indicate clearly that photolytic conversions of **1** to **6** and to **4** and **5** can not involve total transformation to the intermediates (such as **7–9**) formed in thermolysis. Principal formation of **6** by photolysis may thus involve direct or ylidic attack of carbene **12a–12b**, cations **14** and **15**, or/and excited **1** on the hydroxyl groups of the alcohols. The photochemical oxidation–reduction products (**5** and **4**) are minor, and their origins, be they homolytic, cationic, and/or carbenic (singlet or triplet), are as yet totally speculative.

Decomposition of **2** also results in **12a–12b** which inserts in part into the C–H bonds of alcohols. Thus photolysis of **2** at 10–20 °C in ethanol gives **10b** (3%), **11b** (13%), **4** (60%), **5b**, and **6b** (39%). Further, irradiation of **2** in methanol yields **10a** (20%), **4**, **5a**, and **6a**. These results are of possible further significance in that they indicate that decomposition of appropriate triazenes with loss of nitrogen and amines may serve as convenient sources of carbenes.

2,5-Diphenyl-4*H*-imidazolylidene (**16**), generated thermally from **3** at 60 °C, behaves impressively in reactions with C–H bonds. Thus decomposition of **3** in cyclohexane and in benzene yields **17a** (60%) and **17b** (72%),[13] respectively. Of particular
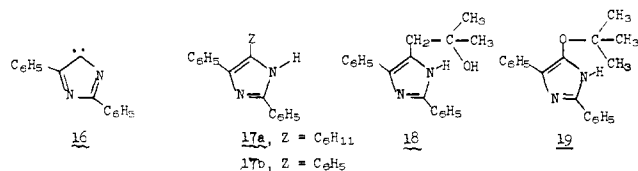
interest is that **3** is converted preparatively by 2-methyl-2-propanol to **18** (80%) and **19** (20%); formation of **18** is the first example of thermal decomposition of a diazo compound in an alcohol resulting in intermolecular C–H penetration. Insertion into the C–H bonds of alcohols by appropriate carbenes appears to be of considerable synthetic promise. It is likely that such reactions will be of advantage with carbenes (and diazo compounds) of limited nucleophilicities and with alcohols which are poor proton donors.

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(2) (a) Decomposition of diazomethane in 2-propanol in sunlight gives mainly methyl 2-propyl ether; 2-butanol and 2-methyl-2-propanol are minor products.[2d] (b) Photolyses of ethyl diazoacetate in methanol and in 2-propanol yield ethyl 3-hydroxypropanoate[2e] (trace) and ethyl 3-hydroxy-3-methylbutanoate (9%),[21] respectively, along with Wolff rearrangement products. (c) In gas phase photolysis of diazomethane in *tert*-butyl alcohol, the reactivity of the O–H bond of the alcohol is 10.9 ± 0.5 times that of any of its single C–H bonds.[2g] (d) H. Meerwein, H. Rathjen, and H. Werner, *Chem. Ber.*, **75**, 1610 (1942). (e) H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *J. Am. Chem. Soc.*, **90**, 4088 (1968). (f) O. P. Strausz, T. DoMinh, and H. E. Gunning, *ibid.*, **91**, 1261 (1969). (g) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 897 (1967).
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(4) (a) Diazoimidazoles **1** and **3** (1.0 g, respectively) were thermolyzed in the various solvents (550 mL) until nitrogen evolution was complete. (b) The products were separated and analyzed by reverse phase, liquid chromatography from aqueous solution on a Bondapak C-18 column (4 ft × ⅜ in., Waters Associates). (c) 2-Azahypoxanthine[1a] was not found in the various reaction mixtures. (d) The products were assigned from their elemental analyses and/or exact masses, NMR (D₂O) and IR spectra, and melting points and by comparison with literature values.
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(7) Photolyses of **1** (1.0 g, respectively) in solvents (550 mL) under nitrogen were effected in Pyrex with a 450-W medium-pressure Hanovia lamp.
(8) (a) The C–H insertions appear subject to statistical steric factors; the conversions to **6** also correlate with the proton donor abilities of the alcohols. (b) 4(5)-[2-(2-Hydroxypropyl)]imidazole-5(4)-carboxamide was not detected.
(9) 1,5-Sigmatropic rearrangements of **13** are allowed.
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(11) Benzylidene[3] and phenyl(ethylphosphonyl)carbene[3] are presumed to insert into the C–H bonds of alcohols in matrix at −110 to −196 °C by triplet abstraction–recombination mechanisms upon repression of the singlet ylidic reactions of the carbenes at the O–H groups. We should like to add that the C–H insertions of alcohols may become prominent because at these temperatures the proton-donor activities of the carbinols are greatly depressed and conversions of the carbenes to their carbonium ions are significantly retarded.
(12) (a) Protonation of **12a–12b** at its carbenic center will also yield a highly energetic cation. (b) **12a–12b** is expected to be very electrophilic because of the 6π-electron character of its imidazole ring, the inductive effect of its ring nitrogens, and the electron withdrawal of its carboxamido group.
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Uan G. Kang, Harold Shechter*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
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Metal–Metal Bonded Clusters in Transition Metal Groups 3 and 4. Synthesis and Structure of Three M₆X₁₂-Type Clusters for Scandium and Zirconium

Sir:

Knowledge of halogen-containing clusters of the types $M_6X_{12}^{n+}$ and $M'_6X_8^{m+}$ (X = Cl, Br, I) has been substantially limited to the well-known examples from group 5 for M = Nb and Ta and n = 2, 3, and 4, and to group 6, M′ = Mo and W and m = 4 principally, together with a few smaller clusters for such elements as rhenium.[1,2] There have been no previous reports of either examples containing fewer than the 14 to 16 bonding electrons per M_6 group or discrete clusters of any sort containing elements earlier in the transition block than group 5. Results reported here for scandium and zirconium suggest that the scarcity of these examples may be attributed to kinetic[3] rather than thermodynamic limitations since metal–metal bonding and extensive halogen bridging appear to contribute appreciably to the stability of the products. In the case of scandium the lower number of valence electrons available for delocalized bonding is remedied through the formation of anionic M_6X_{12} clusters.

Cluster synthesis reactions in these metal–halogen binary systems are carried out under very reducing conditions near 800–1000 °C for several weeks using welded tantalum tubing as a container material; even so they are characteristically very slow, and the yields, low. All products are evidently formed by vapor phase transport. Thus, of the order of 10–20 mg of well-crystallized ZrI_2 is transported in the presence of excess

Table I. Crystal and Bonding Information for the Zirconium and Scandium Cluster Compounds

	ZrI_2	$ZrCl_{2.5}$	$Sc_{1.167}Cl_2$
Space group	$R\bar{3}, Z = 18$	$Ia3d, Z = 96$	$R\bar{3}, Z = 18$
Unit cell, Å	14.502 (2)	21.141 (3)	12.959 (2)
	9.996 (2)		8.825 (2)
Independent reflections	609	404	483
R^a	0.109	0.111	0.053
$R_w{}^a$	0.121	0.096	0.064
Formulation[b,c]	$Zr_6I_6^iI_{12/2}^{i\text{-}a}$	$[Zr_6Cl_{12}^i]Cl_{6/2}^{a\text{-}a}$	$Sc[Sc_6Cl_6^iCl_{12/2}^{i\text{-}a}]$
Bonding electrons/cluster	12	9	9
Distances, Å			
M–M (2 each)	$\begin{cases} 3.195\ (1) \\ 3.204\ (2) \end{cases}$	3.199 (4)	3.204 (2)
		3.215 (4)	3.234 (1)
M–X^i	2.860 (2)	2.494 (6)–2.514 (7)	2.540 (1)–2.591 (4)
M–X^a	2.947 (2)	2.588 (5)	2.755 (1)

[a] Residuals according to the usual definitions.[4] [b] See note 5 for definitions of i and a. [c] Fractional coordinates for atoms in the three structures follow. ZrI_2: Zr, 0.2310 (1), 0.7073 (1), 0.2970 (1); I, 0.4142 (1), 0.4360 (1), 0.1659 (1); I, 0.7181 (1), 0.5110 (1), 0.1579 (1). Zr_6Cl_{15}: Zr, 0.0614 (1), 0.9655 (1), 0.0809 (1); Cl, 0.1568 (3), 0.0296 (3), 0.0508 (3); Cl, 0.1094 (3), 0.8762 (3), 0.0191 (3); Cl, 0.5712 (6), −0.3212 (6), 0.125. Sc_7Cl_{12}: Sc, 0.1725 (1), 0.6232 (1), 0.0191 (1); Sc, 0.0, 0.0, 0.0; Cl, 0.0230 (1), 0.4377 (1), 0.1615 (1); Cl, 0.1801 (1), 0.0503 (1), 0.1660 (1).

metal from a $ZrI_{1.8}$ composition at 800 to a 900 °C zone in 30 days. The gem-like zirconium chloride crystals are obtained from a $ZrCl_{1.6}$ composition using a 750/650 °C gradient for 6 weeks, while crystals of the scandium phase are produced from reaction of powdered metal and $ScCl_3$ (overall composition $ScCl_{1.4}$) in 6 weeks at 890–900 °C.

The cluster compounds discovered are stoichiometrically ZrI_2, $ZrCl_{2.5}$, and $Sc_{1.17}Cl_2$, and, according to the crystal data summarized in Table I, are properly and simply described as Zr_6I_{12}, $(Zr_6Cl_{12}{}^{3+})(Cl^-)_3$, and $Sc^{3+}(Sc_6Cl_{12}{}^{3-})$. (The charges assigned in the last two descriptions ignore halogen bridging which links the ions shown.) In Zr_6Cl_{15} (isostructural with $Ta_6Cl_{15}{}^6$) the three additional chloride ions occupy bridging, exo positions between clusters so that $Zr_6Cl_{12}^iCl_{6/2}^{a\text{-}a}$ [5] is a better description. Metal–metal distances in all of the new clusters are ~0.3 Å longer than in the tantalum and related niobium compounds, reflecting both larger orbitals and a reduction in the number of bonding electrons per cluster from 15 to 9 or 12. The two compounds Zr_6I_{12} and $Sc(Sc_6Cl_{12})$ are closely related and both occur in the same space group. As illustrated in Figure 1 for the former, both structures consist of essentially ccp halogen layers between which triangles of metal atoms occur in pairs and are drawn together through metal–metal bonding to generate M_6 trigonal antiprisms. The halogen site in the central layer which would fall in the center of the M_6 cluster is left vacant. With the lower halogen:metal ratio in Zr_6I_{12} relative to Zr_6Cl_{15} half of the twelve inner halogens in each cluster (those in the middle layer) also occupy exo positions in another cluster, thus giving $M_6X_6^iX_{12/2}^{i\text{-}a}$. In $Sc(Sc_6Cl_{12})$ additional scandium(III) cations are located along the three-fold axis in octahedral interstices generated by the inner type halogens from two clusters. The metal atoms in the two zirconium clusters exhibit octahedral symmetry to within experimental error, while in the scandium example there is a 0.03-Å lengthening in the distances within the scandium triangles.

Metal–metal distances are substantially the same in all three clusters in spite of the difference in electron count between ZrI_2 (12 e) and the other two examples (9 e). Converged refinements of both chloride structures contain a residual of ~6 e Å^{-3} in the center of the cluster, a position of $\bar{3}$ symmetry. Whether this represents a real foreign atom or termination effects awaits improvement of the synthetic routes to the point that greater and more useful quantities of these two compounds will allow additional characterization.

These clusters represent a bridge to structures containing, formally, extended clusters which occur on reduction when there are more electrons and still fewer halogens. This leads
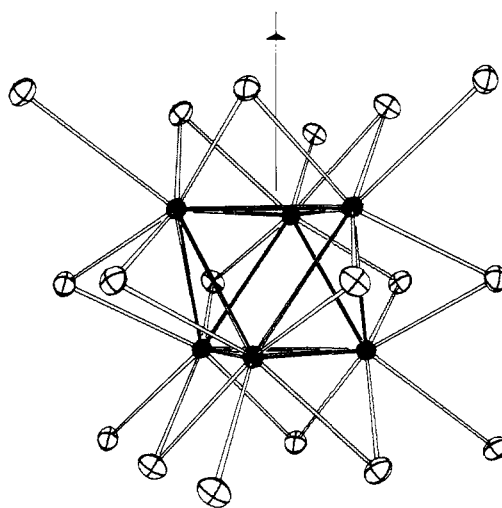

Figure 1. The Zr_6I_{12} cluster with the $\bar{3}$ axis of the metal octahedron vertical. Zirconium atoms are depicted as solid ellipsoids. The portion of three cubic-close-packed iodine layers shown contains all iodine atoms bound to the cluster. The six singly bonded iodine atoms exo to the cluster are inner, edge-bridging members of adjacent clusters.

to double sheets of shared octahedra, $ZrCl^4$ and $ScCl$,[7] or extended chains of edge-shared metal octahedra in Sc_7Cl_{10},[7] Sc_5Cl_8,[8] Gd_2Cl_3,[9] and Tb_2Cl_3.[10] The scandium structure reported here also brings to our attention again[7] a hitherto unappreciated factor, that particularly favorable electronic structures may be achieved for elements in the early groups through formation of poly*anions*, thus providing a cluster $Sc_6Cl_{12}{}^{3-}$ isoelectronic with $Zr_6Cl_{12}{}^{3+}$. It is likely that many more variations of isolated and condensed clusters will be found, among them perhaps stable zirconium anion clusters with additional halide, e.g., $Zr_6Cl_{18}{}^{3-}$.

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octahedron and the latter is bonded to only one metal and lies on or near the proper fourfold axis of the octahedron. Those forming links between two M_8 groups are denoted $X^{i\text{-}i}$, $X^{i\text{-}a}$, or $X^{a\text{-}a}$ depending on the mode.

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John D. Corbett,* Richard L. Daake
Kenneth R. Poeppelmeier, Dennis H. Guthrie

Ames Laboratory—USDOE and Department of Chemistry
*Iowa State University, Ames, Iowa 50011*

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Diastereomeric Transition States. High and Low Energy Reaction Pathways in the Cope Rearrangement

Sir:

It has long been recognized that a variety of conformations are accessible to molecules undergoing Cope and Claisen rearrangement. The traditional chair and boat forms have now been superceded by a more thorough delineation of mechanistic possibilities.[1] An understanding of the relative energy of the individual conformations, coupled with the constraints imposed by orbital symmetry, has greatly expanded the synthetic utility of these reactions.[2] Conformationally flexible 1,5-dienes exhibit a strong preference for a presumed "chair-like" form, making independent observation of the higher energy conformations a challenging experimental task.[3] The high energy form of the Cope rearrangement has only recently yielded to independent study.[4]

We wish to report preliminary results from an investigation of the thermal rearrangements of bis(methylenecycloalkanes), eq 1, a class of molecules that permit independent observation
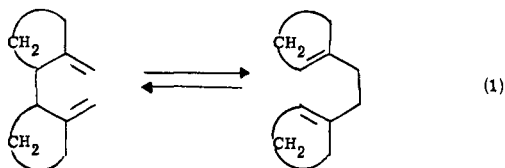
of high and low energy conformations of the Cope rearrangement. This communication describes the Cope rearrangement of *meso*- and *dl*-2-(2-methylenecyclopentane)methylenecyclopentane (**1**), eq 2. Sigmatropic rearrangement requires
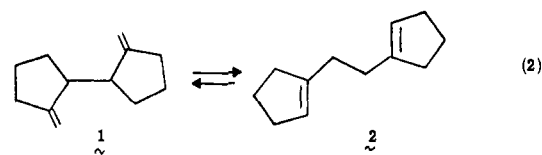
alignment of the two terminal exocyclic methylene carbons. The conformation that each diastereomer must adopt is shown in the figures in Chart I. Drawing upon the analogy of the Cope rearrangement to the dimerization of two allyl radicals,[5] the *meso*-**1** transition state corresponds to the six-center approach while *dl*-**1** corresponds to the four-center approach. These two transition states coincide with the high energy and low energy forms of the Cope rearrangement. This simple analysis predicts a substantial difference in the rate of Cope rearrangement for the two diastereomers. We have verified this prediction experimentally. The half-life for rearrangement of *dl*-**1** at 160 °C is 1 h. Rearrangement of *meso*-**1** occurs at an appreciable rate only at temperatures in excess of 250 °C. At 200 °C, *dl*-**1** is 18 000 times more reactive than the meso diastereomer (extrapolated).[6]

The temperature dependence of the rate constants was examined to obtain the activation parameters for both diastereomers.[7] These, together with the activation parameters of a model compound, 2-methallylmethylenecyclopentane (**3**), and the parent, 1,5-hexadiene,[8] are given in Table I. The similarity of activation parameters between *dl*-**1** and monocyclic 1,5-diene **3** should be noted. The enthalpy and entropy of activation are "normal" for Cope rearrangement.[9] Comparison of the values for *dl*- and *meso*-**1** reveal sizable differences in enthalpy ($\Delta\Delta H^{\ddagger}$ 13.8 kcal/mol) and entropy ($\Delta\Delta S^{\ddagger}$ 11 eu) of activation. These differences parallel those found for the high and low energy Cope rearrangement of parent 1,5-hexadiene (Table I). Discrepancies still remain
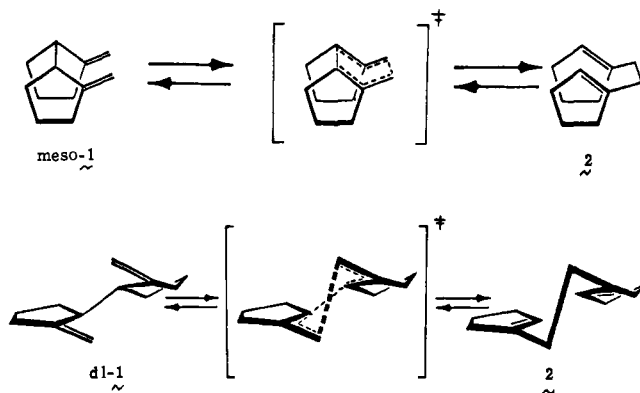
Chart I

Table I. Activation Parameters for Cope Rearrangement[a]

Compd	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}_{523}$	$\Delta G^{\ddagger}_{523}$	$\Delta\Delta H^{\ddagger}$	$\Delta\Delta S^{\ddagger}$	$\Delta\Delta G^{\ddagger}$
3	30.0 ± 0.3	−13.2 ± 1.0	36.9 ± 0.5			
dl-1	28.0 ± 1.1	−11.4 ± 2.6	33.9 ± 1.8			
				13.8	11.0	8.1
meso-1	41.8 ± 0.5	−0.4 ± 1.0	42.0 ± 0.6			
(low)[b]	33.5 ± 0.5	−13.8 ± 1.0	40.5 ± 1.0			
				11.2	10.8	5.8
(high)[c]	44.7 ± 2.0	−3.0 ± 3.6	46.3 ± 3.8			

[a] Units are in kcal/mol for $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ and cal/(mol-deg) for $\Delta S^{\ddagger}$; subscripts are in °K; uncertainties are standard deviations. [b] Reference 8. [c] Reference 4.