6.63, N 1.61.

X-ray Crystallographic Studies of 2 and 3. Crystals of **2** and **3** were grown from hot toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2

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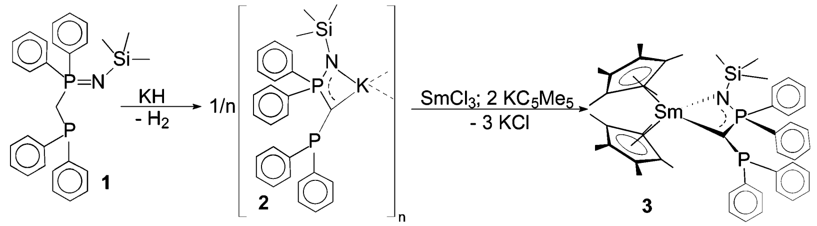
Scheme 3



stream of a Stoe IPDS diffractometer. Subsequent computations were carried out on a Intel Pentium III PC.

All structures were solved by the Patterson method (SHELXS-97[19]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[20] In the final cycles of each refinement, all non-hydrogen atoms except C4−C6, C22−C24, C39−C41, C53−C56, and the toluene molecules in **2** and the toluene molecules in **3** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances, and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-245811 (**2**) and 245812 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The neutral phosphine-phosphinimine ligand $Ph_2PCH_2PPh_2NSiMe_3$ (**1**), was prepared as described in the literature from bis(diphenylphosphino)methane (dppm) and trimethylsilyl azide (Scheme 2). However, compared to the reported procedure[15] we used different reaction conditions to obtain a pure product in high yields. Treatment of **1** with KH in boiling THF followed by crystallization from hot toluene leads to the desired potassium reagent $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ (**2**) in moderate yields (Scheme 3). The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid state structure was established by single-crystal X-ray diffraction. Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2. Compound **2**, which crystallizes in the triclinic space group $P\bar{1}$ with two molecules of toluene, forms infinite chains in the solid state (Figure 1). In the unit cell there are two different $[K(Ph_2PCHPPh_2NSiMe_3)]$ units. In both units the $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand coordinates via the N−P−C backbone in a heteroallylic fashion onto the potassium atom. Thus, K1 is η^3-coordinated by the N1−P1−C1 and K2 by the N2−P3−C29 unit. Inside these units the angles are N1−P1−C1 118.1(3)° and N2−P3−C29 115.9(3)°. The distances of these units to the potassium atoms are N1−K1 2.799(6) Å, N2−K2 2.798(6) Å, C1−K1 3.166(7) Å, and C29−K2 3.002(7) Å and the N−K−C bite angles are N1−K1−C1 56.2(2)° and N2−K2−C29 57.3(2)°.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ (2)

Bond Lengths		Bond Angles	
N1−K1	2.799(6)	N1−P1−C1	118.1(3)
C1−K1	3.166(7)	N1−K1−C1	56.2(2)
C14−K1	3.170(7)	P1−C1−P2	122.5(4)
C15−K1	3.233(8)	N2−P3−C29	115.9(3)
C34−K1	3.218(8)	N2−K2−C29	57.3(2)
C35−K1	3.414(8)	P3−C29−P4	124.8(4)
C1−P1	1.724(6)		
C1−P2	1.739(7)		
N1−P1	1.574(6)		
N2−K2	2.798(6)		
C29−K2	3.002(7)		
C2−K2’	3.496(7)		
C3−K2’	3.394(8)		
C4−K2’	3.329(9)		
C5−K2’	3.384(9)		
C6−K2’	3.424(9)		
C7−K2’	3.491(8)		
C29−P3	1.697(7)		
C29−P4	1.752(7)		
N2−P3	1.587(5)		

Besides the heteroallyl coordination of the ligand, π-coordination of the phenyl rings to the potassium atoms is observed. The coordination number of the potassium atom depends strongly on the considered length of the C−K interaction. In Figure 1 all C−K interactions up to a range of 3.5 Å are marked as dotted lines. By using the criteria, K1 is η^2-coordinated in an intramolecular fashion by one of the phenyl rings, which is bound to P2. Furthermore a η^3-coordination is observed to a phenyl ring of a neighboring $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand. In contrast K2 is intramolecular η^1-coordinated by one of the phenyl rings, which is bound to P4. Additionally, an intramolecular η^6-coordination to one of the phenyl rings, which is attached to P1, is seen. Here, the average C−K distance of these interactions is 3.420(8) Å.

Next, we were interested to learn about the coordination behavior of the $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand in lanthanide chemistry. To get a reliable comparison with other ligands in lanthanide chemistry, we wanted to synthesize a metallocene complex. In a one-pot reaction starting from $SmCl_3$ and the potassium salt **2** followed by an addition of KC_5Me_5 the metallocene complex $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$ (**3**) was obtained (Scheme 3). Compound **3** is an air- and moisture-

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[19] Sheldrick, G. M. *SHELXS-97*, *Program of Crystal Structure Solution*; University of Göttingen: Germany, 1997.

[20] Sheldrick, G. M. *SHELXL-97*, *Program of Crystal Structure Refinement*; University of Göttingen: Germany, 1997.

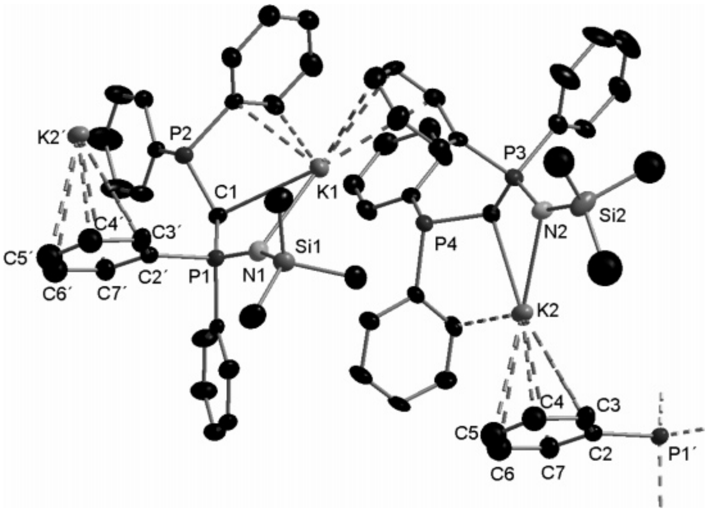

Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms are omitted for clarity. Shown is one unit out of an infinite chain.

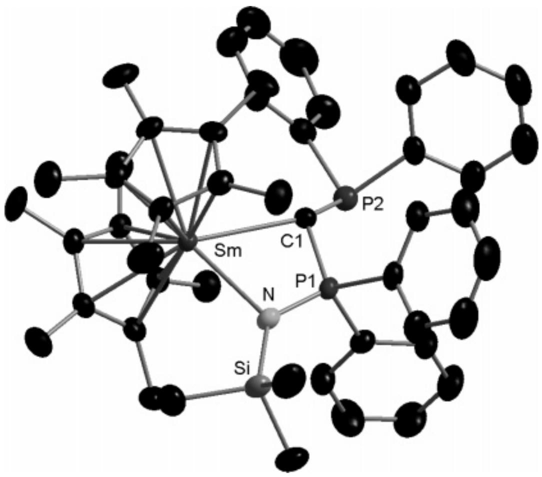

Figure 2. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$ (3)[a]

Bond Lengths		Bond Angles	
C1−P1	1.753(3)	N−Sm−C1	63.41(10)
C1−P2	1.820(3)	N−P1−C1	108.2(2)
C1−Sm	2.698(3)	P1−C1−P2	116.0(2)
N−P1	1.612(3)	P1−C1−Sm	88.49(12)
N−Si	1.738(3)	P2−C1−Sm	138.2(2)
N−Sm	2.478(3)	P1−N−Si	133.0(2)
Cg1−Sm	2.514(9)	P1−N−Sm	99.85(12)
Cg2−Sm	2.509(6)	Si1−N−Sm	127.1(2)
		Cg1−Sm−Cg2	130.77(10)
		Cg1−Sm−N	116.04(10)
		Cg1−Sm−C1	114.68

[a] Cg = C_5Me_5-ring centroid.

sensitive compound, which has been characterized by single-crystal X-ray diffraction and elemental analysis.

The solid state structure of **3** was investigated by single-crystal X-ray diffraction (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 3. The structure reveals a pseudo 4-fold coordination sphere of the ligands around the samarium atom. The $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand is coordinated via the atoms N−P1−C1 to the samarium atom in a chelating heteroallylic (η^3) fashion. Whereas compound **3** is to the best of our knowledge the first lanthanide compound having a η^3-N−P−C heteroallyl ligand, other heteroallyl systems such as benzamidinates,[21] diiminosulfates,[22] and diiminophosphinates[23] are established in lanthanide chemistry.[24] The unusual point in compound **3** is the phosphorus atom (P2) in oxidation state +3, which points away from the center metal. It may be possible to attach other transition metals at this position onto **3**. The bite angle of the ligand in **3** (N−Sm−C1 63.41(10)°) is in the expected range (62.94(13)° in $[\{Ph_2P(NSiMe_3)_2\}_2Sm(\mu\text{-}I)_2Li(THF)_2]$).[23b] The corresponding bond distances C1−Sm (2.698(3) Å) and N−Sm (2.478(3) Å) differ by more than 0.2 Å. Both distances are in agreement with other samarium amido (e.g., Sm−N in $[(\eta^5\text{-}C_5Me_5)_2Sm\{\eta^2\text{-}N(PPh_2)_2\}]$, 2.430(3) Å)[25] and allyl complexes (e.g., Sm−C in the allyl complex $[(\eta^5\text{-}C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)]$ (2.63(2) and 2.64(2) Å).[26] The Cg−Sm (Cg = C_5Me_5-ring centroids) distances (Cg1−Sm 2.514(9) Å, Cg2−Sm 2.509(6) Å, respectively) and the angle Cg1−Sm−Cg2 (130.77(10)°) are in the expected range.[25−27]

Summary

In summary, we have introduced the $(Ph_2PCHPPh_2NSiMe_3)^-$ ligand in organometallic chemistry. Starting from $Ph_2PCH_2PPh_2NSiMe_3$ the potassium salt $[K(Ph_2PCHPPh_2NSiMe_3)]_n$ was prepared and further reacted to the samarium complex $[(\eta^5\text{-}C_5Me_5)_2Sm(Ph_2PCHPPh_2NSiMe_3)]$. The $(Ph_2PCHPPh_2NSiMe_3)^-$

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ligand always coordinates in η^3-heteroallylic fashion via the N atom and the methine group.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2** and **3** are available free of charge via the Internet at http://pubs.acs.org.

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