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2,5-Diphenyl-3,4-bis(trimethylsilyl)-1-phosphacyclopentadienide as a Ligand at Calcium, Strontium, and Tin(II)

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The addition reaction of tetrakis(tetrahydrofuran)calcium or -strontium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne in toluene yields nearly quantitative amounts of slightly yellow tetrakis(tetrahydrofuran)calcium (**1**) and -strontium bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide] (**2**). Due to the fact that the alkaline earth metal bis[bis(trimethylsilyl)amides] do not react with alkynes, colorless (tetrahydrofuran)calcium bis[2,5-bis(*tert*-butyl)-1-azacyclopentadienide] (**3**) was prepared by the transmetalation of *N*-trimethylstannyl-2,5-bis(*tert*-butyl)-1-azacyclopentadiene with distilled calcium. The metathesis reaction of **1** and **2** with $SnCl_2$ gives yellow tin bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide] (**4**).The phosphorus atoms of **1** and **2** are in a planar environment with long M−P distances, whereas in **4** the P atoms comprise a pyramidal coordination sphere. The tin−carbon distances are larger than observed in stannocenes which could be interpreted as a stannylene-like structure with σ-bonded ligands. Crystallographic data for **1**: monoclinic, $C2/c$, $a = 2108.9(3)$ pm, $b = 1296.2(2)$ pm, $c = 2735.3(3)$ pm, $\beta = 93.37(1)°$, $Z = 4$, $wR2 = 0.1381$ (all data, on F^2). Crystallographic data for **2**: monoclinic, $C2/c$, $a = 2104.7(1)$ pm, $b = 1296.43(6)$ pm, $c = 2717.8(1)$ pm, $\beta = 93.189(1)°$, $Z = 4$, $wR2 = 0.0954$ (all data, on F^2). Crystallographic data for **4**: triclinic, $P\bar{1}$, $a = 1253.25(4)$ pm, $b = 1312.58(4)$ pm, $c = 1481.61(5)$ pm, $\alpha = 87.667(1)°$, $\beta = 79.438(1)°$, $\gamma = 72.684(1)°$, $Z = 2$, $wR2 = 0.0692$ (all data, on F^2).

Introduction

The alkaline earth metal bis[bis(trimethylsilyl)amides] are easily accessible by various reactions such as transmetalation and metathesis reactions.[1] These compounds are powerful metalation reagents toward molecules with acidic hydrogen atoms, as, for example, alcohols,[2] selanes,[3] tellanes,[3] phosphanes,[4,5] and arsanes[6] and even alkynes[7] and benzylbenzylidenephosphoranes.[8] The homologous alkaline earth metal bis[bis(trimethylsilyl)phosphanides] are prepared quantitatively by metalation of $HP(SiMe_3)_2$ in tetrahydrofuran or toluene.[4] The bis(amides) and bis(phosphanides) react with benzonitrile to give the alkaline earth metal bis[*N*,*N*′-bis(trimethylsilyl)benzamidinates][9,10] and bis[1,3-bis(trimethylsilyl)-2-phenyl-1,3-azaphosphapropenides];[11] however, no reaction occurs with the less reactive pivalonitrile.[9] The addition reaction of magnesium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne in toluene yields dimeric 1-bis(trimethylsilyl)phosphanyl-1,4-diphenylbut-1-en-3-yn-2-ylmagnesium bis(trimethylsilyl)phosphanide **I** (Chart 1).[12] The performance of this reaction with tetrakis(tetrahydrofuran)barium bis[bis(trimethylsilyl)phosphanide] yields the dimeric THF complex **II** with Ba−C bonds.[12] Another central feature of this latter molecule is the phosphacyclopentadienide moiety, which exhibits distorted η^5-coordination to the barium atom, thus shielding the reactive Ba_2C_2 cycle. The question arising concerns the reaction pathway and products using the calcium and strontium bis(phosphanides) as synthons in this reaction. Furthermore, the phospholide chemistry of the alkaline earth metals opens a new research area. Thus far, interest centers on the phospholides of lithium and the transition metals.[13] The lithium phospholides are usually prepared by cleavage of the

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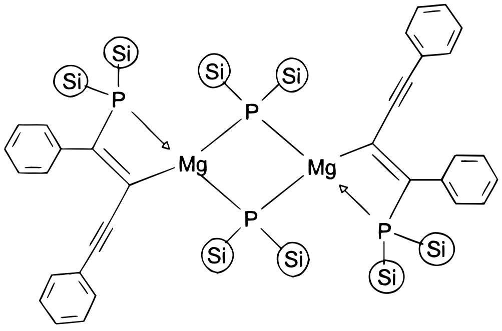
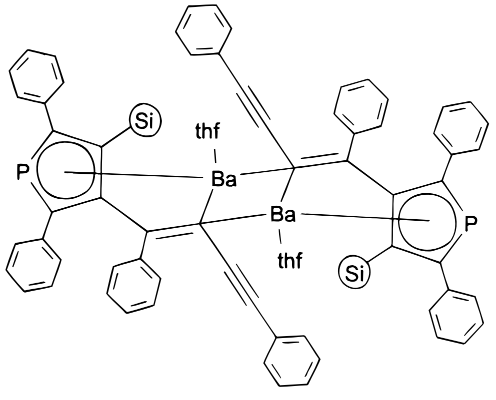
10.1021/ic981132k CCC: $18.00

Chart 1



I

Si = $\mathrm{SiMe_3}$



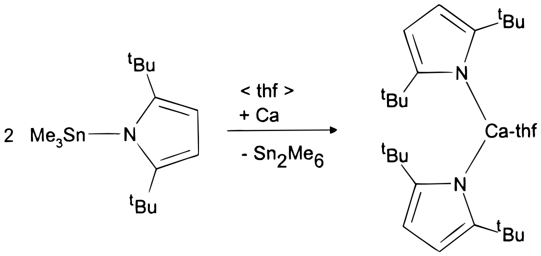
II

phenyl−phosphorus bond of 1-phenylphospholes with lithium metal. The reaction of lithium bis(trimethylsilyl)phosphanide with 2 equiv of diphenylethyne yields lithium tetraphenylphospholide; however, the reaction mechanism is yet not fully understood.[14]

Results and Discussion

Preparation. The slow reaction of tetrakis(tetrahydrofuran)-calcium and -strontium bis[bis(trimethylsilyl)phosphanide] with diphenylbutadiyne in a toluene solution leads to the precipitation of slightly yellow, crystalline tetrakis(tetrahydrofuran)calcium (**1**) and -strontium bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide] (**2**). A proposed reaction mechanism is presented in Scheme 1. The first reaction step is the addition of the alkaline earth metal−phosphorus bond to a C≡C triple bond, which has been verified for a magnesium derivative.[12] The subsequent 1,3-trimethylsilyl shift followed by a second M−P bond addition to the remaining C≡C bond leads to the intermediate, which was already assumed in the case of formation of the barium derivative **II**.[12] However, in the case of Ca−C and Sr−C bonds, respectively, another 1,3-trimethylsilyl migration from the phosphorus to the carbon atom is observed. The alkaline earth metal atoms calcium and strontium are now bonded to the phosphorus atom. The last reaction step can be explained by the hardness of the alkaline earth metal atoms. The rather small dications Ca^{2+} and Sr^{2+} stay coordinated to the THF molecules during the reaction whereas the soft dication Ba^{2+} loses three of the four THF molecules, thus opening a coordination site for diphenylbutadiyne, which inserts into the Ba−C bond. Solvent-free calcium and strontium bis[bis(trimethylsilyl)phosphanides] are polymeric and insoluble in toluene, thus leading to a heterogeneous and complex reaction; therefore, this reaction was performed in the presence of THF, but the influence of the THF molecules is not fully understood.

A similar reaction to build up a pyrrolide from alkaline earth metal bis[bis(trimethylsilyl)amides] is not possible because these amides are too inert to react with butadiynes. Therefore, 2,5-di(*tert*-butyl)-1-trimethylstannylpyrrole was transmetalated by calcium in tetrahydrofuran to give colorless (tetrahydrofuran)calcium bis[2,5-bis(*tert*-butyl)-1-azacyclopentadienide] (**3**) according to eq 1. The formation of hexamethyldistannane was concluded by ^{119}Sn{^{1}H} as well as ^{13}C{^{1}H} NMR spectroscopy. The workup of this insertion reaction has to be performed after a short reaction period, because calcium also inserts into the Sn−Sn bond of the formed hexamethyldistannane, thus giving tetrakis(tetrahydrofuran)calcium bis(trimethylstannanide).[15] Compound **3** is represented with N-bonded pyrrolide ligands; however, we were not able to obtain single crystals suitable for an X-ray structure determination. In agreement with this assumption, bis(tetrahydrofuran)lithium 2,5-di(*tert*-butyl)pyrrolide is bonded end-on to the nitrogen atom and coordinatively saturated by agostic interactions with the *tert*-butyl substituents.[16] Moreover, the alkaline earth metal bis(carbazolide) complexes show η^1 coordination to the nitrogen atoms.[17] The coordination sphere of the metal centers is saturated by neutral coligands such as ether and ammonia. On the other hand, the 2,5-di(*tert*-butyl)pyrrolide ligand forms 2,2′,5,5′-tetrakis(*tert*-butyl)-1,1′-diazastannocene[18] and -plumbocene[19] with η^5 bonded pyrrolide substituents. The interesting coordination behavior is even extended by structures with bridging 2,5-di(*tert*-butyl)-pyrrolide anions.[16]



3 (1)

Compound **1** is a valuable transfer reagent for the sterically shielded phosphacyclopentadienide ligand. The metathesis reaction (eq 2) of **1** with $SnCl_2$ in tetrahydrofuran yields the yellow tin(II) complex **4**. After removal of the solvent in a vacuum the

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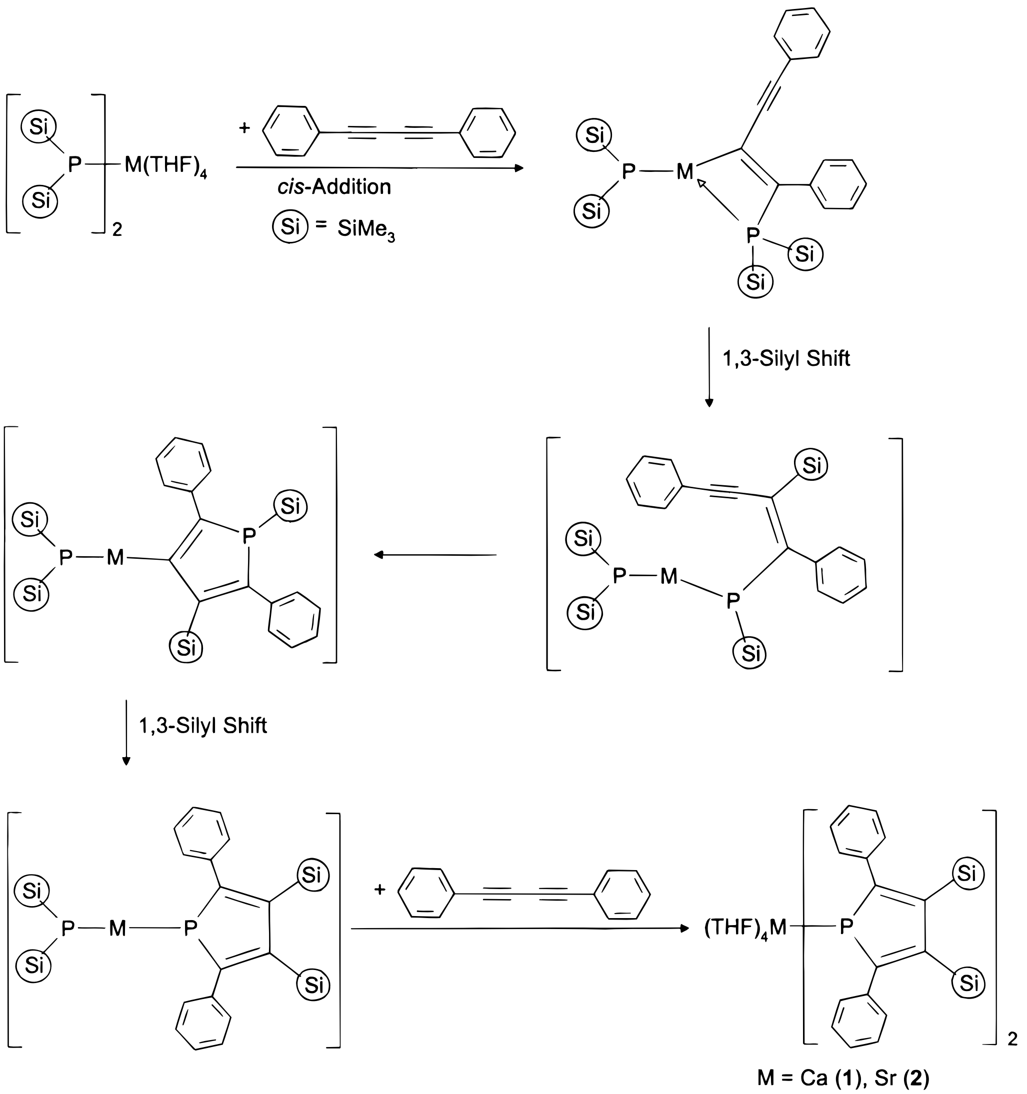
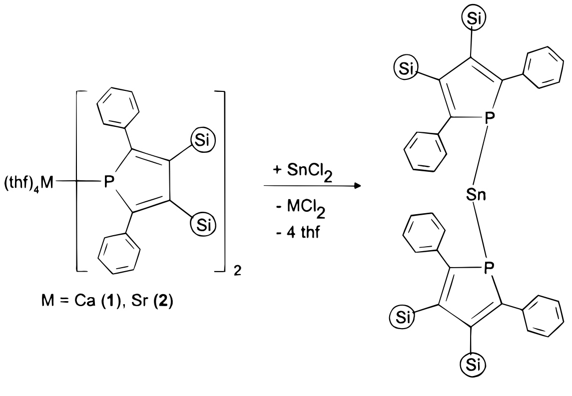
Scheme 1. Proposed Mechanism for the Formation of Products **1** and **2**

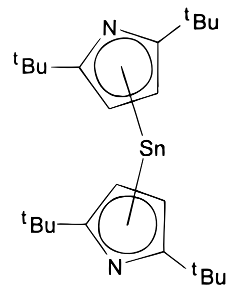


residue is redissolved in *n*-pentane. From this solution were obtained single crystals suitable for an X-ray structure determination. Whereas stannocenes $SnCp'_2$ with C_5H_5 or substituted cyclopentadienyl ligands are a well-investigated class of compounds, only very few results are published dealing with tin(II) bis(pentelacyclopentadienides). Kuhn et al.[18] prepared stannocene **III** (Chart 2) with the pyrrolide ligand also present in **3**. The formal substitution of a CC fragment of a stannocene by a BN moiety yields compound **IV**.[20] The lack of knowledge concerning the 1,1′-dipentelastannocenes of the heavier pentele[21] (pnictogen, group 15 element) atoms is in contrast to the attention which the phosphacyclopentadienide ligands gained within transition metal chemistry.[13]

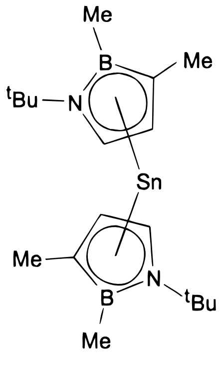


4 (2)

Chart 2



III



IV

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Table 1. Selected NMR Data of $M(NC_4H_2\text{-}2,5\text{-}^tBu_2)_n$ with η^1-Coordinated ($n = 1$; M = Me_3Sn, Me_2Ga, H, $(THF)_2Li$) and η^5-Coordinated ($n = 2$; M = Sn, Pb) Pyrrolide Ligands

M	$SnMe_3{}^a$	$GaMe_2{}^b$	H^c	$Li(THF)_2$	Sn	Pb	Ca(THF) (**3**)
			^1H NMR				
δ(CH)	4.86	6.23	5.93	5.59	5.47	5.51	6.34
$\delta(^tBu)$	1.26	1.24	1.17	1.22	1.39	1.39	1.36
			$^{13}C\{^1H\}$ NMR				
δ(C2/C5)	173.3	145.3	139.5	146.7	162.3	161.7	153.7
δ(C3/C4)	81.4	105.5	102.5	100.1	100.5	105.2	105.3
$\delta(CMe_3)$	34.6	32.9	31.2	33.5	33.8	33.3	34.0
$\delta(CMe_3)$	30.6	32.5	30.7	32.8	32.0	32.7	31.4

[a] $SnMe_3$: $\delta(^1H) = 0.02$, $\delta(^{13}C) = -5.86$. [b] $GaMe_2$: $\delta(^1H) = 0.19$, $\delta(^{13}C) = 0.95$. [c] NH: $\delta(^1H) = 7.53$.

NMR Spectroscopy. The NMR data of **3** do not allow the distinction between a metallocene-like structure as observed for 2,2′,5,5′-tetrakis(*tert*-butyl)-1,1′-diazacalcocene and an N-bonded pyrrolide ligand. Table 1 summarizes the NMR data of selected 2,5-di(*tert*-butyl)pyrrolides of the type $M(NC_4H_2\text{-}2,5\text{-}^tBu_2)_n$ with η^1 ($n = 1$, M = $SnMe_3$, $GaMe_2$, H, $Li(THF)_2$)[16] and η^5 coordination ($n = 2$, M = Sn,[18] Pb[19]). With the exception of the starting material 2,5-di(*tert*-butyl)-1-trimethylstannylpyrrole, which shows rather unique NMR data, the ^1H as well as ^{13}C NMR parameters vary only within a rather narrow range. The chemical ^{13}C shifts of derivative **3** are rather similar to those of the lithium pyrrolide. The coordination behavior seems to have a small influence on the chemical shifts. Furthermore, the importance of the nature of coordination decreases with increasing ionicity of the compound.

The phosphacyclopentadienide substituent shows characteristic chemical ^{31}P shifts not depending on the nature of the metal nor the substituents at this heterocycle. The low-field shift of approximately 60−80 ppm compared to the phospholes[13] accounts for the charge delocalization within the heterocycle as well as for an aromatic character which is comparable to that of the $C_5H_5^-$ anion.[22] The lithium phosphacyclopentadienides[13,23] with phenyl substituents in the 2,5-positions show chemical ^{31}P shifts of $\delta = 79-102$ whereas the resonances of **1** and **2** lie at $\delta = 109$. The coupling constant $^1J(^{119}Sn,^{31}P)$ of 164.3 Hz in **4** with a δ value of 102 is rather small compared to a kinetically stabilized monomeric bis(phosphanyl)stannylene with a $^1J(^{119}Sn,^{31}P)$ value of 1682 Hz.[24] Due to the expectation that the molecular structures of **1** and **2** and on the other hand of **4** should differ drastically, single-crystal structure determinations were undertaken.

Molecular Structures. The compounds **1** and **2** crystallize isotypic in the monoclinic space group *C*2/*c*. Figure 1 shows the molecular structure of **1** and Figure 2 the homologous strontium compound **2**. The molecules lie on crystallographic C_2 axes. The symmetry-generated atoms are marked with primes. Selected structural parameters are summarized in Table 2.

The alkaline earth metal centers are coordinated distorted octahedrally by four oxygen atoms of the THF molecules and two phosphorus atoms in trans positions. The Ca−P1 and Sr−P1 bond lengths of 3.068 and 3.143 Å, respectively, are very large compared with the M−P distances of the alkaline earth metal bis[bis(trialkylsilyl)phosphanides] (Ca−P 2.91 ± 4 Å, Sr−P 3.05 ± 5 Å[1]). This could account for rather loose contact ion pairs and would also explain the insolubility in common organic solvents such as toluene and ethers.

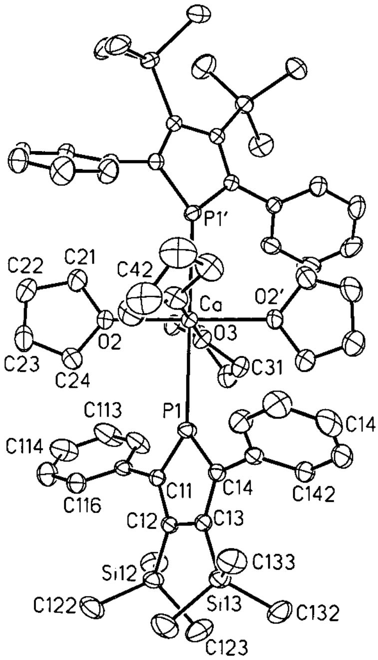

Figure 1. Molecular structure and numbering scheme of **1**. The hydrogen atoms as well as the toluene molecule are omitted for clarity. The ellipsoids represent a 30% probability. The atoms of the symmetry-related half of the molecule are marked with primes.

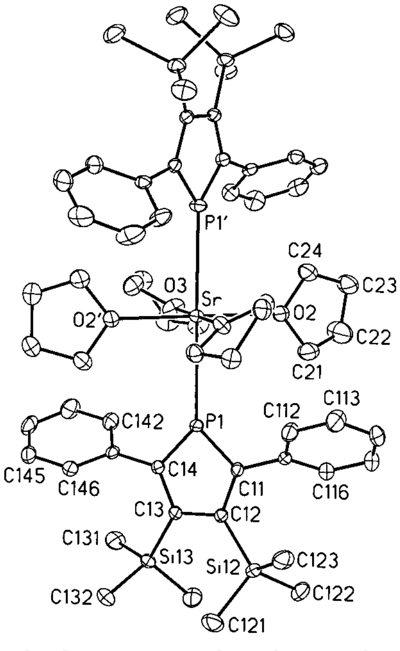

Figure 2. Molecular structure and numbering scheme of **2**. The hydrogen atoms as well as the toluene molecule are omitted for clarity. The ellipsoids represent a 40% probability. The atoms of the symmetry-related half of the molecule are marked with primes.

The phosphacyclopentadienide substituents are η^1 bonded via the phosphorus atom, which is in a distorted trigonal planar environment. The P(*n*)−C(*nm*) distances of 1.75 Å are shorter than P−C single bonds (1.84 Å). Furthermore, the endocyclic C−C bond lengths show also a shortening compared to a C−C single bond between two sp^2-hybridized carbon atoms (1.48 Å); however, the C11−C12 and C13−C14 distances are approximately 5 pm shorter than the C12−C13 bond.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] of the Phospholides **1**, **2**, and **4**

	1 (M = Ca) $n = 1$	**2** (M = Sr) $n = 1$	**4** (M = Sn)[a] $n = 1/n = 2$
	(a) Bond Lengths		
M−P(n)	3.068(1)	3.1426(7)	2.7298(8)/2.7902(8)
M−O2	2.364(2)	2.503(2)	
M−O3	2.355(4)	2.481(3)	
M−O4	2.342(4)	2.483(2)	
P(n)−C(n1)	1.749(4)	1.745(3)	1.781(3)/1.786(3)
P(n)−C(n4)	1.753(4)	1.758(2)	1.777(3)/1.781(3)
C(n1)−C(n2)	1.404(5)	1.414(3)	1.412(4)/1.414(4)
C(n2)−C(n3)	1.451(5)	1.457(3)	1.463(4)/1.466(4)
C(n3)−C(n4)	1.405(5)	1.402(4)	1.405(4)/1.417(4)
C(n2)−Si(n2)	1.892(4)	1.887(3)	1.906(3)/1.916(3)
C(n3)−Si(n3)	1.877(4)	1.876(2)	1.900(3)/1.910(3)
	(b) Bond Angles		
P(n)−M−P(n')	176.80(6)	176.76(3)	103.52(3)
M−P(n)−C(n1)	132.5(1)	132.35(8)	70.53(9)/68.21(9)
M−P(n)−C(n4)	136.0(1)	136.38(9)	73.61(9)/74.27(9)
C(n1)−P(n)−C(n4)	91.5(2)	91.2(1)	89.0(1)/89.8(1)
P(n)−C(n1)−C(n2)	112.4(3)	112.9(2)	113.8(2)/112.8(2)
C(n1)−C(n2)−C(n3)	111.7(3)	111.1(2)	111.4(3)/112.5(2)
C(n2)−C(n3)−C(n4)	112.4(3)	112.5(2)	111.4(3)/111.0(3)
C(n3)−C(n4)−P(n)	111.9(3)	112.2(2)	114.2(2)/113.7(2)

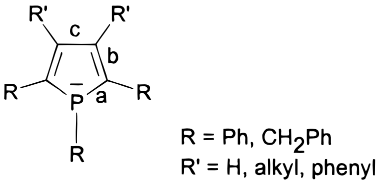
[a] Two crystallographically independent phosphacyclopentadienide ligands.

Table 3. Comparison of the Endocyclic Bond Lengths (Mean Values) in Selected Phospholide Ligands

E	hapticity	a (Å)	b (Å)	c (Å)	Δ[a] (pm)	ref
Ph	η^1	1.822	1.349	1.440	9.1	25
CH_2Ph	η^1	1.783	1.343	1.438	9.5	26
W(CO)$_3$Cp	η^1	1.771	1.371	1.447	7.6	27
W(CO)Cp(PhCCPh)	η^1	1.795	1.363	1.439	7.6	27
Sn	η^1	1.780	1.412	1.465	5.3	
Sr(THF)$_4$	η^1	1.752	1.408	1.457	4.9	
Ca(THF)$_4$	η^1	1.750	1.405	1.451	4.6	
Li(tmeda)	η^5	1.751	1.396	1.424	2.8	28
Fe	η^5	1.780	1.410	1.416	0.6	29
Fe	η^5	1.767	1.412	1.407	−0.5[b]	30

[a] $\Delta = c - b$, see text. [b] Value in the range of the standard deviations of the bond lengths.

Chart 3



V

In Table 3 selected structural data are summarized to focus on the differences of the endocyclic C−C bond lengths. No delocalization of the π electrons is observed for the *P*-alkyl- and *P*-aryl-substituted phosphole; the difference Δ between the C−C distances c and b in **V** (Chart 3) is almost 10 pm.[25,26] The opposite is realized for the 1,1′-diphosphaferrocenes with a Δ value of less than 1 pm.[29,30] A small Δ value of 2.8 pm is also observed for a lithium complex with a η^5-coordinated phosphacyclopentadienide substituent.[28] The σ-bonded phospholide ligand in **1** and **2** shows values of Δ = 4.6 and 4.9 pm, respectively, which demonstrates a slight disturbance of the delocalization of the π electrons.

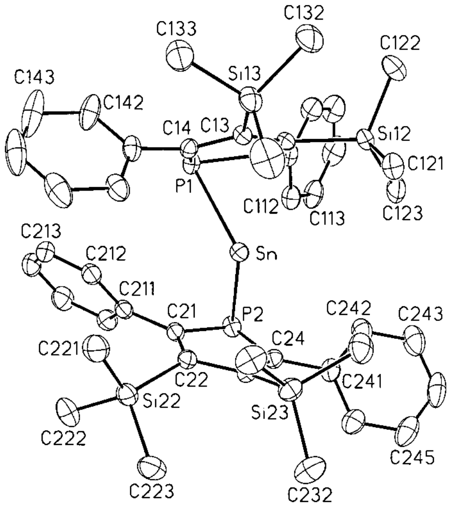


Figure 3. Molecular structure and numbering scheme of **4**. The hydrogen atoms are omitted for clarity. The ellipsoids represent a 40% probability.

In contrast to the long alkaline earth metal−phosphorus bonds, the M−O(n) distances show values in the characteristic region (mean values: Ca−O 2.35 Å; Sr−O 2.49 Å). Due to the coordination of four tetrahydrofuran molecules to the alkaline earth metal centers, the (THF)$_4$M fragments are rather demanding. This could be the reason for the η^1 coordination of the phosphacyclopentadienide at the metal atoms because a metallocene-like structure would lead to enormous intramolecular strain due to repulsion between the substituents and the THF molecules or would enforce an enhanced separation of the phosphacyclopentadienide ligands, thus decreasing the electrostatic attraction between anion and cation.

Figure 3 shows the molecular structure and the numbering scheme of **4**. This tin(II) complex is the first structurally characterized 1,1′-diphosphastannocene. The value Δ (Table 3) is slightly larger than those determined for **1** and **2**. The Sn−P1 and Sn−P2 bond lengths of 2.73 and 2.79 Å are elongated compared to the kinetically stabilized bis(phosphanyl)stannylene with Sn−P distances of 2.57 Å.[24] On the other hand, the phospholide substituent is clearly not η^5-bonded to the tin(II) atom because the Sn···C(nm) contacts vary between 2.718 and 2.988 Å (mean Sn−C distances 2.852 and 2.846 Å) and are larger than observed for even more overcrowded stannocenes such as the bent 1,1′,2,2′,3,3′,4,4′-octaisopropylstannocene (mean Sn−C bond lengths 2.703 and 2.705 Å).[31] The distances between the ring centers of the phospholide ligands and the tin(II) atom are 2.497 and 2.502 Å whereas in Sn($C_5H^iPr_4$)$_2$ the corresponding values are approximately 8 pm smaller. Even the sandwich η^5 decaphenylstannocene displays similar values (Sn−ring center 2.401 Å).[32]

The Δ value of 5.3 pm (Table 3) clearly speaks against an aromatic phospholide which should be supported electronically

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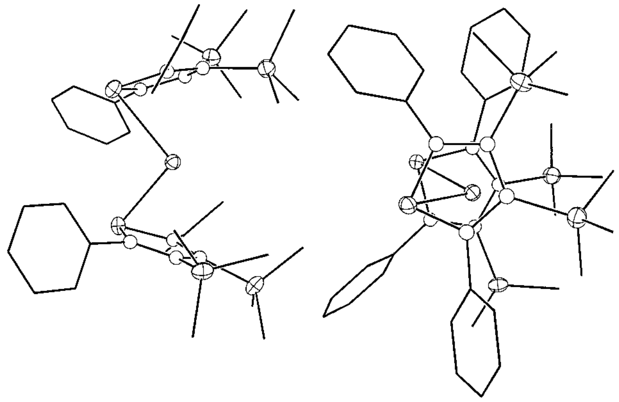
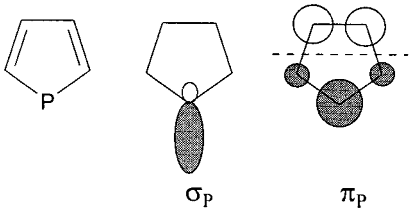


Figure 4. Representatation of projections of **4** with a view of the SnP_2 plane (left) and perpendicular to this plane (right). The H atoms are omitted for clarity. Only the ring carbon atoms are displayed with arbitrary radii, whereas the heavier atoms are shown with a 40% probability.

Chart 4



by the phenyl substituents in the 2,5-positions.[33] On the other hand, the substitution of a CH moiety of a $C_5H_5^-$ anion by a phosphorus atom leads only to a small reduction of the aromaticity of approximately 10%.[34] The large Sn−P(*n*) distances are in accordance with Sn−P bond lengths of heterobimetallic alkaline earth metal/tin(II) phosphanides.

A still remaining question concerns the geometry at the phosphorus atoms. How can it be understood that in **1** and **2** the phosphorus atoms are in a trigonal planar environment, whereas in **4** a pyramidal coordination sphere is realized? The Sn−P(*n*)−C(*nm*) bond angles with values between 68.2° and 73.6° are very small. Kostic and Fenske[35] calculated the relative energies and shapes of the molecular orbitals of a phospholide anion. The occupied σ_P and π_P molecular orbitals (Chart 4) are very close in energy; however, bonding of the metal cation to the σ_P MO yields a trigonal planarily surrounded phosphorus atom (which is realized in **1** and **2**) whereas a bonding to the π_P MO leads to a metal located above the heterocyclic plane as seen in **4**. The small population at the neighboring carbon atoms explains the Sn−P−C angles with values even smaller than 90° which could be interpreted as a η^3 coordination (Figure 4). Due to the small energy difference, steric arguments gain in importance. The rather small tin(II) atom fits between the phospholide ligands whereas the tetrakis(tetrahydrofuran) alkaline earth metal atoms enforce disfavor of this geometry. Another characteristic feature is the rather high negative charge at the phosphorus atom thus explaining the coordination of a cation to this atom. These considerations are also in agreement with the small $^1J(^{119}Sn,^{31}P)$ coupling constant, since the interaction of the tin dication with the phosphorus atom occurs nearly exclusively with the π_P orbitals.

This argumentation is supported by a comparison with the structures of $(THF)_2Li-NC_4H_2$-2,5-$^tBu_2$[16] and $Sn(\eta^5$-NC_4H_2-2,5-$^tBu_2)_2$ **III**.[18] Whereas for the 2,2′,5,5′-tetra(*tert*-butyl)-1,1′-diazastannocene **III** the endocyclic C−C distances are alike, small differences are observed within the nitrogen-bonded 2,5-di(*tert*-butyl)pyrrolide ligand ($\Delta = 2.0$ pm) of the lithium compound. Furthermore, the distance between the tin(II) atom and the ring center in **III** is 2.428 Å[18] and lies in the characteristic range.

Conclusion

The 2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide ligand coordinates in a η^1 fashion to the alkaline earth metal dications $(THF)_4Ca^{2+}$ and $(THF)_4Sr^{2+}$. A criterion for the charge delocalization is the difference between the endocyclic C−C bond lengths. Even though an alkaline earth metal−phosphorus σ bond is realized, a delocalization is observed although less effective than in ferrocene derivatives. Preliminary calculations for solvent-free monomeric 1,1′-diphosphacalcocene favor the 1,1′-diphospha alkaline earth metallocene structure with η^5-coordinated aromatic heterocycles over the η^1 coordination at a metal center.[36] The observation of the unfavorable structures is best explained as a consequence of steric repulsion between coordinated THF molecules and the substituents at the heterocycle.

Experimental Section

General Methods. All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The compounds $(THF)_4Ca[P(SiMe_3)_2]_2$[4] and $(THF)_4Sr[P(SiMe_3)_2]_2$[4] were prepared by literature procedures. NMR spectra were recorded on JEOL spectrometers GSX270 and EX400. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were measured in Nujol between CsBr windows (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The frequencies in the region of the Nujol vibrations were not listed. Due to the sensitivity of even crystalline **2**−**4** toward moisture and air and formation of carbonates and carbides during combustion, no satisfactory analytical data were obtained, although these compounds were spectroscopically pure.

Synthesis of Tetrakis(tetrahydrofuran)calcium Bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide], 1. A V-shaped Schlenk tube with a diaphragm separating the sides was filled with 10 mL of toluene. To one side 0.40 g of tetrakis(tetrahydrofuran)calcium bis[bis(trimethylsilyl)phosphanide] (0.65 mmol) was added. On the other side 0.26 g of diphenylbutadiyne (1.30 mmol) was dissolved. After approximately 10−12 h on both sides of the diaphragm 0.58 g of yellow crystalline **1** (0.53 mmol; yield: 82%) had formed. Mp: 137−140 °C. ^{1}H NMR (THF-d_8, 30 °C): δ 0.00 (s, $SiMe_3$),1.77 and 3.62 (THF), 6.9−7.4 (m, phenyl). $^{13}C\{^1H\}$ NMR (THF-d_8, 30 °C): δ 5.46 [s, $SiMe_3$, $^1J(Si,C) = 50.5$ Hz], 26.26 and 68.13 (THF), 124.30 (s, phenyl, *p*-C), 127.29 (s, phenyl, *m*-C), 131.01 [d, phenyl, *o*-C, $^2J(P,C) = 6.7$ Hz], 137.61 (s, phospholide, C3/C4), 148.57 [d, phenyl, ipso-C, $^2J(P,C) = 23.5$ Hz], 163.06 [d, phospholide, C2/C5, $^1J(P,C) = 23.5$ Hz]. $^{29}Si\{^1H\}$ NMR (THF-d_8, 30 °C): δ −13.40 [d, $^3J(P,Si) = 4.1$ Hz]. $^{31}P\{^1H\}$ NMR (THF-d_8, 30 °C): δ 109.30 (s). IR (KBr, Nujol): 1590 m, 1540 vw, 1478 s, 1459 m, 1376 w, 1369 w, 1353 w, 1295 vw, 1261 w, 1242 s, 1221 m, 1186 m, 1067 w, 1026 s, 1003 w, 986 w, 918 w, 907 w, 886 m, 868 vs, 781 w, 758 s, 732 s, 700 m, 683 w, 673 w, 638 w, 625 vw, 608 vw, 543 w, 521 vw, 466 w. Anal. Calcd for toluene adduct $CaP_2Si_4C_{67}H_{96}O_4$: C, 68.21; H, 8.20. Found: C, 67.84; H, 7.87.

Synthesis of Tetrakis(tetrahydrofuran)strontium Bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide], 2. The reaction was performed as described for **1**. The V-shaped Schlenk tube

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Table 4. Crystallographic Data for **1**, **2**, and **4** as Well as Details of the Structure Solution and Refinement Procedures

compd	**1**·toluene	**2**·toluene	**4**
empirical formula	$C_{74}H_{104}CaO_4P_2Si_4$	$C_{74}H_{104}O_4P_2Si_4Sr$	$C_{44}H_{56}P_2Si_4Sn$
fw (g·mol^{-1})	1271.95	1319.49	877.88
temp *T* (K)	298	173	173
space group[37]	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
unit cell dimens			
a (Å)	21.089(3)	21.047(1)	12.5325(4)
b (Å)	12.962(2)	12.9643(6)	13.1258(4)
c (Å)	27.353(3)	27.178(1)	14.8161(5)
α (deg)	90	90	87.667(1)
β (deg)	93.37(1)	93.189(1)	79.438(1)
γ (deg)	90	90	72.684(1)
V (Å^3)	7464(2)	7404.3(6)	2287.1(1)
Z	4	4	2
ρ_{calcd} (g·cm^3)	1.132	1.184	1.275
λ (Å)	0.710 73	0.710 73	0.710 73
μ (cm^{-1})	2.36	8.81	7.82
R indices (all data)	4377	6228	7128
wR2[a]	0.1381	0.0954	0.0692
R1[a]	0.0740	0.0544	0.0400
R indices with $I > 2\sigma(I)$ (data)	3347	5282	6136
R1[a]	0.0521	0.0426	0.0304
goodness-of-fit s[b] on F^2	1.075	1.090	1.092
residual density (e·Å^{-3})	0.405; −0.352	0.335; −0.329	0.335; −0.346

[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] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

was filled with 17 mL of toluene. Tetrakis(tetrahydrofuran)strontium bis[bis(trimethylsilyl)phosphanide] (0.68 g) (1.16 mmol) and 0.47 g of diphenylbutadiyne (2.32 mmol) were dissolved on each side of that tube. After 10 days the solution did not contain any starting material, and 1.17 g of yellow crystalline **2** (0.89 mmol; yield: 76%) precipitated within a few hours after cooling to 5 °C. Mp: 158−160 °C (dec). ^{1}H NMR (THF-d_8, 30 °C): *δ* −0.01 (s, SiMe$_3$), 1.77 and 3.61 (THF), 6.9−7.6 (m, phenyl). ^{13}C{^{1}H} NMR (THF-d_8, 30 °C): *δ* 4.56 (s, SiMe$_3$), 25.46 and 67.29 (THF), 123.62 (s, phenyl, *p*-C), 126.57 (s, phenyl, *m*-C), 130.14 [d, phenyl, *o*-C, ^3J(P,C) = 7.1 Hz], 137.39 (s, phospholide, C3/C4), 147.50 [d, phenyl, ipso-C, ^2J(P,C) = 23.9 Hz], 162.50 [d, phospholide, C2/C5, ^1J(P,C) = 23.8 Hz]. ^{29}Si{^{1}H} NMR (THF-d_8, 30 °C): *δ* −13.09 [d, ^3J(P,Si) = 3.5 Hz]. ^{31}P{^{1}H} NMR (THF-d_8, 30 °C): *δ* 109.76 (s). IR (KBr, Nujol): 1594 sh, 1590 m, 1569 w, 1487 s, 1461 m, 1442 m, 1409 w, 1378 w, 1367 w, 1354 m, 1308 vw, 1295 w, 1280 w, 1261 m, 1243 s, 1220 s, 1185 m, 1169 sh, 1156 w, 1067 m, 1028 vs, 1003 m, 987 m, 918 s, 907 m, 887 s, 869 vs, 861 vs, 839 vs, 781 s, 758 vs, 732 vs, 700 vs, 684 m, 673 m, 638 m, 625 w, 608 w, 585 vw, 574 vw, 542 w, 521 w, 481 vw, 466 w, 398 s, 358 m, 302 vw. Anal. Calcd for coligand-free complex $SrP_2Si_4C_{44}H_{56}$: C, 62.40; H, 6.67. Found: C, 61.28; H, 6.51.

Synthesis of (Tetrahydrofuran)calcium Bis[2,5-di(*tert*-butyl)-pyrrolide], 3. To a solution of 0.97 g of *N*-trimethylstannyl-2,5-di-(*tert*-butyl)pyrrole (2.84 mmol) in 15 mL of THF was added 0.18 g of distilled calcium (4.49 mmol). This solution was stirred at room temperature for approximately 12 days. During this time the solution turned brown. The solution was decanted from the solid materials, and then all volatiles were removed in a vacuum. The oily residue was dissolved in 7 mL of *n*-pentane, and a yellow-brown solution was formed. At −60 °C compound **3** precipitates as a colorless solid. Recrystallization from *n*-pentane affords 0.95 g of colorless **3** (2.03 mmol; yield: 71%). Mp: 95−102 °C (dec). ^{1}H NMR (benzene-d_6, 30 °C): *δ* 1.25 and 3.83 (m, THF), 1.36 (s, ^{t}Bu), 6.34 (s, pyrrolide). ^{13}C NMR (benzene-d_6, 30 °C): *δ* 25.32 (THF), 31.40 [C*Me*$_3$, ^1J(C,H) = 125.7 Hz, ^3J(C,H) = 4.8 Hz], 33.95 [*C*Me$_3$, ^2J(C,H) = 3.8 Hz], 70.44 (THF), 105.33 [C3/C4, ^1J(C,H) = 163.7 Hz, ^2J(C,H) = 6.3 Hz], 153.68 (C2/C5). IR (KBr, Nujol): 1638 vw, 1613 vw, 1582 w, 1519 w, 1484 vs, 1349 vs, 1286 m, 1264 m, 1246 vs, 1204 vs, 1164 w, 1134 w, 1106 w, 1071 vw, 1040 s, 1023 s, 999 sh, 969 w, 958 m, 922 w, 908 sh 893 m, 872 m, 842 w, 820 vw, 799 w, 763 vs, 735 w, 702 w, 691 w, 671 vw, 618 w, 567 vw, 544 w, 520 m, 500 w, 471 w. Anal. Calcd for coligand-free complex $CaN_2C_{24}H_{40}$: C, 72.67; H, 10.16; N, 7.06. Found: C, 71.43; H, 10.14; N, 6.97.

Synthesis of Tin(II) Bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienide], 4. To a stirred solution of 0.22 g of **1** (0.17 mmol) in 3.5 mL of THF was added 30 mg of anhydrous tin(II) chloride (0.17 mmol) at room temperature. After 72 h no starting material was detectable NMR spectroscopically. All volatile components were removed in a vacuum at room temperature and the residue was extracted with 20 mL of *n*-pentane. This solution was cooled to −30 °C. Within a few days yellow crystals of **4** precipitated. Mp: 196−201 °C. ^{1}H NMR (benzene-d_6, 30 °C): *δ* 0.25 (s, SiMe$_3$), 6.9−7.6 (m, phenyl). ^{13}C{^{1}H} NMR (benzene-d_6, 30 °C): *δ* 4.73 (s, SiMe$_3$), 128.31 (s, phenyl, *m*-C), 130.36 [d, phenyl, *o*-C, ^3J(P,C) = 7.8 Hz], 139.79 [d, phospholide, C3/C4, ^2J(P,C) = 20.7 Hz], 151.91 [d, phenyl, ipso-C, ^2J(P,C) = 7.2 Hz], 167.03 [d, phospholide, C2/C5, ^1J(P,C) = 41.4 Hz], the *p*-C signal is covered by the solvent resonances. ^{29}Si{^{1}H} NMR (benzene-d_6, 30 °C): *δ* −8.04 (s). ^{31}P{^{1}H} NMR (benzene-d_6, 30 °C): *δ* 102.45 [s, ^1J(^{119}Sn,P) = 164.3 Hz]. IR (KBr, Nujol): 1597 w, 1574 vw, 1490 w, 1484 sh, 1462 s, 1457 sh, 1407 vw, 1373 m, 1303 vw, 1261 m, 1249 s, 1184 vw, 1155 vw, 1133 vw, 1073 w, 1031 w, 1002 vw, 909 w, 871 s, 840 vs, 755 s, 722 w, 698 s, 626 w, 567 m, 527 vw, 495 vw, 487 vw, 396 vw, 376 vw. Anal. Calcd for $SnP_2Si_4C_{44}H_{56}$: C, 60.19; H, 6.43. Found: C, 58.87; H, 6.59.

Structure Determinations of 1, 2, and 4. A suitable crystal of **1** was sealed under argon in a thin-walled glass capillary and mounted on the automatic four-circle diffractometer Nonius CAD4/MACH3 with graphite-monochromated Mo Kα radiation. The data were collected at room temperature; details of the data collection and refinement procedures are listed in Table 4. The crystal showed an intensity decay of 34%. Suitable single crystals of **2** and **4** were covered with Nujol and mounted on a glass fiber.[38] The crystal structure analyses were performed at −100 °C on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation and a SMART-CCD area detector. The crystallographic data as well as details of the structure solution and refinement procedures are summarized in Table 4.

The crystal structures were solved by direct methods with the program SHELXTL Plus.[39] The refinement of the structures succeeded with the program packages SHELXL-93 and SHELXL-97,[40] where the

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function $\Sigma[w(F_o^2 - F_c^2)^2]$ was minimized. The displacement parameters of all non-hydrogen atoms were treated anisotropically. For all calculations the atom form factors of the neutral atoms C, Ca, O, P, Si, Sn, and Sr[41] as well as hydrogen[42] were used. The H atoms were taken into account in idealized positions with C−H distances of 96 pm and taken into account with a riding model.

Acknowledgment. This research was financially supported by the "Deutsche Forschungsgemeinschaft" (DFG) and the "Fonds der Chemischen Industrie".

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determinations of **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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