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Trialkylsilyl-Substituted Pentalene Ligands

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Summary: The reaction between $[C_8H_6][Li(DME)]_2$ and chlorotrimethylsilane affords the trimethylsilyl-substituted dihydropentalene $C_8H_6(SiMe_3\text{-}1,4)_2$, which may be deprotonated with ${}^nBuLi$ in dimethoxyethane to give $[C_8H_4(SiMe_3\text{-}1,4)_2][Li(DME)]_2$; the latter reacts with chlorotrimethylsilane to give $C_8H_4(SiMe_3\text{-}1,1',4,4')_4$. Similarly, treatment of $[C_8H_6][Li(DME)]_2$ with triisopropylsilyl triflate gives $C_8H_6(Si^iPr_3\text{-}1,4)_2$; deprotonation of the latter with KNH_2 in diethyl ether affords $[C_8H_4(Si^iPr_3\text{-}1,4)_2][K]_2$, which has been crystallographically characterized and exhibits a chain structure in the solid state.

Introduction

The aromatic 10π-electron pentalene dianion, $[C_8H_6]^{2-}$, was first prepared by Katz and Rosenberger[1] via the flash vacuum pyrolysis (FVP) of isodihydrodicyclopentadiene and subsequent deprotonation of the resultant 1,3-dihydropentalene with ^{n}BuLi in THF. Subsequently, FVP of cyclooctatetraene under a variety of conditions was found to yield a mixture of isomeric dihydropentalenes,[2−4] which could be collectively deprotonated with ^{n}BuLi-DME to afford crystallographically characterized $[C_8H_6][Li(DME)]_2$,[5] or with ^{n}BuLi-TMEDA to give $[C_8H_6][Li(TMEDA)]_2$.[6] A non-FVP, multistep route to $[C_8H_6]Li_2$, based on ring expansion of cycloheptatriene, has also been reported.[7]

Recently we described the synthesis of the silyl-substituted pentalene complex $[Ta(\eta^8\text{-}C_8H_4\{SiMe_3\text{-}1,5\}_2)Cl_3]$, which represented the first example of η^8 ligation for a pentalene ligand.[8] Accordingly, we were interested in developing a rational synthesis of bis(trialkylsilyl)-pentalene ligands, and herein we describe the preparation of pentalene dianions bearing trimethylsilyl or triisopropylsilyl substituents. The use of the latter for the synthesis of $[Th(\eta^8\text{-}C_8H_4\{Si^iPr_3\text{-}1,4\}_2)_2]$ and $[Mo(C_8H_4\{Si^iPr_3\text{-}1,4\}_2)]_2$ has been previously communicated.[9,10]

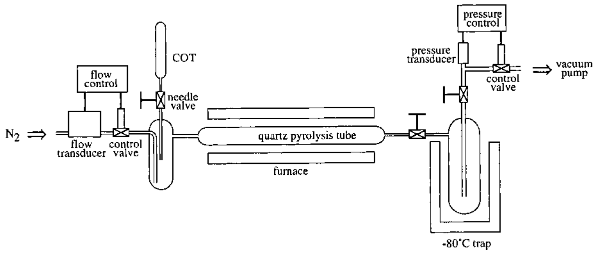

Figure 1. Flash vacuum pyrolysis apparatus.

Results and Discussion

By analogy with the synthesis of the bis(trimethylsilyl)cyclooctatetraene dianion, the starting point for the synthesis of trialkylsilyl pentalene derivatives was the pentalene dianion.[11] The synthesis of the latter has been effected by a number of routes (vide supra), but the one employed here was the FVP of cyclooctatetraene and deprotonation of the resultant dihydropentalenes with ^{n}BuLi-DME.[5] Previously reported temperatures for this pyrolysis vary from 400 to 675 °C, with optimum conversion at 550−600 °C to give dihydropentalenes in up to 90% (nonisolated) yield.[3,4]

The FVP apparatus employed in this work is shown in Figure 1.

Precise, reproducible control of N_2 carrier gas flow rate and partial pressure was achieved by use of closed-loop flow and pressure transducers (MKS Instruments); admission of cyclooctatetraene into the system was controlled by a high-precision needle valve (Parker HR Series). The pyrolysis zone was a quartz tube 300 mm in length × 27 mm i.d., heated by a tube furnace. The mixture of dihydropentalenes was collected in a dry ice trap, dissolved in −80 °C hexane, and immediately treated with 2 equiv of ^{n}BuLi-DME in hexane to afford a precipitate of $[C_8H_6][Li(DME)]_2$ (which is essentially insoluble in aliphatic hydrocarbons). Under carefully optimized conditions (N_2 flow rate 1.5 $cm^3\ min^{-1}$, operating pressure 1.0 mbar, COT introduction rate 0.5 $cm^3\ h^{-1}$, pyrolysis temperature 615 °C), a typical isolated yield of $[C_8H_6][Li(DME)]_2$ was 87% (based on COT), and on a scale of some 25 g.

Treatment of $[C_8H_6][Li(DME)]_2$ in THF with 2 equiv of chlorotrimethylsilane afforded the pale yellow, crystalline bis(trimethylsilyl)dihydopentalene $C_8H_6(SiMe_3\text{-}1,4)_2$, **1**, as a mixture of racemic and meso isomers (see Figure 2).

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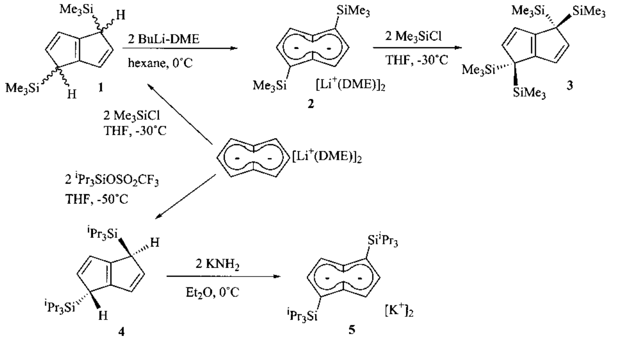

Figure 2. Synthesis of trialkylsilyl pentalene derivatives.

1 is exceedingly soluble in hydrocarbon solvents and oligomerizes to unidentified oily products on standing at room temperature but is stable for long periods at −20 °C. **1** may be readily deprotonated with ^{n}BuLi-DME to give the dilithium bis(trimethylsilyl)pentalenide $[C_8H_4(SiMe_3\text{-}1,4)_2][Li(DME)]_2$, **2** (Figure 2). **2** readily loses coordinated DME in the solid state and, as isolated, displays two resonances (at δ −8.4 and −10.8) in the ^{7}Li spectrum in toluene-d_8; however, addition of excess (ca. 10 equiv) DME to the NMR sample results in the observation of a single resonance at δ −8.1. We therefore conclude that **2** has an analogous structure to that of $[C_8H_6][Li(DME)]_2$ (Figure 2), which has been crystallographically characterized.[5]

Attempts to introduce further trimethylsilyl substitution into the pentalene ring system, by treatment of **2** with 2 equiv of chlorotrimethylsilane, resulted in the isolation of the tetrakis(trimethylsilyl)pentalene $C_8H_4(SiMe_3\text{-}1,1',4,4')_4$, **3**, as the only observed isomer (Figure 2). **3** is considerably more thermally robust than **1**, and survives unchanged (by NMR) at 60 °C in benzene-d_6 solution; **3** may thus find application as an alternative transfer reagent for the $C_8H_4(SiMe_3\text{-}1,4)_2$ ring via elimination of chlorotrimethylsilane in reactions with metal halides. The ^{1}H NMR spectrum of **3** in toluene-d_8 is invariant down to −80 °C, and we therefore conclude that silyl group migration, via the metallotropic shifts seen in the bis(trimethylsilyl)-substituted cyclopentadiene $C_5H_4(SiMe_3\text{-}5,5')_2$,[12] around the pentalene ring system does not occur. **3** is correspondingly resistant to deprotonation by either ^{n}BuLi or KNH_2, whereas the equilibrium concentration of $C_5H_4(SiMe_3\text{-}1,3)_2$ in $C_5H_4(SiMe_3\text{-}5,5')_2$ enables deprotonation of the latter to form $[C_5H_3(SiMe_3\text{-}1,3)_2]^-$.[12]

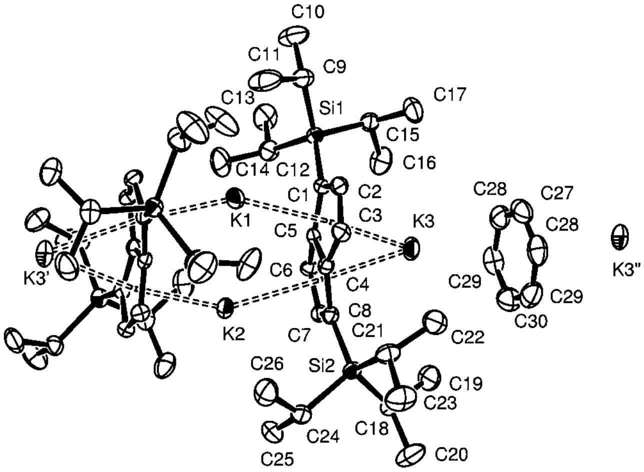

Figure 3. ORTEP[18] representation of the molecular structure of **5**. Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Distances for Compound 5[a]

K(1)−C(1)	2.887(4)	K(1)−C(2)	2.865(4)	C(1)−C(2)	1.433(5)
K(1)−C(3)	3.037(4)	K(1)−C(4)	3.182(4)	C(2)−C(3)	1.376(5)
K(1)−C(5)	3.057(4)	K(2)−C(4)	3.091(4)	C(4)−C(5)	1.449(5)
K(2)−C(5)	3.233(4)	K(2)−C(6)	3.102(4)	C(5)−C(6)	1.431(5)
K(2)−C(7)	2.919(4)	K(2)−C(8)	2.937(4)	C(7)−C(8)	1.430(5)
K(1)···K(2)	3.332(2)	K(3)−C(1)	3.062(4)	C(1)−C(5)	1.456(5)
K(3)−C(2)	3.175(4)	K(3)−C(3)	3.042(4)	C(3)−C(4)	1.433(5)
K(3)−C(4)	2.722(4)	K(3)−C(5)	2.732(4)	C(4)−C(8)	1.456(5)
K(3)−C(6)	3.064(4)	K(3)−C(7)	3.190(4)	C(6)−C(7)	1.393(5)
K(3)−C(8)	3.029(4)	K(3)−M(1)[b]	3.271(5)		

[a] Bond distances are given in angstroms. Pentalene fold angle is 14.38(07)°. [b] M(1) is the centroid of the C(27)−C(30) benzene ring.

We were particularly interested in the synthesis of bulkier variants of **1,** and hence **2**, as a potential ligand in f-element chemistry, and we therefore chose to employ triisopropylsilyl groups as the substituents. $[C_8H_6][Li(DME)]_2$ fails to react with chlorotri(isopropylsilyl)silane but reacts smoothly with tri(isopropyl)silyl triflate at ca. −50 °C in THF to afford $C_8H_6(Si^iPr_3\text{-}1,4)_2$, **4**, as a white crystalline solid in high yield after crystallization from pentane (Figure 2). Only one isomer is observed in the NMR spectra of **4**, in contrast to **1** (vide supra): we assume this to be the trans (meso) isomer (Figure 2) on the basis of the steric influence of the -Si^iPr_3 groups during attack on $[C_8H_6][Li(DME)]_2$. The bulky nature of these substituents also confers a fair degree of thermal stability on **4**, which is unchanged after several days at room temperature. It was felt desirable to prepare the dipotassium salt of the bis(triisopropylsilyl)pentalene dianion, again for reasons associated with the intended use of the latter in f-element chemistry, where employment of lithium transfer reagents often results in salt incorporation and formation of "ate" complexes. Hence **4** was deprotonated with potassium amide in ether to give an essentially quantitative yield of base-free $[C_8H_4(Si^iPr_3\text{-}1,4)_2]K_2$, **5** (Figure 2). As initially isolated, **5** is a tan-colored solid of sufficient purity (>99% by NMR) for further reactions;[9,10] recrystallization from benzene at room temperature provided X-ray-quality, pale yellow crystals of analytically pure **5**. The molecular structure has been determined by X-ray crystallography, and the structure is shown in Figure 3, with selected bond lengths collated in Table 1. **5** crystallizes with one molecule of benzene, and the structure consists of chains of alternating $[K_2\{C_8H_4(Si^iPr_3\text{-}1,4)_2\}_2]$ and $[K_2(C_6H_6)]$ units, with another benzene solvate molecule in the lattice. The $[K_2\{C_8H_4(Si^iPr_3\text{-}1,4)_2\}_2]$ unit has a bimetallic sandwich structure similar to that seen in $[Mo(C_8H_4\{Si^iPr_3\text{-}1,4\}_2)]_2$,[10] although the pentalene rings in the latter are essentially planar while those in **5** are folded (by ca. 14°) away from K(1) and K(2) as a result of η^8-ligation to the neighboring $[K_2(C_6H_6)]$ unit. The K−C bond lengths for the bonding of K(1) and K(2) to the two five-membered rings of the pentalene ligand [C(1)−C(5) and C(4)−C(8), respectively] lie in the range 2.865(4)−3.233(4) Å, comparable to the K-ring C distances in

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potassium cyclopentadienyl derivatives, e.g., $[K(\eta-C_5H_5)]_n$ [2.955(5)−3.140(6) Å] and $[K(\eta-SiMe_3C_5H_4)]_n$ [2.988(8)−3.074(10) Å].[13] For the η^8-ligated K(3), the K−C bond lengths range from 2.722(4) to 3.190(4) Å, considerably longer than the V−C bond distances [2.042(6)−2.310(6) Å] for the covalently bound, and significantly folded (43°) η^8-pentalene ring in $[V(\eta-C_5H_5)(\eta-C_8H_6)]$; the C−C distances within the pentalene ring in **5**, which range from 1.376(5) to 1.456(5) Å, are, however, remarkably similar to those in the latter [1.374(6)−1.456(6) Å].[14] In the $[K_2(C_6H_6)]$ unit, the K(3)−benzene ring centroid distance of 3.271(5) Å is in the normal range for such interactions.[13]

Conclusion

We have described a high-yield route, starting from cyclooctatetraene, to 1,4-bis(trialkylsilyl)pentalene dianions, which represent a new class of ligand in organometallic chemistry. Additionally, these ligands are C_2-symmetric and facially enantiotopic, and we therefore anticipate that they will find application for the synthesis of novel compounds that have potentially useful stereochemical features.

Experimental Section

Unless otherwise stated, all experimental procedures were carried out under standard high-vacuum and Schlenk techniques, under an atmosphere of dry argon, or under dinitrogen in an MBraun or a Miller−Howe glovebox. Glassware was dried in an oven at 150 °C prior to use. *n*-Pentane and diethyl ether were distilled from sodium/potassium alloy, and tetrahydrofuran, *n*-hexane, and 1,2-dimethoxyethane (DME) from potassium metal under dinitrogen prior to use; benzene-d_6, toluene-d_8, and tetrahydrofuran-d_8 were dried over molten potassium and then vacuum-transferred to, and stored in, an ampule under dinitrogen prior to use. NMR spectra were recorded at 295 K on a Bruker DPX 300 MHz spectrometer, with chemical shifts (δ) reported in parts per million (ppm), relative to the residual proton chemical shifts of the internal deuterated solvent (^{1}H and ^{13}C) set relative to external TMS, and relative to external LiCl (^{7}Li). Coupling constants are quoted in hertz. Electron impact mass spectra were recorded on a VG Autospec mass spectrometer. Elemental analyses were carried out by Mikroanalytisches Labor Pascher, Remagen, Germany, and the University of North London Elemental Analysis Service, London, U.K.

Chlorotrimethylsilane and triisopropylsilyl triflate were purchased from Aldrich and used as received. Cyclooctatetraene (Fluorochem) was dried over 4A molecular sieves and vacuum-distilled before use. Potassium amide was prepared by reaction of potassium metal with liquid ammonia in the presence of a catalytic amount of iron(III) chloride.

Synthesis of $[C_8H_6][Li(DME)]_2$. Cyclooctatetraene (11.3 g, 0.108 mol) in a slow stream (1.5 cm^3 min^{-1} at STP) of dinitrogen was passed through a quartz tube at 615 ± 1 °C under a controlled dynamic vacuum of 1.0 ± 0.05 mbar over a period of 24 h in the FVP apparatus shown in Figure 2; the resultant mixture of dihydropentalenes (which must be maintained below −50 °C) was collected in a trap at −78 °C. The contents of the latter were then dissolved in precooled (−78 °C) hexane (100 cm^3) and DME (23 cm^3, 0.22 mol) added, followed by ^{n}BuLi (2.5 M in hexanes, 88 cm^3, 0.22 mol) dropwise with stirring, which resulted in the precipitation of white $[C_8H_6][Li(DME)]_2$. After warming to room temperature, the latter was isolated by filtration on a frit, washed with hexane (3 × 50 cm^3), and dried under vacuum. Yield 27.8 g, 87% based on cyclooctatetraene. The exact amount of coordinated DME varies between 1 and 2 and must be determined by ^{1}H NMR before use. NMR data (THF-d_8): ^{1}H, δ 5.76 (t, 2H, ring C*H*, J_{HH} = 3.0 Hz), 5.00 (d, 4H, ring C*H*, J_{HH} = 3.0 Hz), 3.42 (s, 8H, DME C*H*$_2$), 3.27 (s, 12H, DME C*H*$_3$); ^{7}Li{^{1}H}, δ −8.57 (s).

Synthesis of $C_8H_6(SiMe_3\text{-}1,4)_2$, 1. To a stirred solution of $[C_8H_6][Li(DME)]_2$ (2.95 g, 10 mmol) in THF (100 cm^3) at −30 °C was added chlorotrimethylsilane (2.38 g, 22 mmol) dropwise; the mixture was then allowed to warm to 0 °C and stirred for 2 h. The solvent was removed in vacuo at this temperature. The resultant pale yellow solids were extracted with pentane (2 × 50 cm^3) and filtered at 0 °C, and the yellow filtrates were pumped to dryness at 0 °C to afford a pale yellow semicrystalline mass of **1**. Further purification was hampered by the extreme solubility of **1**, coupled with its thermal sensitivity, and was found to be unnecessary (NMR purity > 90%). Yield 1.75 g, 70%. **1** requires storage under inert atmosphere at −20 °C or below. NMR data (minor isomer, benzene-d_6): ^{1}H, δ 6.79 (d, 2H, ring C*H*, J_{HH} = 4.6 Hz), 6.41 (d, 2H, ring C*H*, J_{HH} = 4.6 Hz), 3.15 (s, 2H, ring C*H*), −0.11 (s, 18H, Si−C*H*$_3$); ^{13}C{^{1}H}, δ 152.9 (ring *C*), 133.7 (ring *C*H), 127.3 (ring *C*H), 44.3 (ring *C*HSiMe$_3$), −1.8 (Si*C*H$_3$). NMR data (major isomer, benzene-d_6): ^{1}H, δ 6.72 (d, 2H, ring C*H*, J_{HH} = 5.1 Hz), 6.45 (d, 2H, ring C*H*, J_{HH} = 5.1 Hz), 3.19 (s, 2H, ring C*H*), −0.05 (s, 18H, Si−C*H*$_3$); ^{13}C{^{1}H}, δ 152.1 (ring *C*), 133.3 (ring *C*H), 126.9 (ring *C*H), 44.4 (ring *C*HSiMe$_3$), −1.9 (Si*C*H$_3$). HRMS (EI): 248.142687 (calculated 248.141658)

Synthesis of $[C_8H_4(SiMe_3\text{-}1,4)_2][Li(DME)_x]_2$, 2. To a stirred solution of $C_8H_6(SiMe_3\text{-}1,4)_2$ (2.48 g, 10 mmol) in a mixture of hexane (50 cm^3) and DME (10 cm^3) at −30 °C was added ^{n}BuLi in hexane (20 mmol, 8 cm^3 of 2.5 M solution) dropwise; the mixture was then allowed to warm to room temperature and stirred for 2 h, and the solvent was removed in vacuo. The resultant orange solids were washed with cold (−78 °C) pentane (2 × 10 cm^3), and dried in vacuo to afford orange **2** (x = 1.1). Yield 2.1 g, 60%. Meaningful microanalysis was not possible due to ready loss of DME. NMR data (toluene-d_8): ^{1}H, δ 6.17 (br s, 2H, ring C*H*), 5.89 (br s, 2H, ring C*H*), 2.59 (s, C*H*$_3$), 2.37 (s, C*H*$_2$), 0.48 (s, 18H, SiC*H*$_3$); ^{13}C{^{1}H}, δ 131.4 (ring *C*), 117.0 (ring *C*H), 91.4 (ring *C*H), 84.7 (ring *C*SiMe$_3$), 69.8 (*C*H$_2$), 58.8 (*C*H$_3$), 1.6 (Si*C*H$_3$); ^{7}Li{^{1}H}, δ −8.4 (s), −10.8 (s); ^{7}Li{^{1}H} (+ ca.10 equiv of DME): δ −8.1 (s).

Synthesis of $C_8H_4(SiMe_3\text{-}1,1',4,4')_4$, 3. To a stirred solution of $[C_8H_4(SiMe_3\text{-}1,4)_2][Li_2]\cdot DME_{1.1}$, (1.08 g, 3 mmol) in THF (50 cm^3) at −30 °C was added chlorotrimethylsilane (0.70 g, 6.5 mmol) dropwise; the mixture was allowed to warm to room temperature and stirred for 2 h, and the solvent was removed in vacuo at this temperature. The resultant orange solids were extracted with pentane (2 × 25 cm^3) and filtered, and the yellow filtrates were pumped to dryness at 0 °C to afford a yellow semicrystalline mass of **3**. Crude yield 1.0 g (92%). Further purification was hampered by the extreme solubility of **3** and was found to be unnecessary (NMR purity >99%). **3** requires storage under inert atmosphere at 20 °C or below. NMR data (benzene-d_6): ^{1}H, δ 6.76 (d, 2H, ring C*H*, J_{HH} = 4.4 Hz), 6.44 (d, 2H, ring C*H*, J_{HH} = 4.4 Hz), 0.04 (s, 36H, SiC*H*$_3$); ^{13}C{^{1}H}, δ 154.6 (ring *C*), 135.7 (ring *C*H), 126.4 (ring *C*H), 47.8 (ring *C*SiMe$_3$), 0.3 (Si*C*H$_3$). HRMS (EI): 392.221349 (calculated 392.220715).

Synthesis of $C_8H_6(Si^iPr_3\text{-}1,4)_2$, 4. To a stirred solution of $[C_8H_6][Li(DME)]_2$ (2.95 g, 10 mmol) in THF (100 cm^3) at −78 °C was added tri(isopropylsilyl) triflate (6.12 g, 20 mmol) dropwise; the mixture was allowed to warm to 0 °C and the solvent was removed in vacuo at this temperature. The resultant white solids were extracted with pentane (3 × 100 cm^3) and filtered, and the pale yellow filtrates were concentrated and cooled to −40 °C to afford white crystals of **4**. These

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were collected and washed with pentane (2×10 cm^3) at −78 °C. Total yield (two crops) 3.2 g, 77%. **4** is best stored under inert atmosphere at 0 °C or below. Microanalysis (%); found: C, 75.13; H, 11.83. Calculated for $C_{26}H_{48}Si_2$: C, 74.92; H, 11.61. HRMS (EI): 416.330456 (calculated 416.329459). NMR data (benzene-d_6): ^{1}H, δ 6.82 (d, 2H, ring C*H*, $J_{HH} = 4.8$ Hz), 6.65 (d, 2H, ring C*H*, $J_{HH} = 4.8$ Hz), 3.56 (s, 2H, ring C*H*), 1.12 (m, 6H, ^{i}Pr C*H*), 1.08 (d, 18H, ^{i}Pr C*H*$_3$, $J_{HH} = 6.4$ Hz), 1.01 (d, 18H, ^{i}Pr C*H*$_3$, $J_{HH} = 6.4$ Hz); ^{13}C{^{1}H}, δ 153.0 (ring *C*), 134.3 (ring *C*H), 127.9 (ring *C*H), 39.7 (ring *C*HSi^{i}Pr$_3$), 19.3 (^{i}Pr *C*H$_3$), 19.1 (^{i}Pr *C*H$_3$), 12.7 (^{i}Pr *C*H).

Synthesis of [C_8H_4(Si^{i}Pr$_3$-1,4)$_2$][K]$_2$, 5. To a stirred, solid mixture of [C_8H_6(Si^{i}Pr$_3$-1,4)$_2$] (2.08 g, 5 mmol) and [KNH_2] (0.55 g, 10 mmol) in a −78 °C bath was added diethyl ether, precooled to −78 °C, and the mixture was allowed to warm to room temperature overnight. The orange solution was then filtered from small amounts of insoluble material and evaporated to dryness in vacuo to afford tan-colored **5** in essentially quantitative yield. NMR data (benzene-d_6): ^{1}H, δ 6.41 (d, 2H, ring C*H*, $J_{HH} = 3.2$ Hz), 5.80 (d, 2H, ring C*H*, $J_{HH} = 3.2$ Hz), 1.45 (m, 6H, ^{i}Pr C*H*, $J_{HH} = 7.1$ Hz), 1.28 (d, 36H, ^{i}Pr C*H*$_3$, $J_{HH} = 7.1$ Hz); ^{13}C{^{1}H}, δ 139.2 (ring *C*), 121.6 (ring *C*H), 94.1 (ring *C*H), 79.5 (ring *C*Si^{i}Pr$_3$), 20.5 (^{i}Pr *C*H$_3$), 13.6 (^{i}Pr *C*H). Recrystallization of a small sample from benzene at room temperature afforded X-ray quality crystals of **5**·C_6H_6. Microanalysis (%) found: C, 67.52; H, 9.21. Calculated for $C_{26}H_{46}Si_2K_2 \cdot C_6H_6$: C, 67.30; H, 9.18.

X-ray Structure Determination of 5. Crystals of **5** of sufficient quality for single-crystal X-ray determination of the molecular structure were grown from a saturated benzene solution at 20 °C. Data were collected on an Enraf-Nonius Kappa CCD diffractometer from a crystal of dimensions $0.3 \times 0.3 \times 0.2$ mm mounted in oil at 173(2) K. A total of 5864 unique reflections were measured for $2° < 2\theta < 25°$, 3420 reflections with $|F^2| > 2\sigma(F^2)$ being used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04i)^2]^{0.5}/L_p$. The structure was solved by use of SHELXS-86[15] and refined with SHELXL-93.[16] All non-H atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. Interactive graphics and final drawing were obtained with CAMERON.[17] Crystal data are given in Table 2.

Table 2. Crystallographic Details

empirical formula	$C_{32}H_{52}K_2Si_2$	Z	8
crystal system	orthorhombic	density$_{calc}$ (Mg/m^3)	1.14
space group	*Pbcn* (no.60)	radiation [λ (Å)]	Mo−Kα (0.71073)
temp (K)	173 (2)	fw (g/mol)	571.1
a (Å)	11.419(3)	μ (mm^{-1})	0.37
b (Å)	34.713(5)	range 2−2θ (deg)	25
c (Å)	16.858(8)	F(000)	2480
α (deg)	90	R1 [$I > 2\sigma$(I)]	0.060
β (deg)	90	wR2 (all data)	0.144
γ (deg)	90	S	1.023
V (Å^3)	6682(4)		

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Supporting Information Available: NMR spectra for **1**, **2**, and **3**, tables of crystal and intensity data, complete fractional atomic coordinates, interatomic distances and angles, anisotropic thermal displacement parameters, and fully labeled ORTEP figure for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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