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3,4-Dimethyl-2,5-bis(trimethylsilyl)phospha- and 3,4-Dimethyl-2,5-bis(trimethylsilyl)arsacyclopentadienides of Calcium

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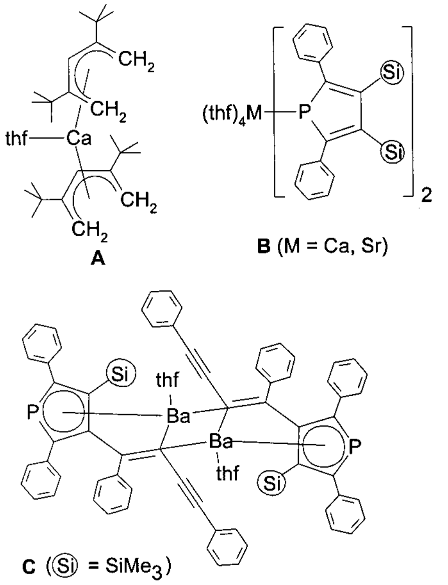
The reaction of zirconocene dichloride with 2 equiv of butyllithium and 1-trimethylsilylpropyne yields yellow 1,1-bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)zirconacyclopenta-2,4-diene, **1**. The metathesis reaction of **1** with PCl_3 gives a mixture of 1-chloro- and 1-cyclopentadienyl-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-phosphacyclopenta-2,4-diene, which was allowed to react in THF with distilled calcium. Crystallization of the product from THF solution gave dimeric bis(tetrahydrofuran-*O*)dicalcium bis[3,4-dimethyl-2,5-bis(trimethylsilyl)-1-phosphacyclopenta-2,4-dienide] cyclopentadienide chloride, **2**. The metathesis reaction of **1** with $AsCl_3$ yielded nearly quantitatively 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-arsacyclopenta-2,4-diene, **3**. 3,4-Dimethyl-2,5-bis(trimethylsilyl)-1-arsacyclopentadienyl bis(tetrahydrofuran-*O*)calcium chloride, **4**, was isolated from the reduction of **3** with distilled calcium.

Introduction

Scheme 1



Since the determination of the molecular structure of polymeric calcocene $CaCp_2$,[1] the field of substituted calcocenes and the heavier alkaline earth metallocenes has experienced active development.[2,3] (Tetrahydrofuran-*O*)calcium bis[2,4-di(*tert*-butyl)pentadienide] (**A**)[4,5] (Scheme 1) was the first structurally characterized example of an open alkaline earth metallocene which opened the research field of side-on bonded π-systems.[6] Examples of the phosphametallocenes of the group 2 metals were first synthesized by the reaction of diphenylbutadiyne to calcium and strontium bis[bis(trimethylsilyl)phosphanide]. However, these tetrakis(tetrahydrofuran-*O*)alkaline earth metal bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phosphacyclopentadienides] (**B**)[7] (Scheme 1) show metal−phosphorus σ-bonds rather than a metallocene-like structure. On the other hand, $(THF)_4Ba[P(SiMe_3)_2]_2$ reacts differently with diphenylbutadiyne,[8] and a η^5-bonded phospholide ligand was observed (**C**, Scheme 1).

The reaction of $M[P(SiMe_3)_2]_2$ with butadiynes forms products with the trimethylsilyl groups in 3,4-position; stabilization of the phosphacyclopentadienides by 2,5-bis(trimethylsilyl) substituents is not possible. For that reason, 1-chloro-2,5-bis(trimethylsilyl)phosphole would be an alternate starting material for these purposes. Access to this substance class is given by the metathesis reaction of ECl_3 (E = P, As, Sb, Bi) with bis(cyclopen-

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[‡] Crystal structure analysis.

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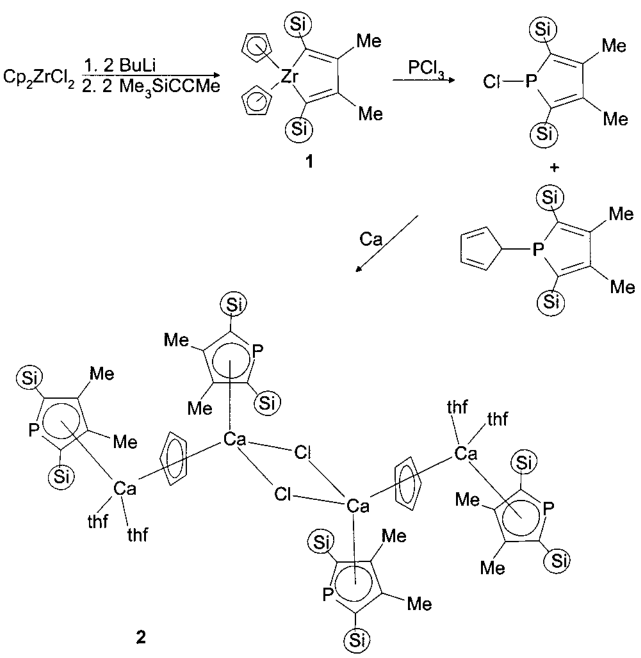
tadienyl)zirconacyclopentadienes. However, Fagan[9] described the chlorostiboles and bismoles as thermolabile compounds whose isolation was not possible. Furthermore, Nief and Mathey[10] synthesized the instable chloroarsole, whereas Douglas and Theopold[11] reported NMR data for yellow 1-chloro-2,3,4,5-tetramethylphosphole and described this phosphole as a stable oil at very low temperatures. Here we report the synthesis of 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)arsole as well as of a mixture of 1-chloro- and 1-cyclopentadienyl-3,4-dimethyl-2,5-bis(trimethylsilyl)phosphole, as well as the reduction of these pentelacyclopentadienes with calcium metal. Although phospholide anions are widely used ligands within the transition metal chemistry,[12] alkaline earth metal phospholides are only mentioned as unisolated magnesium derivatives used as intermediates.[13] To our knowledge, isolated species have not been reported thus far.

Results and Discussion

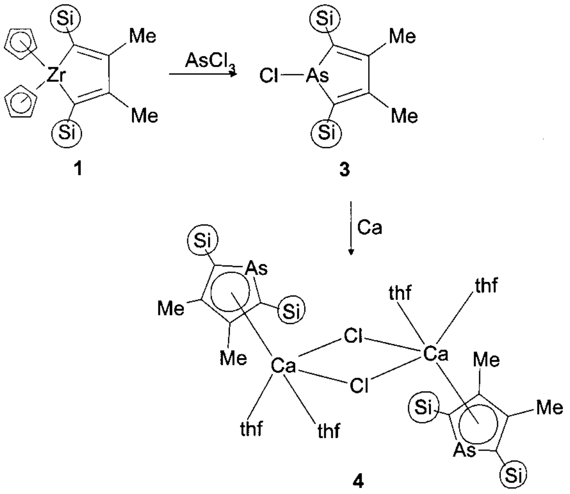
Synthesis. The synthesis of bis(cyclopentadienyl)zirconacyclopenta-2,4-dienes starting from zirconocene dichloride is well-known.[14] At low temperatures the metathesis reaction of Cp_2ZrCl_2 with 2 equiv of *n*-butyllithium yields $Cp_2Zr^nBu_2$,[15] which reacted with 2 molar equiv of 1-trimethylsilylpropyne to give yellow 1,1-bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-zirconacyclopenta-2,4-diene, **1**. The metathesis reaction of **1** with PCl_3 gave a mixture of 1-chloro- and 1-cyclopentadienyl-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-phosphacyclopenta-2,4-diene. Neither variations of the reaction temperature, of the solvent, nor of the reaction time allowed the isolation of pure 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)-1-phosphacyclopenta-2,4-diene. Distillation of the reaction mixture resulted in decomposition of the phosphacyclopentadienes to as yet unknown compounds. Therefore, the phosphacycles were not isolated, and the reaction mixture was stirred with distilled calcium metal for several days. According to our expectations, the calcium atom inserted into the Cl−P bond, but the cyclopentadienyl substituent reacted as a pseudohalide and 3,4-dimethyl-2,5-bis(trimethylsilyl)-1-phosphacyclopenta-2,4-dienyl calcium chloride and the cyclopentadienide were isolated. These two derivatives form adduct **2** as shown in Scheme 2, and, due to this fact, a separation by recrystallization failed.

The chemical shift of the phosphorus nucleus at $\delta(^{31}P\{^1H\}) = +149$ is within the characteristic range for phosphacyclopentadienides.[12] The fact that only one resonance was detected could be explained by exchange reactions. On the other hand, the ionicity of the bond between calcium and the phospholide anion would reduce the influence of the coligands on the chemical ^{31}P shift. Due to its sensitivity toward moisture and air, satisfactory analytical data could not obtained for **2**.

Scheme 2



Scheme 3



The metathesis reaction of **1** with $AsCl_3$ yielded 1-chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)arsole, **3**. A chlorocyclopentadienyl exchange reaction, as observed for the phosphorus analogue, did not occur. The reduction of **3** with distilled calcium gave dimeric 3,4-dimethyl-2,5-bis(trimethylsilyl)-1-arsacyclopentadienyl bis(tetrahydrofuran-*O*)calcium chloride, **4**, as shown in Scheme 3.

Molecular Structures. Figure 1 shows the molecular structure and the numbering scheme of **1**. The structural parameters agree well with those data of already published bis(cyclopentadienyl)zirconacyclopenta-2,4-dienes. The deviations from a best plane of the atoms Zr1, C2, C3, C4, and C5 are smaller than 2.1 pm. The Zr−C distances of **1** with values of 2.244(3) and 2.248(2) Å lie in the narrow region between 2.20 and 2.27 Å.[16−20] The substituents at the carbon atoms show a very small influence on the endocyclic C−C bonds. However, phenyl substituents lead to a smaller differ-

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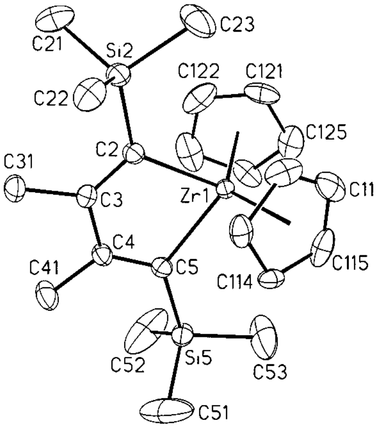

Figure 1. Molecular structure and numbering scheme of **1**. The ellipsoids represent a probability of 40%. The hydrogen atoms are omitted for clarity. Only one orientation of the disordered cyclopentadienyl ligands is represented. Selected bond lengths (Å): Zr1−C2 2.248(2), Zr1−C5 2.244(3), C2−C3 1.351(4), C3−C4 1.519(4), C4−C5 1.365(4), C2−Si2 1.871(3), C3−C31 1.522(4), C4−C41 1.518(4), C5−Si5 1.858(3). Bond angles (deg): C2−Zr1−C5 81.8(1), Zr1−C2−C3 107.5(2), C2−C3−C4 121.8(2), C3−C4−C5 121.4(3), C4−C5−Zr1 107.4(2).

ence between the endocyclic C−C and C=C bond lengths,[16] whereas exocyclic ring strain increases this difference.[17]

Figure 2 shows the molecular structure as well as the numbering scheme of **2**. This tetranuclear complex contains a central Ca_2Cl_2 ring with nearly equal Ca2−Cl1 distances of 2.71 Å and a Cl1−Ca2−Cl1′ angle of 84.87°. A similar Ca_2X_2 ring was reported by Hanusa and co-workers.[21] The calcium atoms Ca1 and Ca2 are bridged by a cyclopentadienide anion with mean Ca1−C and Ca2−C bond lengths of 2.756 and 2.790 Å, respectively. This structural motif is already known in the coligand-free calcocene.[1] The phospholide anions are η^5-coordinated to the calcium atoms. The Ca1−P1 as well as Ca2−P2 distances with values of 2.933 and 2.912 Å lie in the range of Ca−P bond lengths of calcium bis(phosphanides).[22] The mean calcium−carbon bond distances to the phospholide ligands lie in the characteristic range of calcocenes (Ca1−C(1m) 2.805 Å, Ca2−C(2m) 2.845 Å). The short Ca1−O(1m) bond lengths of 2.362 and 2.406 Å indicate an only weak steric shielding of the calcium center by the anionic ligands.

The P(n)−C(n1) as well as P(n)−C(n4) bond lengths of the planar phospholide ligands of approximately 1.78 Å show a partial double bond, as expected for a delocalized system. However, this distance is sligthly larger than that observed in phosphinines (phosphabenzenes).[23,24] The endocyclic C(n1)−P(n)−C(n4) angle has a value of 91.8°, which is approximately 10° smaller than the corresponding value of the phosphinines. The endocyclic C−C distances vary only slightly within twice the estimated standard deviations. In contrast to these findings, the η^1-P-bonded phospholide anions in tetrakis(tetrahydrofuran-*O*)calcium bis[2,5-diphenyl-3,4-bis(trimethylsilyl)phospholide][7] show a less effective delocalization of the anionic charge within the aromatic system. Due to the steric repulsion between the methyl and trimethylsilyl groups of the phospholide substituents of **2**, the C−C−Si angles are widened compared to the P−C−Si values; significant elongations of the C−Si bonds are not observed.

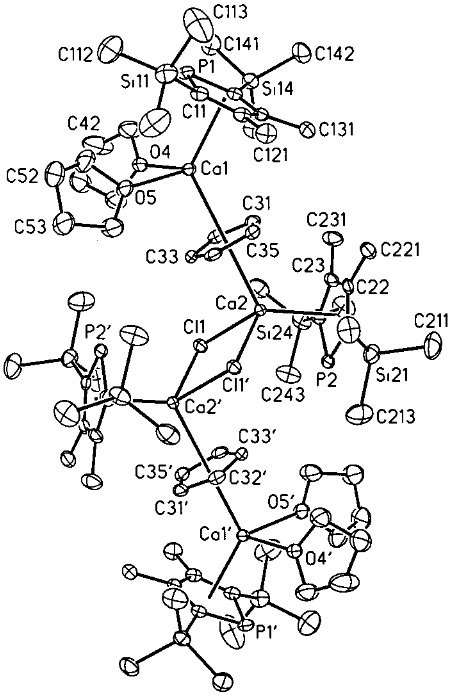

Figure 2. Molecular structure as well as numbering scheme of dimeric **2**. The ellipsoids represent a probability of 30%. The hydrogen atoms are omitted for clarity. Symmetry-related atoms ($-x+1$, $-y+1$, $-z+1$) are marked with an apostrophe. Selected bond lengths (Å): Ca1−P1 2.933(2), Ca1−C11 2.826(5), Ca1−C12 2.813(6), Ca1−C13 2.793(5), Ca1−C14 2.786(5), Ca1−C31 2.724(5), Ca1−C32 2.733(5), Ca1−C33 2.761(5), Ca1−C34 2.78.6(5), Ca1−C35 2.774(5), Ca1−O4 240.6(4), Ca1−O5 236.2(4), Ca2−Cl12.725(2), Ca2−Cl1′ 2.698(2), Ca2−P2 2.912(2), Ca2−C21 2.832(5), Ca2−C22 2.871(5), Ca2−C23 2.862(5), Ca2−C24 2.816(5), Ca2−C31 2.790(5), Ca2−C32 2.742(5), Ca2−C33 2.768(5), Ca2−C34 2.818(5), Ca2−C35 2.830(5), P1−C11 1.773(6), C11−C12 1.412(8), C12−C13 1.421(7), C13−C14 1.415(7), P1−C14 1.781(5), P2−C21 1.779(6), C21−C22 1.411(7), C22−C23 1.402(8), C23−C24 1.424(7), P2−C24 1.774(5). Bond angles (deg): Ca2−Cl1−Ca2′ 95.13(5), C11−P1−C14 91.8(2), C21−P2−C24 91.7(3).

Figure 3 shows the molecular structure as well as the numbering scheme of dimeric **4**. The central moiety is

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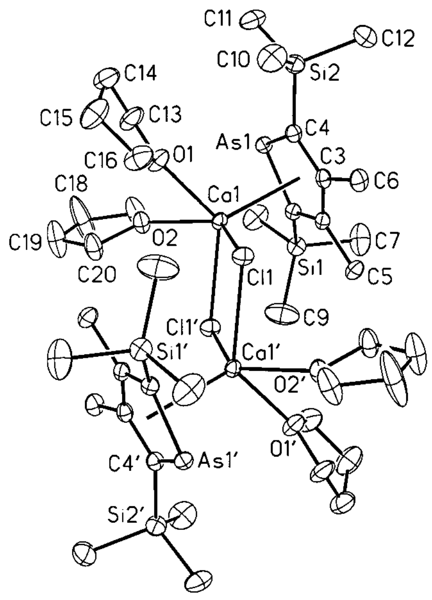

Figure 3. 3,4-Dimethyl-2,5-bis(trimethylsilyl)-1-arsacyclopentadienyl bis(tetrahydrofuran-*O*)calcium chloride, **4**. The ellipsoids represent a probability of 30%. Hydrogen atoms are omitted for clarity and symmetry related atoms ($-x+1$, $-y+1$, $-z+1$) marked with an apostrophe. Selected bond lengths (Å): Ca1−Cl1 2.714(1), Ca1−Cl1′ 2.724(1), Ca1−As1 3.0737(8), Ca1−C1 2.832(3), Ca1−C2 2.770(3), Ca1−C3 2.817(3), Ca1−C4 2.903(4), Ca1−O1 2.408(3), Ca1−O2 2.411(2), As1−C1 1.890(4), C1−C2 1.409(5), C2−C3 1.423(5), C3−C4 1.406(5), C1−Si1 1.861(3), C2−C5 1.514(5), C3−C6 1.510(5), C4−Si2 1.859(4). Bond angles (deg): Cl1−Ca1−Cl1′ 79.25(3), C1−As1−C4 87.9(2), As1−C1−C2 110.6(2), C1−C2−C3 115.5(3), C2−C3−C4 115.1(3), C3−C4−As1 110.8(2).

a centrosymmetric Ca_2Cl_2 ring with Ca−Cl distances of 2.72 Å. The Cl1−Ca1−Cl1′ angle of 79.25° is smaller than the corresponding value in **2**. This finding indicates a higher steric strain on the calcium atom of **4** than for Ca1 of **2**.

The planar arsolide anion is η^5-bonded with As−C bond lengths of 1.89 Å, which are larger than As═C double bonds and only marginally larger than those in arsinine (arsabenzene) derivatives.[24,25] The endocyclic C−C bonds show very small differences of approximately 1.5 pm, thus proving the charge delocalization within the arsacyclopentadienide ligand. The Ca1−As1 bond length of 3.074 Å is slightly longer than the calcium arsenic distances in tetrakis(tetrahydrofuran-*O*)calcium bis[bis(trimethylsilyl)arsanide].[26] The Ca−C distances vary between 2.77 and 2.90 Å (mean Ca−C bond length 2.83 Å), more widely than the corresponding distances of the above-mentioned calcium phospholide moiety. The C1−As1−C4 angle of 87.9° is slightly smaller than the corresponding CPC angle.

Conclusion

The aromaticity of the phospholide anions leads to an increasing similarity of the endocyclic C−C bond lengths. According to calculations,[27,28] the aromaticity is comparable with that of the carbon analogue. The calculated structural parameters of the phospholide anion are rather similar to those of **2** ($H_4C_4P^-$: P−C 1.773 Å, CPC 89.89°, C═C 1.396 Å, C−C 1.418 Å)[28] with a small difference of 2.2 pm between endocyclic CC bonds, even smaller than the corresponding value of a lithium phospholide.[11] Similar structural parameters are reported for phospholes with a planar-coordinated phosphorus atom, whereas a pyramidal environment enforces a less effective delocalization of the anionic charge, thus leading to larger P−C distances of 1.815 Å and a difference between the endocyclic C═C and C−C bond lengths of 10.4 pm.[28] Similar findings compared with **2** concerning the aromaticity are published for 1,1′-diphosphaferrocenes.[29] Consequently, the degrees of aromaticity within the arsolide anion of **4** and of the 1,1′-diarsaferrocenes[30,31] are of the same order of magnitude.

Experimental Section

All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed using standard Schlenk techniques and dried using thoroughly deoxygenated solvents. 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 plates. The frequencies in the region of the Nujol vibrations were not listed. The low carbon values at the elemental analysis result from carbide and carbonate formation as well as loss of neutral coligands during handling and combustion of the compounds. We were unable to get reasonable results for even crystalline **2** due to decomposition during handling.

1,1-Bis(cyclopentadienyl)-3,4-dimethyl-2,5-bis(trimethylsilyl)zirconacyclopenta-2,4-diene (1). A solution of 19.53 g of zirconocene dichloride (66.82 mmol) and 15.0 g of 1-trimethylsilylpropyne in 100 mL of THF was cooled to −78 °C, and 66.8 mL of a 1.6M *n*-butyllithium/hexane solution (133.6 mmol) was added dropwise. This solution was slowly warmed to room temperature and stirred for an additional 2 h. All volatile materials were removed in a vacuum at room temperature, and the residue was dissolved in 50 mL of toluene. The remaining solids were filtered, and again, the solvent was removed at room temperature in a vacuum. The residue was dissolved in pentane, and the clear solution was reduced to 30 mL and then cooled to −30 °C. Within a few days yellow crystals precipitated. Yield: 21.4 g (48.1 mmol) or 72%. Mp: 56 °C. ^1H NMR (THF-d_8, 30 °C, 399.785 MHz): $\delta = 0.05$ ($SiMe_3$), 1.74 (Me), 6.21 (C_5H_5). $^{13}C\{^1H\}$ NMR (THF-d_8, 30 °C, 100.536 MHz): $\delta = 1.71$ ($SiMe_3$), 25.12 (Me), 110.80 (C_5H_5), 146.10 (C2 and C5), 201.60 (C3 and C4). $^{29}Si\{^1H\}$ NMR (THF-d_8, 30 °C, 100.536 MHz): $\delta = -17.20$. IR: 1916 vw, 1871 vw, 1783 w, 1685 w, 1592 w, 1504 m, 1474 w, 1438 sh, 1424 s, 1365 w, 1355 m, 1294 w, 1256 s, 1246 vs, 1241 vs, 1205 sh, 1197 w, 1123 vw, 1085 s, 1075 sh, 1015 vs, 1007 vs, 991 sh, 976 w, 887 sh, 841 vs, 804 sh, 793 vs, 770 s, 749 s, 725 m, 676 s, 629 s, 536 m, 481 w, 430 m, 385 vw, 351 s. Anal. Calcd for $C_{22}H_{34}Si_2Zr$ (445.89): C 59.26, H 7.69. Found: C 59.25, H 7.12.

Dimeric Bis[3,4-dimethyl-2,5-bis(trimethylsilyl)phosphacyclopentadienyl] bis(tetrahydrofuran-*O*)dicalcium Cyclopentadienide Chloride (2). To a solution of 2,00 g of

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

	1	2	4
empirical formula	$C_{25}H_{37}Si_2Zr$	$C_{39.5}H_{75}Ca_2ClO_2P_2Si_4$	$C_{21.25}H_{40}AsCaClO_2Si_2$
fw (g·mol^{-1})	484.95	871.91	534.16
temp T (°C)	−100	−100	−100
space group[33]	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimens			
a (Å)	12.1740(1)	13.6678(1)	10.1842(1)
b (Å)	13.6539(2)	14.7296(1)	12.0737(2)
c (Å)	15.1495(1)	16.6057(2)	12.9866(3)
α (deg)	90	68.917(1)	106.535(1)
β (deg)	91.541(1)	80.610(1)	91.290(1)
γ (deg)	90	64.858(1)	96.721(1)
V (Å^3)	2517.28(5)	2823.56(4)	1517.67(5)
Z	4	2	2
ρ_{calcd} (g·cm^{-3})	1.280	1.026	1.169
λ (Å)	0.71073	0.71073	0.71073
μ (cm^{-1}, Mo Kα)	5.40	4.17	14.68
no. of data collcd	14070	16491	8955
no. of params	345	490	265
no. of restraints	0	12	4
goodness-of-fit s on F^2 [a]	1.041	1.071	1.062
R indices [all data (R_{int})][b]	4666 (0.0222)	8907 (0.0363)	4837 (0.0148)
R_1	0.0424	0.1099	0.0463
wR_2	0.0995	0.2203	0.1318
R indices[b] [data $I > 2\sigma(I)$]	4103	5877	4204
R_1	0.0359	0.0660	0.0385
wR_2	0.0939	0.1781	0.1210
residual dens (e·Å^{-3})	0.563; −0.504	0.724; −0.472	0.928; −0.320

[a] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. [b] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.[35]

1 (4.48 mmol) in 30 mL of THF was added 0.39 mL of PCl_3 (4.49 mmol). After 15 min the solvent was removed by distillation. The residue was dissolved in 30 mL of pentane and filtered to remove the solid materials. The solvent was distilled and the residue redissolved in 15 mL of THF. Then 0.4 g of distilled calcium (10 mmol) was added and the solution stirred at room temperature for 6 days. All solid materials were removed, and the reddish brown filtrate was stored at 7 °C to give crystalline **2**. Yield: 0.53 g (0.32 mmol) or 25%. Mp: 80−82 °C (dec). ^{1}H NMR (THF-d_8, 30 °C, 399.785 MHz): $\delta = 0.23$ ($SiMe_3$), 2.31 (Me), 5.80 (C_5H_5), 1.76 and 3.61 (THF). ^{29}Si{^{1}H} NMR (THF-d_8, 30 °C, 79.425 MHz): $\delta = -10.42$ (d, ^2J(PSi) = 31.4 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 30 °C, 109.365 MHz): $\delta = 148.95$. IR: 1580 m, 1558 w, 1462 sh, 1448 m, 1405 m, 1378 w, 1362 m, 1308 m, 1247 vs, 1182 s, 1154 vs, 1072 s, 1038 m, 984 s, 921 m, 890 vw, 840 vs, 720 vw, 690 w, 665 vw, 641 w, 553 w, 519 m, 487 vw, 445 vw, 392 w, 354 w, 331 w, 297 w.

1-Chloro-3,4-dimethyl-2,5-bis(trimethylsilyl)arsacyclopenta-2,4-diene (3). $AsCl_3$ (0.37 mL, 4.3 mmol) was added at room temperature to a solution of 1.93 g of **1** (4.33 mmol) in 25 mL of THF. After 1 h the solvent was removed at room temperature by distillation under reduced pressure. The yellow residue was dissolved in pentane, and insoluble materials were filtered. After removal of volatile materials, a viscous oil of **3** remained. Yield: 1.13 g (3.37 mmol) or 78%. ^{1}H NMR (THF-d_8, 30 °C, 270.168 MHz): $\delta = 0.29$ ($SiMe_3$), 2.13 (Me). ^{13}C{^{1}H} NMR (THF-d_8, 30 °C, 100.536 MHz): $\delta = -0.09$ ($SiMe_3$), 19.06 (Me), 151.26 (C3, C4), 162.27 (C2, C5; AsC). ^{29}Si{^{1}H} NMR (THF-d_8, 30 °C, 53.674 MHz): $\delta = -7.60$. IR (pure **3** between KBr plates): 3004 sh, 2953 vs, 2916 s, 2850 m, 1942 vw, 1876 vw, 1570 w, 1517 m, 1444 m, 1430 m, 1405 m, 1377 m, 1367 w, 1319 w, 1259 vs, 1131 s, 1035 m, 1001 vw, 862 vs, 839 vs, 792 m, 756 s, 740 m, 691 m, 634 s, 550 w, 502 m, 442 w, 404 w, 362 s, 306 w, 294 w. Anal. Calcd for $C_{12}H_{24}AsClSi_2$ (334.86): C 43.04, H 7.22. Found: C 41.34, H 7.53.

Dimeric Bis[3,4-dimethyl-2,5-bis(trimethylsilyl)arsacyclopentadienyl] bis(tetrahydrofuran-*O*)calcium Chloride (4). Compound **3** (1.33 g, 3.97 mmol) was dissolved in 15 mL of THF, and 0.33 g of distilled calcium metal (8.23 mmol) was added. After stirring of this solution for 2 days at room temperature volatile materials were removed in a vacuum. The residue was redissolved in 20 mL of pentane, and the remaining solids were filtered. Cooling of this yellow solution to 5 °C resulted in the precipitation of yellow single-crystalline **4**. Yield: 0.45 g (0.43 mmol) or 22%. Decomposed without melting. ^{1}H NMR (THF-d_8, 30 °C, 399.785 MHz): $\delta = 0.05$ and 0.20 ($SiMe_3$), 1.72 and 1.74 (Me), 1.80 and 3.57 (THF). ^{29}Si{^{1}H} NMR (THF-d_8, 30 °C, 53.674 MHz): $\delta = -9.70$. IR: 1448 w, 1431 w, 1406 w, 1352 vw, 1315 vw, 1295 vw, 1245 vs, 1187 vw, 1145 w, 1132 m, 1074 w, 1034 s, 952 w, 910 sh, 876 sh, 863 vs, 837 vs, 753 m, 742 sh, 683 m, 634 m, 513 w, 505 vw, 457 w, 423 vw, 369 w, 325 w. Anal. Calcd for bis(THF) complex $C_{32}H_{64}As_2Ca_2Cl_2O_2Si_4$ (894.09): C 42.98, H 7.22. Found: C 42.58, H 7.21.

Structure Determinations of 1, 2, and 4. Suitable single crystals were covered with Nujol and mounted on a glass fiber.[32] The crystal structure analysis was performed on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation and a SMART area detector. The crystallographic data as well as details of the structure solution and refinement procedures are summarized in Table 1.

The crystal structures were solved by direct methods with the program SHELXTL Plus.[34] The refinement of the structures succeeded with the program packages SHELXL-97[35] and SHELXTL PC, version 5.03,[34] where the function $\sum[w(F_o^2 - F_c^2)^2]$ was minimized. The displacement parameters of all nonhydrogen atoms were treated anisotropically. For all calculations the atom form factors of the neutral atoms As, C, Ca, Cl, O, P, Si, and Zr[36] as well as hydrogen[37] were used. The H

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atoms were taken into account in idealized positions with fixed *U* values and C−H distances of 0.96 Å. The cyclopentadienyl ligands of **1** show a two-site disorder with refined population ratios of 0.57(3)/0.43(3) and 0.53(2)/0.47(2). The asymmetric unit contains half of a benzene molecule. The elementary cells of **2** and **4** contain each a disordered pentane molecule, which is not shown in Figures 2 and 3, respectively. These solvent molecules were refined isotropically.

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Supporting Information Available: A Listing of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters of non-hydrogen atoms for **1**, **2**, and **4**. This material, as well as an X-ray crystallographic file in CIF format, is available free of charge via the Internet at http://pubs.acs.org.

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