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Notes

Synthesis and Structure of Alkali-Metal Triorganozincates

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Summary: The potassium and sodium trialkylzincates $KZn(CH_2CMe_3)_3$ (**1**), $NaZn(CH_2CMe_3)_3$ (**2**), and $KZn(CH_2SiMe_3)_3$ (**3**) were isolated from reactions between the alkali metal and R_2Zn in benzene. The compounds all metalate benzene, and in fact $KZn(CH_2SiMe_3)_2Ph$ (**4**) was isolated during the synthesis of **3**. The crystal structures of **1**-**4** show all four complexes to consist of ZnR_3^- and K^+ or Na^+ ions. Potassium ions in **4** join the ZnR_3^- ions into a polymeric lattice, while **1**-**3** crystallize as discrete dimers. The K^+ ions in **1** are solvated with weakly coordinated benzene, while the Na^+ ions in **2** and the K^+ ions in **3** have weak contacts outside the dimeric unit. Only the Na complex **2** sublimes under vacuum.

Organozinc compounds of the form $MZnR_3$ (M = alkali metal) have been known since 1858, when Wanklyn prepared "sodium ethyl" ($NaZnEt_3$) and "potassium ethyl" ($KZnEt_3$) from a reaction between $ZnEt_2$ and the alkali metal.[2] However, very little has been reported on such compounds since that time.[3] As part of an effort to prepare volatile sodium- and potassium-zinc alkyls, we reexamined this chemistry. Since $NaZnEt_3$ is nonvolatile, we decided to turn to sterically demanding ligands without β-hydrogens, such as neopentyl and (trimethylsilyl)methyl. Such ligands should help to improve thermal stability and reduce intermolecular association, which might allow the complex to sublime before its decomposition temperature is reached.

The reactions between R_2Zn and the alkali metal were conducted in benzene solution or without solvent (eq 1).

$$R_2Zn + \tfrac{2}{3}M \rightarrow \underset{\mathbf{1\text{-}3}}{\tfrac{2}{3}MZnR_3} + \tfrac{1}{3}Zn \qquad (1)$$

$KZn(CH_2CMe_3)_3$ (**1**), $NaZn(CH_2CMe_3)_3$ (**2**), $KZn(CH_2SiMe_3)_3$ (**3**)

Only the Na complex **2** sublimes under vacuum. While **1**-**3** readily dissolve in benzene, they are all insoluble in hexane. This large difference in solubility can be attributed to the ability of benzene to act as a weakly coordinating solvent, as illustrated in the crystal structure of $\mathbf{1}\cdot C_6H_6$ (Figure 1). These trialkylzincates all metalate benzene (eq 2), as evidenced by the growth of a RD peak in NMR samples (in C_6D_6), with the relative order of reactivity being $\mathbf{1} \approx \mathbf{2} \gg \mathbf{3}$.[4] The resulting $MZnR_2Ph$ compounds are substantially less soluble than **1**-**3** and precipitate in the NMR tubes. Crystals of one such compound, $KZn(CH_2SiMe_3)_2Ph$ (**4**), were isolated during the synthesis of **3**. As alkali-metal alkyls are known to metalate benzene, none of this is surprising.[5]

$$MZnR_3 + C_6H_6 \xrightarrow{\Delta} MZnR_2Ph + RH \qquad (2)$$

$KZn(CH_2SiMe_3)_2Ph$ (**4**)

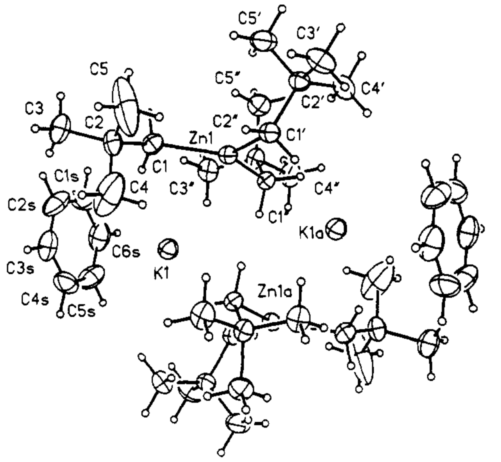

Figure 1. Thermal ellipsoid plot for $\mathbf{1}\cdot C_6H_6$. Atoms with the suffix "a" are symmetry-related atoms via inversion listed in Table II. Other unlabeled atoms are also related by the same symmetry operation.

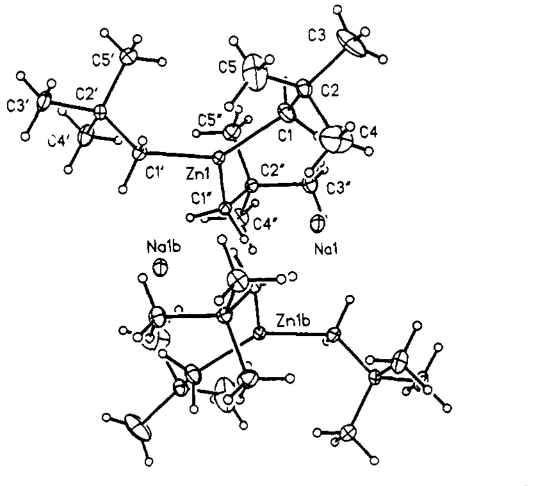

Figure 2. Thermal ellipsoid plot of **2**. Atoms with the suffix "b" and unlabeled atoms are related by an inversion center.

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[1] SFA Inc. employee at the Naval Research Laboratory.

[2] (a) Wanklyn, J. A. *Proc. R. Soc. London* **1858**, 341-345. (b) Wanklyn, J. A. *Justus Liebigs Ann. Chem.* **1858**, 67-79. (c) NMR data for $NaZnEt_3$ have not been previously reported: ^1H NMR δ -0.26 (CH_2, q, $^3J_{HH}$ = 8.05 Hz), 1.55 (CH_3, t); ^{13}C NMR δ 3.89 (CH_2, ^1J = 109 Hz), 13.21 (CH_3, ^1J = 123 Hz).

[3] Rochow, E. G.; Hurd, D. T.; Lewis, R. N. *The Chemistry of Organometallic Compounds*; Wiley: New York, 1957; pp 100-105.

[4] Freshly prepared C_6D_6 solutions of **1**-**3** in NMR tubes were heated at 76 °C for 2 h, resulting in >75% completion for **1** and **2** and very little reaction for **3**. Heating another 111 h brought the reaction with **3** to ~20% completion.

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Table I. Crystal and Refinement Data

formula	$KZnC_{15}H_{33}\cdot C_6H_6$	$NaZnC_{15}H_{33}$	$KZn_{12}H_{33}Si_3$	$KZnC_{14}H_{27}Si_2\cdot(1/x)$solvent
cryst syst	monoclinic	triclinic	monoclinic	trigonal
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$R\bar{3}$
a, Å	9.795 (2)	9.877 (3)	10.106 (2)	30.157 (3)
b, Å	13.382 (3)	10.152 (2)	22.265 (5)	30.157 (3)
c, Å	18.266 (3)	10.285 (4)	10.274 (2)	12.831 (2)
α, deg	90	81.89 (3)	90	90
β, deg	97.97 (2)	75.85 (3)	113.29 (2)	90
γ, deg	90	60.59 (2)	90	120.0
V, Å^3	2371.1 (8)	870.9 (5)	2123.4 (8)	10 106 (3)
Z	4	2	4	18
fw	396.0	301.8	366.1	356^{d}
$F(000)$	856	328	784	3491^{e}
ρ(calc), g cm^{-3}	1.109	1.151	1.145	1.053^{d}
temp, °C	22	−50	−40	22
cryst dimens, mm	0.17 × 0.20 × 0.62	0.14 × 0.26 × 0.64	0.38 × 0.42 × 0.52	0.22 × 0.35 × 0.36
μ, abs coeff, cm^{-1}	12.4	14.5	15.3	42.7
$2\theta_{max}$, deg	45	45	50	115
ω scan speed, deg/min	variable, 5.0–15.0	constant, 15	varible, 10.0–30.0	variable, 5.0–15.0
2θ scan range, deg	$1.8 + \Delta\alpha_1\alpha_2$	$2.0 + \Delta\alpha_1\alpha_2$	$1.8 + \Delta\alpha_1\alpha_2$	$2.0 + \Delta\alpha_1\alpha_2$
data collected, hkl	0–10, 0–14, −19 to 19	−12 to 12, −13 to 13, −13 to 0	−12 to 11, 0–26, 0–12	−32 to 15, 0–32, 0–13
no. of unique data	3125	4022	3744	1907
R_{int}	0.023	0.010	0.011	0.011
no. of unique data, $F_o > 3\sigma(F_o)$	2214	3062	2784	1907
std reflns	2.6% random	2.8% linear decay	6.7% linear decay	2.5% random
no. of params refined	209	173	181	167
R,^{a} R_w,^{b} S^{c}	0.053, 0.051, 1.64	0.056, 0.053, 1.49	0.039, 0.038, 1.23	0.088, 0.074, 1.79
Fourier excursions, e Å^{-3}	0.53, −0.35	1.26, −0.64	0.28, −0.33	0.56, −0.61

[a] $\sum|\Delta|/\sum|F_o|$. [b] $\sum[(w\Delta^2)/\sum(wF_o^2)]^{1/2}$. [c] $[\sum w(\Delta^2)/(N_o - N_p)]^{1/2}$; $w^{-1} = \sigma^2(F_o) + gF_o^2$; $g = 0.000\,23$. [d] Does not include fractional weight of solvate. [e] Includes electron density attributed to solvate.

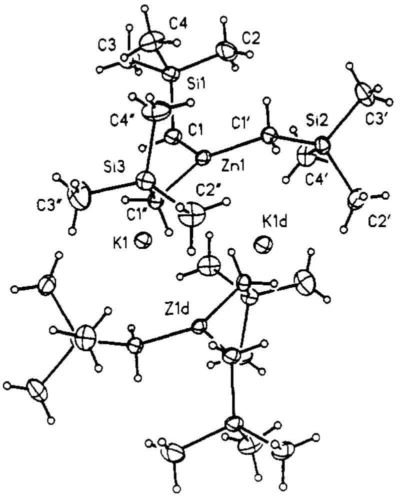

Figure 3. Thermal ellipsoid plot of **3**. K(1)d and Zn(1)d are symmetry-related atoms, as are unlabeled atoms.

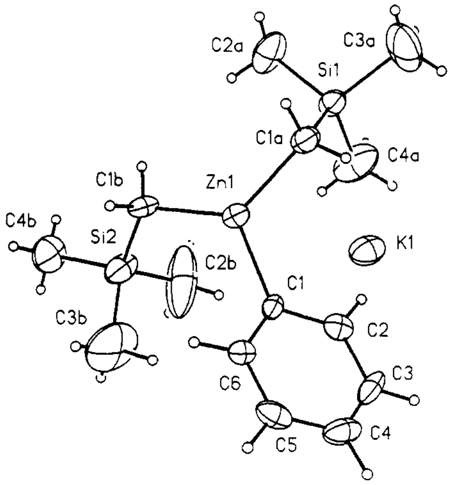

Figure 4. Thermal ellipsoid plot of **4**.

The structural features of these related complexes (Figures 1–4) show a number of similarities. They all share the $\{ZnC_3\}$ moiety in which the bonding environment for Zn is trigonal-planar with average deviations from a least-squares plane for the $\{ZnC_3\}$ plane of 0.026, 0.019, 0.024, and 0.010 Å, respectively, for **1**·C_6H_6 through **4**. In addition, in complexes **1**·C_6H_6, **2**, and **3** there is a common geometry with respect to the alkali-metal cations and the ZnR_3 anions. Each complex is located near an inversion center about which the complexes form "dimers" that are all similarly oriented. The $\{ZnC_3\}$ planes and the planar $\{Zn_2M_2\}$ (M = Na, K) "rings" intersect with dihedral angles of 128.4, 127.8, and 126.6°, respectively. Selected interatomic distances and angles, given in Tables II and III, detail the alkali-metal environment. In **1**·C_6H_6 that environment includes a benzene which is coordinated to the K^+ ion so that within the dimer the K^+ ions are effectively contained by the cage formed by the benzenes and $Zn(CH_2CMe_3)_3^-$ pairs around the inversion center. In complexes **2** and **3** the alkali-metal ions are not as well shielded and the environment sphere[6] includes a contact less than 3.5 Å outside the dimer (Na- - -C = 3.16 Å in **2**, and K- - -C = 3.23 Å in **3**). Other than within the dimer the alkali-metal ions are well separated with the next nearest alkali-metal-ion to alkali-metal-ion separation of K(1)- - -K(1) = 8.97 Å, Na(1)- - -Na(1) = 6.71 Å, and K(1)- - -K(1) = 7.79 Å for **1**·C_6H_6, **2**, and **3**. The smaller size of the Na^+ ion vs that of the K^+ ion results in Na–Zn and Zn–Zn distances shorter than are found in **3** and thus a "tighter" dimer, which may account for the volatility of **2**. Although the K^+ ions in **1**·C_6H_6 are better shielded, easy loss of C_6H_6 under vacuum at room temperature prevents that shielding from enhancing volatility.

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(5) Wardell, J. L. *The Chemistry of the Metal-Carbon Bond*; Wiley: New York, 1987; Vol. 4, pp 35–37.

(6) Does not include H- - -M separations.

Table II. Selected Interatomic Distances (Å) and Angles (deg)

	$1\cdot C_6H_6$	2	3	4
	Bond Distances			
Zn–C(1)	2.045 (6)	2.032 (5)	2.043 (3)	2.06 (1)
Zn–C(1′)	2.069 (6)	2.055 (5)	2.026 (3)	2.03 (1)
Zn–C(1″)	2.107 (5)	2.129 (5)	2.086 (4)	2.04 (1)
$(C–C)_{mean}$	1.51 (4), 1.33 (2)[f]	1.52 (2)		1.38 (2)[f]
$(C–Si)_{mean}$			1.86 (1)	1.81 (3)
Zn- - -X	3.440 (2)	2.894 (3)	3.419 (1)	3.884 (3)
Zn- - -X[e]	3.493 (2)[a]	3.034 (2)[b]	3.328 (1)[c]	3.582 (3)[d]
Zn- - -Zn[e]	4.832[a]	4.399[b]	4.786[c]	4.328[d]
X- - -X[e]	4.973[a]	3.976[b]	4.757[c]	6.091[d]
	Bond Angles			
C(1)–Zn–C(1′)	121.2 (2)	126.0 (2)	123.0 (1)	126.8 (5)
C(1)–Zn–C(1″)	119.5 (2)	118.1 (2)	113.0 (1)	111.6 (4)
C(1″)–Zn–C(1′)	119.0 (2)	115.8 (2)	123.7 (1)	121.7 (5)
$(C–C–C)_{mean}$	109.5 (21), 120.0 (5)[f]	109.3 (36)		120.0 (40)[f]
$(C–Si–C)_{mean}$			109.4 (26)	109.4 (37)
Zn- - -X- - -Zn[e]	88.3	95.8	90.3	
X- - -Zn- - -X[e]	91.7	84.2	89.7	
	Torsion Angles			
C(1)–Zn–C(1′)–C(2′)[Si(2)]	−97.7	92.6	[−59.2]	[138.3]
C(1′)–Zn–C(1″)–C(2″)[Si(3)]	−127.6	131.0	[47.2]	136.3
C(1″)–Zn–C(1)–C(2)[Si(1)]	156.7	−153.9	[121.1]	[117.0]

[a–d] Symmetry operations are as follows: $a = -x, 1.0 - y, 2.0 - z$; $b = c = 1.0 - x, 1.0 - y, 1.0 - z$; $d = 1.0 - x, -y, 2.0 - z$. [e] Symmetry related, X = K or Na. [f] Aromatic.

Table III. Alkali-Metal-Ion Environment (Å)

$1\cdot C_6H_6$		2		3		4	
K(1)–C(1″)[a]	3.093 (6)	Na(1)–C(1″)[b]	2.703 (4)	K(1)–C(1″)	3.150 (4)	K(1)–C(1′)[f]	3.10 (1)
–C(3″)	3.237 (6)	–C(1)	2.841 (6)	–C(1)	3.163 (4)	–C(1″–6″)	3.10 (1)–3.65 (1)
–C(1)	3.240 (6)	–C(1″)	2.848 (4)	–C(1′)[d]	3.180 (4)	–C(1″–6″)[g]	3.21 (1)–3.67 (1)
–C(1′)[a]	3.312 (6)	–Zn(1)	2.894 (2)	–C(1″)[d]	3.184 (4)	–C(1)[f]	3.61 (1)
–C(1″)	3.327 (6)	–C(3″)	2.945 (5)	–C(2″)[d]	3.184 (4)	–C(2)[f]	3.66 (1)
–C(1s–6s)	3.38 (1)–3.79 (1)	–C(1′)[b]	2.973 (5)	–C(3)[e]	3.225 (4)	–Zn(1)	3.884 (3)
–Zn(1)	3.440 (2)	–Zn(1)[b]	3.034 (2)	–C(2′)[d]	3.271 (4)	–Zn(1)[f]	3.583 (3)
–Zn(1)[a]	3.493 (2)	–C(3′)[c]	3.161 (6)	–Zn(1)[d]	3.328 (1)		
–C(4)	3.761 (6)	–C(2″)	3.469 (6)	–Zn(1)	3.419 (1)		

[a–g] Symmetry operations are as follows: $a = -x, 1.0 - y, 2.0 - z$; $b = 1.0 - x, 1.0 - y, 1.0 - z$; $c = x - 1.0, y, z$; $d = 1.0 - x, 1.0 - y, 1.0 - z$; $e = -x, 1.0 - y, -z$; $f = 1.0 - x, -y, 2.0 - z$; $g = {}^2/_3 - x + y, {}^1/_3 - x, {}^1/_3 + z$.

The geometric arrangement of the K cations and the $Zn(CH_2SiMe_3)_2Ph$ anions is substantially different in **4**, where a polymeric geometry is observed with coordination of the K^+ ion to the phenyl ligand and a symmetry-related phenyl ligand along a crystallographic 3-fold screw axis. The K–C distances to the phenyl carbons range from 3.10 (1) to 3.65 (1) Å with a mean of 3.38 Å, and from 3.21 (1) to 3.67 (1) Å with a mean of 3.48 Å to the symmetry-related ligand. The K to ring centroid distances (M1 and M2) are 3.09 and 3.19 Å, respectively, with a M1–K–M2 angle of 106.7° so that the K^+ ions are distributed along a spiral between the phenyls (Figure 5). The K^+ to benzene coordination observed in $1\cdot C_6H_6$ is to a single benzene, where the K–C distances range from 3.38 (1) to 3.79 (1) Å, with a 3.59-Å mean and a K to ring centroid distance of 3.34 Å. While the aromatic to alkali-metal ion coordinations in **1** and **4** differ in geometry, the coordination in both is likely due to induced dipole interactions.[7]

Although uncommon, the K–aromatic coordination in **4** is similar to that observed in $Lu\{CH(SiMe_3)_2\}_3(\mu\text{-}Cl)K(\eta^6\text{-}C_7H_8)_2$[7b] and in the related dimer $[(C_6H_6)_2Ga(GaCl_4)]_2$.[7c] The C_6H_6–K coordination of $1\cdot C_6H_6$ is more common and is similar to the aromatic–K coordination in $K[AlMe_3NO_3]\cdot C_6H_6$[7d] and $K[Al_7O_6Me_{16}]\cdot C_6H_6$.[7e] In these compounds the mean K–C distances are 3.36 and 3.33 Å. The longer 3.59-Å mean in $1\cdot C_6H_6$ is likely due to steric requirements imposed by the bulky CH_2CMe_3 ligands.

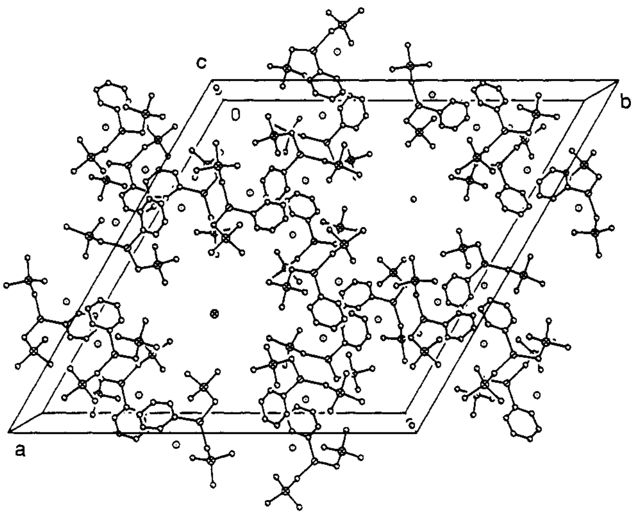

Figure 5. Packing diagram of **4** viewed down the *a* axis.

The trigonal-planar coordination of Zn observed in $1\cdot C_6H_6$ through **4** is also uncommon in that these compounds

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[7] (a) Atwood, J. L.; Newberry, W. R., III. *J. Organomet. Chem.* **1974**, *65*, 145–154. (b) Schaverien, C. J.; van Mechelen, J. B. *Organometallics* **1991**, *10*, 1704–1709. (c) Schmidbaur, H.; Thewalt, U.; Zafiropoulos, T. *Organometallics* **1983**, *2*, 1550. (d) Atwood, J. L.; Crissinger, K. D.; Rogers, R. D. *J. Organomet. Chem.* **1978**, *155*, 1–14. (e) Atwood, J. L.; Hrncir, D. C.; Priester, P. D.; Rogers, R. D. *Organometallics* **1983**, *2*, 985–989. (f) Atwood, J. L.; Seale, S. K. *J. Organomet. Chem.* **1976**, *114*, 107–118.

contain planar $\{ZnC_3\}$ moieties for which structural parameters have not previously been reported.[8] In trigonal-planar Zn complexes containing (<3) Zn–C bonds,[9] these distances are in the range 1.94–2.00 Å. The Zn–C distances here are nearly equal in **4** but unequal in **1**·C_6H_6, **2**, and **3** with differences of 0.062, 0.097, and 0.060 Å. The range of distances is 2.026–2.129 Å, longer than in the trigonal complexes but within the range Zn–C = 1.98–2.17 Å observed in four-coordinate Zn complexes.[10] Other bond distances and angles in **1**·C_6H_6 through **4** are normal, as are intermolecular distances. In **4**, however, there is a solvent channel with an approximately 8.0-Å diameter in which the unidentified and disordered solvate or solvates are present at partial occupancy.

Table IV. Atomic Coordinates (×10⁴) for 1•C_6H_6 and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	*y*	*z*	*U*(eq)[a]
K(1)	752 (1)	4285 (1)	8865 (1)	78 (1)
Zn(1)	−534 (1)	6549 (1)	9343 (1)	56 (1)
C(1)	−630 (6)	6365 (5)	8226 (3)	74 (2)
C(2)	−1947 (6)	6221 (5)	7678 (3)	78 (2)
C(3)	−1717 (7)	6193 (6)	6880 (3)	118 (3)
C(4)	−2559 (11)	5266 (9)	7825 (5)	286 (4)
C(5)	−2932 (11)	6985 (10)	7743 (5)	332 (4)
C(1′)	−2124 (5)	7225 (4)	9795 (3)	66 (2)
C(2′)	−1938 (6)	8327 (4)	10014 (3)	65 (2)
C(3′)	−3291 (6)	8787 (5)	10173 (4)	106 (3)
C(4′)	−879 (7)	8446 (5)	10695 (3)	93 (2)
C(5′)	−1457 (7)	8904 (5)	9385 (4)	107 (3)
C(1″)	1300 (5)	6190 (4)	10040 (3)	56 (2)
C(2″)	2691 (5)	6543 (5)	9838 (3)	65 (2)
C(3″)	3089 (6)	6003 (5)	9169 (3)	85 (2)
C(4″)	3855 (6)	6367 (5)	10477 (3)	90 (2)
C(5″)	2602 (6)	7660 (5)	9664 (4)	89 (2)
C(1S)	2982 (11)	4649 (7)	7347 (5)	129 (3)
C(2S)	1680 (11)	4503 (8)	6991 (5)	130 (3)
C(3S)	1075 (8)	3640 (9)	7055 (4)	114 (3)
C(4S)	1724 (11)	2926 (7)	7462 (5)	116 (3)
C(5S)	2998 (11)	3068 (8)	7804 (5)	123 (3)
C(6S)	3607 (9)	3928 (10)	7750 (5)	129 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Atomic Coordinates (×10⁴) for 2 and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	*y*	*z*	*U*(eq)[a]
Na(1)	6962 (2)	4225 (2)	5715 (2)	43 (1)
Zn(1)	4128 (1)	3921 (1)	6765 (1)	25 (1)
C(1)	5968 (6)	2409 (5)	7637 (5)	47 (2)
C(2)	6945 (5)	715 (5)	7434 (5)	36 (2)
C(3)	7952 (9)	−143 (7)	8437 (7)	99 (3)
C(4)	8221 (8)	529 (8)	6140 (7)	104 (3)
C(5)	6089 (9)	−1 (7)	7102 (9)	117 (3)
C(1′)	2540 (5)	3485 (5)	6186 (4)	32 (2)
C(2′)	1009 (5)	3812 (5)	7236 (4)	31 (2)
C(3′)	85 (6)	3139 (6)	6807 (5)	47 (2)
C(4′)	−62 (6)	5507 (5)	7388 (6)	52 (2)
C(5′)	1413 (6)	3092 (6)	8578 (5)	55 (2)
C(1″)	3660 (5)	6215 (4)	6557 (4)	26 (2)
C(2″)	3690 (5)	6933 (5)	7767 (4)	29 (2)
C(3″)	5390 (5)	6366 (5)	7929 (5)	42 (2)
C(4″)	2915 (6)	8651 (5)	7590 (5)	47 (2)
C(5″)	2765 (6)	6549 (6)	9042 (5)	47 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Experimental Section

General Comments. All manipulations were performed under vacuum or under an inert atmosphere (He) using a Vacuum Atmospheres Dri-Lab. All solvents were distilled from $NaOCPh_2$ prior to use. Zinc chloride was purified by vacuum sublimation, and Me_3CCH_2Cl (Lancaster Synthesis) was vacuum-distilled from P_2O_5. All other reagents were used as received. The zinc alkyls $Zn(CH_2CMe_3)_2$ and $Zn(CH_2SiMe_3)_2$ were prepared by literature procedures.[11] NMR spectra were obtained on C_6D_6 solutions using a Bruker MSL-300 instrument. Elemental analyses were performed by E+R Microanalytical Laboratory Inc., 96-34 Corona Ave., Corona, NY 11368.

$KZn(CH_2CMe_3)_3$ (1). Freshly cut K (0.123 g, 3.14 mmol), $Zn(CH_2CMe_3)_2$ (1.00 g, 4.81 mmol), and C_6H_6 (10 mL) were mixed in an H-tube equipped with a stirbar, Kontes valves, and a fine frit. After it was stirred for 1 day, the black mixture was filtered and washed with benzene. Some of the finely divided zinc produced in the reaction passed through the frit. The solvent was removed under vacuum, affording crude **1** in 86% yield. Material was recrystallized by dissolving in benzene and adding hexane. The colorless crystals were washed with hexane and dried under vacuum, during which time they turned opaque (0.18 g isolated); the crystals used for the structure determination were not dried. Data for **1**: ^1H NMR δ 1.39 (Me), 0.09 (CH_2, br); $^{13}C\{^1H\}$ NMR δ 36.43 (Me), 40.74 (CH_2); mp 154–162 °C dec. Anal. Found (calcd) for $C_{15}H_{33}KZn$: C, 57.08 (56.67); H, 10.19 (10.46); K, 12.25 (12.30); Zn, 20.39 (20.57).

$NaZn(CH_2CMe_3)_3$ (2). Sodium chunks (0.0733 g, 3.19 mmol), $Zn(CH_2CMe_3)_2$ (0.99 g, 4.76 mmol), and C_6H_6 (5 mL) were mixed in an H-tube as before. The mixture was heated with a heat gun until the sodium started to melt and then stirred at room temperature for 2 days and filtered. The solvent was removed from the filtrate in vacuo, and the residue was dissolved in warm benzene and this solution layered with hexane. An isolated yield of 0.34 g (35%) of the colorless crystals was obtained. Data for **2**: ^1H NMR δ 1.32 (Me), 0.14 (CH_2): $^{13}C\{^1H\}$ NMR δ 36.22 (Me), 38.17 (CH_2); sublimation point 100 °C; mp 146–157 °C dec. Anal. Found (calcd) for $C_{15}H_{33}NaZn$: C, 59.91 (59.70); H, 10.95 (11.02); Na, 7.72 (7.62).

Reactions between K and $Zn(CH_2SiMe_3)_2$. (a) Potassium (0.11 g, 2.8 mmol), $Zn(CH_2SiMe_3)_2$ (1.00 g, 4.17 mmol), and C_6H_6 (3 mL) were mixed in an H-tube, heated with a heat gun to dislodge potassium from the walls of the flask, and stirred at room temperature for 24 h. After filtration and removal of solvent, the residue was dissolved in ~2 mL of C_6H_6 and layered with hexane. The system formed two layers, from which crystals deposited over several weeks. The first crop (0.10 g) (mixture of **3** and **4**) was covered with a sticky substance that was removed by washing with a 1:2 benzene/hexane mixture. The second crop of crystals formed from the mother liquor of the first (0.25 g). A third crop (0.13 g) consisted only of large, well-formed colorless crystals of **3**. The crystals used for the structure determination of **3** and **4** came from the third and first crops, respectively. Data for **3**: mp 94–96 °C; dec pt 160 °C (under He) and only slightly above melting point (in vacuo); ^1H NMR δ 0.41 (Me), −1.15 (CH_2); $^{13}C\{^1H\}$ NMR 4.41 (CH_2), 5.46 (Me). Anal. Found (calcd) for $C_{12}H_{33}Si_3KZn$: C, 39.00 (39.37): H, 9.06 (9.08); K, 10.93 (10.68).

(b) Potassium (0.075 g, 1.9 mmol), $Zn(CH_2SiMe_3)_2$ (0.68 g, 2.8 mmol), and C_6H_6 (7 mL) were stirred in an H-tube for 1 day and stirred at 75 °C for another day. After filtration, the solvent was removed in vacuo and the resulting residue was recrystallized from a hot hexane/xylene mixture. The off-white crystals were washed with a benzene/hexane mixture, dried in vacuo, and identified as $KZn(CH_2SiMe_3)_2Ph$ (**4**; 0.10 g, 15%). Data for **4**: mp 115–139

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Table VI. Atomic Coordinates (×10^4) for 3 and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)^a
K(1)	3378 (1)	4396 (1)	3145 (1)	57 (1)
Zn(1)	3512 (1)	5868 (1)	4138 (1)	42 (1)
Si(1)	922 (1)	6313 (1)	1217 (1)	52 (1)
Si(2)	6145 (1)	6815 (1)	4075 (1)	54 (1)
Si(3)	2954 (1)	5560 (1)	7056 (1)	57 (1)
C(1)	2172 (4)	5696 (2)	2084 (3)	54 (2)
C(2)	1803 (6)	6923 (2)	634 (5)	98 (3)
C(3)	−642 (4)	6041 92)	−394 (4)	73 (2)
C(4)	144 (5)	6644 (2)	2423 (5)	92 (2)
C(1′)	4755 (4)	6614 (2)	4734 (4)	50 (2)
C(2′)	7980 (4)	6569 (2)	5319 (5)	86 (2)
C(3′)	6252 (6)	7641 (2)	3828 (6)	94 (3)
C(4′)	5824 (5)	6456 (2)	2333 (5)	84 (2)
C(1″)	3300 (4)	5247 (2)	5564 (3)	49 (1)
C(2″)	4672 (5)	5677 (2)	8641 (4)	85 (2)
C(3″)	1811 (7)	5065 (3)	7641 (6)	112 (4)
C(4″)	2053 (6)	6303 (2)	6592 (6)	98 (3)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Atomic Coordinates (×10^4) for 4 and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)^a
K(1)	4048 (1)	−247 (1)	11261 (2)	86 (2)
Zn(1)	4761	238	8622	65 (1)
Si(1)	4414 (1)	−940 (1)	7838 (3)	80 (2)
Si(2)	5255 (2)	1152 (2)	6910 (3)	112 (3)
C(1″)	4251 (4)	412 (4)	9276 (7)	52 (5)
C(2″)	3724 (4)	72 (4)	9202 (7)	66 (6)
C(3″)	3361 (4)	145 (5)	9740 (9)	89 (7)
C(4″)	3508 (6)	537 (5)	10411 (10)	98 (9)
C(5″)	4020 (6)	886 (5)	10481 (8)	85 (7)
C(6″)	4373 (4)	816 (4)	9920 (8)	66 (6)
C(1)	4574 (4)	−503 (4)	8938 (8)	80 (6)
C(1′)	5377 (3)	765 (4)	7800 (7)	71 (6)
C(2)	4996 (4)	−790 (5)	7118 (9)	142 (8)
C(3)	4140 (6)	−1619 (5)	8247 (14)	212 (10)
C(4)	3937 (5)	−927 (6)	6993 (10)	170 (10)
C(2′)	4709 (6)	775 (8)	6152 (14)	355 (12)
C(3′)	5080 (8)	1564 (8)	7599 (14)	335 (13)
C(4′)	5784 (5)	1560 (5)	6046 (10)	141 (9)
Sol(1)	3333	−3333	6667	300
Sol(2)	3333	−3333	1667	300
Sol(3)	3333	−3333	4947 (35)	300
Sol(4)	3333	−3333	147 (40)	300

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

°C dec; ^{1}H NMR δ 0.39 (s, Me), −0.94 (s, CH_2), 7.01, 7.17, 7.74 (m, Ph); $^{13}C\{^1H\}$ NMR 3.12 (br, CH_2), 4.32 (Me), 125.5, 127.7, 139.5 (Ph). Anal. Found (calcd) for $C_{14}H_{27}Si_2KZn$: C, 47.32 (47.23); H, 7.79 (7.64); K, 11.10 (10.98).

(c) Stirring potassium (0.108 g, 2.76 mmol) and $Zn(CH_2SiMe_3)_2$ (0.95 g, 3.96 mmol) under 1 atm of He in a Pyrex tube for 1 day resulted in a black coating on the potassium. The reaction became rapid as soon as the temperature was raised above the melting point of potassium, and the mixture was stirred for 20 min at 95 °C. The gray solid was mixed with benzene, the mixture was filtered, and the filtrate was reduced in vacuo to a yellow gum, which slowly crystallized. NMR spectroscopy showed **3** only.

Crystallographic Studies on 1–4. Suitable crystals were mounted in thin-walled glass capillaries. Data collection for all four structures utilized automated Siemens R3m/V diffractometers with incident-beam graphite monochromators. Mo Kα (λ = 0.710 73 Å) radiation was used for **1**·C_6H_6 through **3** and Cu Kα (λ = 1.541 78 Å) radiation for **4**. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on the ϕ dependence of 10–12 reflections with χ ca. 90° were applied. Maximum and mininum transmissions were 0.62 and 0.43, 0.98 and 0.80, 0.89 and 0.82, and 0.75 and 0.38, respectively, for **1**·C_6H_6 through **4**. Space group determinations were based on extinctions present and confirmed by the structure solutions. In each case the structures were determined by direct methods and refined using full-matrix least-squares methods as implemented by the program SHELEXTL.[12] In all structures the parameters refined included the coordinates and anisotropic thermal parameters for all but the hydrogen atoms. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å), and the coordinate shifts for carbon were applied to the bonded hydrogens. In **2** and **3** methyls were treated as rigid groups and allowed to rotate. In all cases the isotropic thermal parameters for the hydrogens were fixed. In **4** the solvate is disordered and is present in only partial occupancy. No identification of the solvate could be made, and only electron density as a fraction of carbon on the $\bar{3}$ axis was included, although the space available could accommodate hexane or benzene. Additional data collection and refinement parameters are given in Table I. Thermal ellipsoid plots in Figures 1–4 are drawn at the 20% probability level.

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Registry No. **1**·C_6H_6, 140411-47-8; **2**, 140411-48-9; **3**, 140411-49-0; **4**, 140411-50-3; $Zn(CH_2CMe_3)_3$, 54773-23-8; $Zn(CH_2SiMe_3)_2$, 41924-26-9.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates for **1**·C_6H_6, **2**, **3**, and **4** (16 pages). Ordering information is given on any current masthead page.

OM910792T

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Photoactivated Gas-Phase Ligand Switching

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Summary: The photoinitiated ligand-switching reaction of $VC_6H_6^+$ with CH_3CN at 604 nm to generate VCH_3CN^+ is reported. Photodissociation measurements indicate the reaction proceeds on a single minimum potential surface with an endothermic activation barrier.

Condensed-phase ligand photosubstitution reactions have been examined in great detail.[1-4] The vast majority of these reactions proceed by dissociative mechanisms

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