To prove the stereochemistry which has been drawn for these products, a chemical correlation with cytochalasin D has been performed. The details are described in the supplementary material, but the key experiments involve ozonolysis, $NaBH_4$ reduction, and acylation of **18**, the diastereomer pair **20** (derived from **6**), and **21** (derived from natural **1**). This degradation sequence converts **20** into two isomeric tetraacetates, **22** and **23**. Similar degradation of **21** affords **23** while synthetic **18** gives **22**. These results prove that isoindolone Diels–Alder stereochemistry is correct and is retained to the end of our synthesis.

In conclusion, we have developed an approach for synthesis of the zygosporin G–cytochalasin D ring systems, 3% overall from succinimide. Subsequent papers will deal with 11-membered ring stereochemistry and functionality.

Acknowledgment. This work was supported by the National Institutes of Health (CA 17918).

Registry No. 1, 22144-77-0; **1**-6-en-12-ol (7-dehydroxy), 83071-41-4; **1**-6-enal (7-dehydroxy), 90741-92-7; **2**, 25374-69-0; (±)-**3**, 90741-72-3; (±)-**4**, 90741-73-4; **5**, 90741-74-5; (±)-**6**, 90741-75-6; (±)-**7**, 90741-76-7; (±)-**8**, 90741-77-8; (±)-**9** (isomer 1), 90741-78-9; (±)-**9** (isomer 2), 90741-79-0; (±)-**10**, 90741-80-3; (±)-**11**, 90741-81-4; (±)-**12**, 90741-82-5; (±)-**14** (isomer 1), 90741-83-6; (±)-**14** (isomer 2), 90821-11-7; (±)-**15**, 90741-84-7; (±)-**16**, 90741-85-8; (±)-**17**, 90741-86-9; (±)-**18**, 90741-87-0; (±)-**19**, 90741-88-1; (±)-**20**, 90741-89-2; **21**, 90865-40-0; (±)-**21**, 90762-73-5; (±)-**22**, 90741-90-5; (±)-**23**, 90741-91-6; PhC(O)-CH_2SH, 2462-02-4; 2-(*tert*-butyldimethylsiloxy)-1,3-butadiene, 80738-05-2; (±)-(3α,3aα,4β,7β,7aα)-2-benzoyl-3-benzyl-4-methyl-5-[(trimethylsilyl)methyl]-7-(3-hydroxyprop-1(*E*)-enyl)-7a-[(chloromethyl)carbonyl]-1,3,3a,4,7,7a-hexahydroisoindol-1-one, 90741-93-8; (±)-(3α,3aα,4β,7β,7aα)-2-benzoyl-3-benzyl-4-methyl-5-[(trimethylsilyl)methyl]-7-(3-acetoxyprop-1(*E*)-enyl)-7a-[(chloromethyl)carbonyl]-1,3,3a,4,7,7a-hexahydroisoindol-1-one, 90762-74-6; (±)-(3α,3aα,4β,7β,7aα)-2-benzoyl-3-benzyl-4-methyl-5-[(trimethylsilyl)methyl]-7-(3-acetoxyprop-1(*E*)-enyl)-7a-[(acetoxymethyl)carbonyl]-1,3,3a,4,7,7a-hexahydroisoindol-1-one, 90741-94-9.

Supplementary Material Available: NMR data for key intermediates and correlation schemes (6 pages). Ordering information is given on any current masthead page.

A Remarkable Alkali-Metal-Centered Zirconium Cluster in Potassium Hexazirconium Tetradecaiodide ($Zr_6I_{14}K$): Synthesis and Characterization

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Synthetic efforts to identify important products in the reactions of zircaloy (~98% Zr) cladding with prominent fission products have led to the discovery of two zirconium iodides containing octahedral metal clusters, purportedly Zr_6I_{12} and $CsZr_6I_{14}$.[2-4] The generally low yield of these products led us to attempt syntheses of the ternary phase utilizing other alkali metals. Reaction of KI, ZrI_4, and Zr metal resulted in a product with powder pattern closely resembling that of $CsZr_6I_{14}$ but, surprisingly, with larger lattice parameters. Subsequent studies indicate this compound is the first example of an unprecedented configuration, an octahedral metal cluster the center of which is occupied by an alkali metal, namely, $Zr_6I_{14}K$. The single-crystal X-ray diffraction results, electron microprobe analysis, magnetic susceptibility data, photoelectron spectroscopic measurements, and extended Hückel calculations on this novel cluster are reported here.

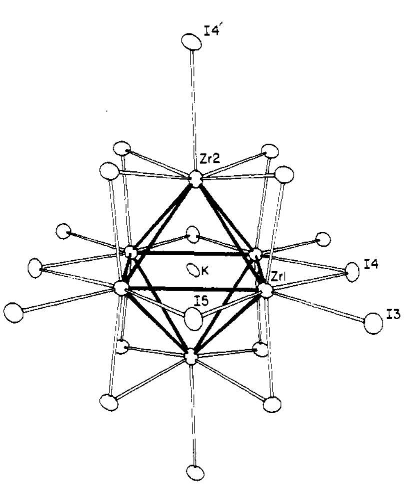

Figure 1. $Zr_6I_{14}K_{1.0}$ cluster with all exo iodines (50% thermal ellipsoids). A C_{2h} symmetry results from a 2-fold axis that passes through I5 and K together with a mirror plane that contains atoms K, I4, and Zr2.

Table I. Comparison of Important Bond Distances (Å) in $CsZr_6I_{14}$, $Zr_6I_{14}K$, and $Zr_6I_{14}K_{0.46}$

		$CsZr_6I_{14}$[a]	$Zr_6I_{14}K$	$Zr_6I_{14}K_{0.46}$
Zr–Zr	interlayer[b]			
	Zr1–Zr1	3.350 (3)	3.494 (3)	3.478 (3)
	Zr1–Zr2 (×2)	3.286 (2)	3.427 (2)	3.408 (3)
	interlayer			
	Zr1–Zr1	3.343 (3)	3.462 (3)	3.447 (3)
	Zr1–Zr2 (×2)	3.298 (2)	3.436 (2)	3.424 (3)
$Zr–I^{a-i}$[c]	Zr2–I4	3.494 (3)	3.408 (2)	3.377 (2)
$Zr–I^a$	Zr1–13	3.186 (2)	3.124 (2)	3.118 (2)
Zr–K	Zr1–K (×4)		2.460 (1)	2.448 (2)
	Zr2–K (×2)		2.393 (2)	2.382 (3)
$Zr–I^i$(av)		2.884 (2)	2.898 (2)	2.883 (2)

[a] Reference 3. [b] The structure can be described as layered perpendicular to [001], this direction lying approximately from lower left to upper right in Figure 1. [c] Superscripts on I refer to bridging functions (i = inner, edge bridging within cluster; a = outer or exo, bridging between clusters).

Sublimed KI, ZrI_4 (K:I, 1:14), and a large excess of reactor-grade Zr strips were sealed in a tantalum container and heated for 4–6 weeks in a 840–860 °C gradient. The air-sensitive product (10–20% yield) grew as clumps of shiny black gems on the zirconium in the hot end of the container. The clumps were visually separated from the remaining reaction products, α-ZrI_2, β-ZrI_2,[5] ZrI_3, and unreacted KI.

Pertinent X-ray data for two single crystals studied together with those for $CsZr_6I_{14}$ are available as supplementary material. Intensities for two octants were measured by using a four-circle automated diffractometer. The data were corrected for absorption effects by a method previously described.[3] With $Zr_6I_{14}K$, a peak ($Z \sim 18$) was observed in the center of the cluster in an electron density map ($R = 14.0\%$) and a potassium atom was included in the model at that position. The refinement proceeded smoothly ($R = 4.5$, $R_w = 6.3\%$) with all atoms refined anisotropically and with a potassium occupancy of 1.05 (3). The position of cesium in $CsZr_6I_{14}$ within an iodine polyhedron was empty. Subsequent reactions also formed $Zr_6I_{14}K$-type phases with somewhat smaller cell parameters, and refinement ($R = 5.8$, $R_w = 8.1\%$) of occupancy and anisotropic thermal parameters (but with K isotropic) led to an X-ray stoichiometry of $Zr_6I_{14}K_{0.46(2)}$.

The $Zr_6I_{14}K_x$ structure is isostructural with Nb_6Cl_{14} and Ta_6I_{14}[6,7] as well as $CsZr_6I_{14}$ (excluding the Cs and K positions). A view of the isolated potassium cluster along with iodine atoms

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[1] Operated for the U. S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

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[4] Occupation of the centers of the octahedral clusters in these compounds by light nonmetals has been suggested previously[3] and is under investigation.

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that are shared between it and other clusters is shown in Figure 1. The rather complex connectivity between clusters that goes with the stoichiometry has been described previously.[3,6,7] This connectivity results in a compression of the zirconium octahedron along a pseudo-4-fold axis as noted in $CsZr_6I_{14}$. A noteworthy difference between the $Zr_6I_{14}K$ and $CsZr_6I_{14}$ structures is the markedly longer Zr–Zr bond distances and the shorter $Zr–I^a$ distances in the former (see Table I) that result from the overall expansion of the Zr_6 octahedron necessary for inclusion of the potassium. The zirconium–potassium separation, 2.44-Å average, is remarkably close to the sum of their six-coordinate crystal radii, 2.38 Å.[8]

Because of the unusual nature of a potassium atom within a cluster, some additional measurements have been made. An electron microprobe analysis of single crystals of the X-ray sample $Zr_6I_{14}K_{1.0}$ showed only K, Zr, and I, excluding the possibility of a heavy nonmetal occupying the K position, and quantitization of the microprobe results gave a composition very consistent with the X-ray formulation. Magnetic susceptibilities of the $Zr_6I_{14}K_{0.46}$ sample measured on a Faraday balance yielded a Curie–Weiss behavior from 298 to 100 K, with $\mu_{eff} = 0.82\ (1)\ \mu_B$ and $\chi_{mol} = 2.71 \times 10^{-4}$ emu/mol at 298 K (corrected for temperature-independent terms). This result is very consistent with the presence of an average of ~0.5 unpaired electron per cluster.

In an attempt to understand the bonding and stability of these unusual clusters, extended Hückel calculations[9] have been carried out on three models of isolated clusters with added exo iodine atoms to correctly reproduce the local environment: $Zr_6I_{18}^{5-}$ with Zr and I positions from $CsZr_6I_{14}$, $Zr_6I_{18}^{5-}$ with Zr and I positions from $Zr_6I_{14}K$ (K^+ removed), and $Zr_6I_{18}K^{4-}$. The results suggest that the stability of the cluster results in part from improved Zr–I bonding that compensates for the loss of Zr–Zr bonding upon expansion of the cluster plus some small but significant bonding interactions of the K 3s and 3p orbitals with both Zr–Zr bonding orbitals and, to a lesser extent, low-lying I orbitals. Of course, the K–Zr interaction is not so unusual if viewed as intermetallic-like. The increased Zr–I bonding mentioned above arises not only from shorter $Zr–I^a$ distances but also from improved $Zr–I^i$ overlap as the Zr atoms are pushed toward their "ideal" positions in a square plane of inner iodines (see Zr2 in Figure 1). Calculations using an iterative, extended Hückel program[10] give a charge on the potassium of +0.4. Although this is probably not of high numerical accuracy, it is lower than one might expect to find in an ionic salt of potassium. A significant shift of the core binding energy of potassium to a lower value in such an electron-rich environment was first considered possible. Careful measurements in fact showed an opposite shift of 0.4 eV in $Zr_6I_{14}K$ vs. K_2ZrI_6 (relative to the internal iodine standard), presumably because of the unusual coulombic effect that a somewhat positive zirconium cluster would have on ionization of the enclosed potassium compared with potassium surrounded by iodide ions in K_2ZrI_6.

Similar reactions of NaI or LiI with ZrI_4 metal also give small yields of $Zr_6I_{14}K$-type phases with lattice parameters that are also larger than those of $CsZr_6I_{14}$ and decrease in magnitude for the series K, Na, Li. Presumably these phases also contain the alkali metal within the cluster, but this has not yet been confirmed by single-crystal studies. Smaller lattice constants for the rubidium product suggest a more normal, cesium-like structure.

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Supplementary Material Available: Pertinent crystal data and a listing of positional and thermal parameters for $Zr_6I_{14}K$ and $Zr_6I_{14}K_{0.46}$ (2 pages). Ordering information is given on any current masthead page.

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Methane Dication as Reagent? Cation-Substituted Methonium Ions, CH_4X^{2+}

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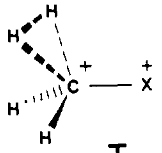
CH_6^{2+}, the parent *hexacoordinate* carbodication, is a minimum on the potential energy surface and awaits experimental verification.[1] We demonstrated by ab initio molecular orbital theory that CH_6^{2+} may result from the exothermic reaction of CH_4^{2+} with H_2.[1] This is in particular of interest, because the trivalent *tetracoordinate* CH_4^{2+} dication has been observed by charge-stripping mass spectrometry, with a minimal lifetime of 3 μs.[2] For this reason and in light of the recent experimental[3] and theoretical[4] interest in dications, we were intrigued to further explore the reactivity behavior of CH_4^{2+}. Here we address the interaction of CH_4^{2+} with CO, NH_3, N_2, and OH_2 by ab initio theoretical methods. Additional impetus for the present study comes from the recognition that the formed species (CH_4X^{2+}) represents a new class of hypercoordinate dication I.



X = CO, NH_3, N_2, OH_2

I

The ab initio calculations for CH_4CO^{2+}, $CH_4NH_3^{2+}$, $CH_4N_2^{2+}$, $CH_4OH_2^{2+}$, their dissociative products (deprotonation and dehydrogenation), and some of their isomers were performed within the Hartree–Fock limit with geometries optimized at the 3-21G and 6-31G* levels (Table I).[5,6] All species reported are equi-

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