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) μ_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.

Acknowledgment. We are indebted to R. A. Jacobson for continued crystallographic advice, to J. Anderegg for the XPS data, to F. Laabs for the microprobe analysis, to K. A. Gschneidner and R. Stierman for the use of the magnetic susceptibility apparatus, and to S. Wijeyesekera for assistance in obtaining and interpreting the extended Hückel results.

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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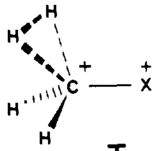
CH_6^{2+}, the parent *hexacoordinate* carbodication, is a minimum on the potential energy surface and awaits experimental verification.[1] We demonstrated by ab initio molecular orbital theory that CH_6^{2+} may result from the exothermic reaction of CH_4^{2+} with H_2.[1] This is in particular of interest, 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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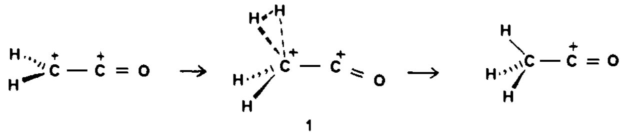
Table I. HF/6-31G* Energies in Hartrees

geometry	symmetry	energy
$H_4C^+—CO^+$	C_s	−151.966 33
$H_3C—C^+{=}O^+—H$	C_{3v}	−152.005 57
$H_3C—C^+{=}O$	C_{3v}	−152.059 30
$H_2C^+—C^+{=}O$	C_{2v}	−150.754 25
$H_4C^+—NH_3^+$	C_s	−95.532 49
$H_2C^+—NH_3^+$	C_s	−94.360 88
$H_4C^+—N_2^+$	C_s	−148.122 40
$H_3C—N^+{\equiv}N^+—H$	C_{3v}	−147.256 26[a]
$H_2C{=}N^+{=}NH_2^+$	C_{2v}	−148.201 28
$H_3C—N_2^+$	C_{3v}	−148.216 05
$H_2C^+—N_2^+$	C_{2v}	−146.924 14
$H_4C^+—OH_2^+$	C_s	−115.280 68

[a] HF/3-21G energy; for H_4C^+-N_2^+ this energy is −147.274 33 au (C_{4v}).

librium structures (minima), because no negative eigenvalues in the force constant matrices of the 3-21G optimized geometries were obtained.[7]

CH_4^{2+} has an empty p_z orbital perpendicular to its planar structure.[2c,d] The intrinsic strong electrostatic repulsion can be alleviated by interaction of this p_z orbital with an electron donor as an alternative to unimolecular fragmentation (deprotonation to CH_3^+).[8] One possibility is to correlate the empty p_z orbital with a free electron pair (n donor) to give a σ-bond. The result of such an interaction is a cation-substituted methonium ion as illustrated in structure I. This qualitative argument is supported by the calculations. At the HF/6-31G*//6-31G* level the formation of I from CH_4^{2+} and CO, NH_3, N_2, and OH_2 is exothermic by 113.9 (**1**), 189.0 (**2**), 82.5 (**3**), and 139.9 (**4**) kcal/mol, respectively.[6] In the present context, the earlier reported[9] carbenium–carbonium dication $C_2H_6^{2+}$ may be viewed as the product of CH_4^{2+} and singlet carbene, exothermic by 215.4 kcal/mol. In each of these examples, a different type of n donor X interacts with CH_4^{2+}. The generality of the product CH_4^+-X^+ dication is underlined by the presence of varying degrees of unsaturation, of free electron pairs, and of different first row-elements in X.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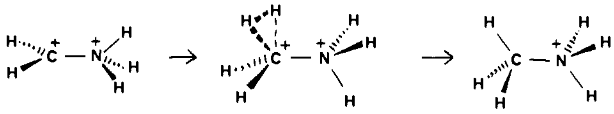
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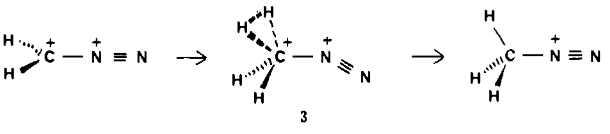
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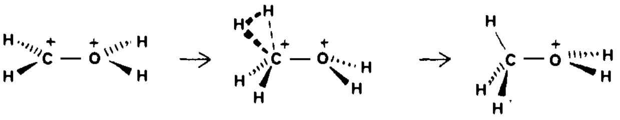
4

The n-donor interaction with CH_4^{2+} results in a formal charge separation. The remaining single positive charge on the now pentacoordinate carbon is best accommodated in a 3c–2e interaction,[10] as depicted in I.[7] Accordingly I may be viewed as a complex between hydrogen and the trivalent carbon in the dication H_2C^+-X^+. Similarly, we have discussed recently $C_2H_6^{2+}$ and $C_2H_8^{2+}$ as hydrogenated ethylene dication[4a] complexes.[1b] It is then expected that also in the present case the hydrogenation of the precursor dication is exothermic. Indeed at the HF/6-31G*//6-31G* level the heats of hydrogenation for the ketene (H_2CCO^{2+}), $H_2CNH_3^{2+}$, diazomethane ($H_2CN_2^{2+}$), and $H_2COH_2^{2+}$ [4b] dications are 53.5, 28.1, 44.8, and 15.4 kcal/mol, respectively.

Although I can be formed calculationally in an exothermic reaction, using either CH_4^{2+} or hydrogenation of a precursor dication, no thermodynamic stability is predicted for I. The important fragmentation pathway is expected to be C-deprotonation.[9] At the HF/6-31G*//6-31G* level this reaction to the acetyl (CH_3-CO^+), methylammonium (CH_3-NH_3^+),[6] methyldiazonium (CH_3-N_2^+), and methyloxonium (CH_3-OH_2^+)[6] ion is exothermic by 58.3, 25.7, 58.8, and 36.6 kcal/mol, respectively. Although these calculated heats of deprotonation are significant, substantial barriers for these processes are anticipated, as based on previous dication studies.[8] Therefore dication I could be a viable species.

Experimental verification of metastable I in the gas phase using CH_4^{2+} and the described n donors, however, is likely hampered by the magnitude of the exothermicity of reaction. This could make accessible fragmentation and isomerization routes for I, unless the excess potential energy can be otherwise accommodated. The hydrogenation route on the other hand appears more promising but would need the prior search for the precursor dications by, e.g., mass spectroscopic charge stripping.

Different from gas phase strongly acidic solutions may cause protio solvation of electrophiles and can thus be viewed as a means of generating transient dications. In the case of the acetyl cation the C-protonated structure $CH_4^+—CO^+$ is less stable than the O-protonated structure $H_3C—C^+{=}O^+—H$ (isoelectronic with propyne), but by only 24.6 kcal/mol (6-31G*). The reverse, however, is found for the protonation of the methyldiazonium ion, where $CH_4^+—N_2^+$ is now 12 kcal/mol (3-21G) more stable than $H_3C—N^+{\equiv}N^+—H$, with the latter surprisingly being a transition structure. Interestingly the di-N-protonated structure $H_2C{=}N^+{=}NH_2^+$ (isoelectronic with allene) is 49.5 kcal/mol (6-31G*) more stable than CH_4^+-N_2^+; apparently the stability order of C- and N-protonated diazomethane[13] is reversed for the dications.

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(6) The HF/6-31G* structural parameters and energies of CO (−112.737 88 au), NH_3 (−56.184 36 au), N_2 (−108.943 95 au), OH_2 (−76.010 75 au), methylammonium ion (−95.573 49 au), and methyloxonium ion (−115.338 99 au) were taken from: Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University; Pittsburgh, PA, 1981. For the HF/6-31G* energy of CH_4^{2+} (−39.046 94 au) see ref 2c.

(7) In some cases the 3-21G optimized geometry differs from the one obtained with the 6-31G* basis set, i.e., CH_4^+–CO^+ and CH_4^+–N_2^+. For these dications the 3-21G geometry has C_{4v} symmetry. A similar situation has been observed for CH_4^+–CH_2^+.[9] It is well-known that in order to describe hypercoordinate ions, and is particular 3 center–2 electron interactions, inclusion of d-polarization functions in the basis set (6-31G*) is a necessity.[1,10] We therefore assume that the lower C_s symmetry 6-31G* geometries I are equilibrium structures.

(8) The barrier for CH_4^{2+} deprotonation is 16.8 kcal/mol, the reaction being exothermic by 105.7 kcal/mol (MP_4/6-311G*//6-31G* + ZPE).[2c] These values are 15.8 and 115.3 kcal/mol, respectively, at the 6-31G* level as employed in the present report.[2c] It appears that most carbodications have a substantial barrier for proton loss. They are at the HF/6-31G* level, with the corresponding exothermic heat of deprotonation in parentheses, e.g., CH_2^{2+}, CH_6^{2+}, $C_2H_2^{2+}$, $C_2H_4^{2+}$, $C_2H_6^{2+}$, and CH_4O^{2+} 37.5 (59.7),[2c] 31.4 (70.1),[1a] 72.6 (6.8),[4c] 87.0 (0.0),[4a] 30.5 (~30),[1b] and 1.7 (63.3)[4b] kcal/mol, respectively.

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Our data appear in agreement with a recent experimental study on diazomethane.[14]

In conclusion we have shown a new class of dications with the general structure I, methonium ions with a cationic substituent. Their formation both from CH_4^{2+} with n donors and from hydrogenation of precursor dications is highly exothermic. The experimental verification of I depends on the balance of the heats of reaction vs. the activation energy of fragmentation and isomerization and further on how excess potential energy can be accommodated otherwise. We encourage mass spectroscopists to search for I.

Acknowledgment. The cooperation of the USC (Los Angeles, where part of the work was done) and UAB computer centers greatly facilitated the present investigation. The author is indebted to Dr. M. Barzaghi who implemented and modified the programs and thanks Professor G. A. Olah for his continuous encouragement.

Registry No. H_4C^+—CO^+, 62655-44-1; H_3C—C^+=O, 15762-07-9; H_2C^+—C^+=O, 85491-02-7; H_4C^+—NH_3^+, 91158-04-2; H_2C^+—N_2^+, 91158-05-3; H_4C^+—N_2^+, 91158-06-4; H_2C=N^+=N^+H_2, 91158-07-5; H_3C—N_2^+, 20404-06-2; H_4C^+—OH_2^+, 91158-08-6.

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(14) McGarrity, J. F.; Cox, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 3961.

Chiral Recognition of the Twisted Cyclohexene Conformation in β-Cyclocitral Schiff Bases

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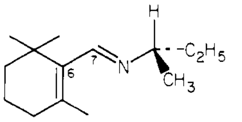
Steric interactions cause the well-documented[1–4] nonplanarity between the cyclohexene double bond and the polyene chain in retinal-type molecules. We now wish to report what we believe is proof of the twist inherent in the β-ionyl system in solution.

Starting with β-cyclocitral and optically active amines the two chiral Schiff bases **1** and **2**[5] were prepared by standard procedures.[6]



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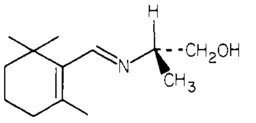

2

The UV and CD spectra of both compounds show a remarkable solvent and temperature dependence. For **1** the results are collected in Table I. In methanol the extinction of the only prominent absorption band (maximum at 241 nm) is less than 40% the value in isopentane with little change when the temperature is lowered. In isopentane on the other hand the extinction drops significantly between −50 and −100 °C, approaching at even lower temperatures the value found in methanol. A prominent feature of the CD spectrum is a negative band with maximum at 264 nm in methanol (267 nm in isopentane), which, however, develops only at low temperatures and at a different rate in both solvents. The methanol data can be interpreted on the basis of a temperature-dependent equilibrium between two chiral species.[7] In a plot of $1/(1 + e^{-\Delta G°/(RT)})$ against the observed rotatory strength, excellent linearity (0.998) is obtained for $\Delta G° = -2.0$ kJ/mol corresponding to rotatory strengths for the two components of −2.4 and +4.5 × 10^{-39} cgs, respectively. In isopentane, the same $\Delta G°$ and rotatory strengths of the same order of magnitude result[8] if only the data below −60 °C are considered.

Table I. Solvent and Temperature Dependence of the UV (241 nm) and CD Spectra of **1**

	ε, L mol^{-1} cm^{-1}		$10^{40}R$, cgs	
T, °C	isopentane	methanol	isopentane	methanol
10	13700	5150	−0.58	−3.9
−20	13000	5400	−1.3	−4.6
−40	12300	5200	−1.6	−6.2
−60	11400	5000	−2.0	−7.2
−80	9300	4400	−4.2	−9.0
−100	7100	4300[a]	−8.2	−10.6[a]
−120	6600		−12.0	−12.6[a]
−140	6200		−16.6	−14.6[a]
−150	5900		−18.5	
−160				−17.0[a]

[a] Methanol/ethanol (1:4).

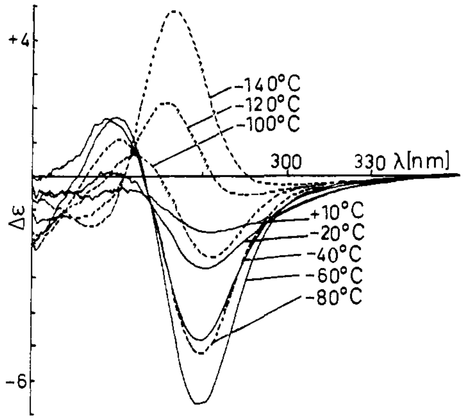

Figure 1. Temperature-dependent CD spectra of **2** in isopentane.

To interprete these results, we have to consider and evaluate the different conformational equilibria that might play a role in **1**. Hindered rotation around the C–N single bond cannot account for the observed effects since open-chain analogues of **1** which we synthesized do not show them. The *E*/*Z* equilibrium at the C=N double bond may be ruled out because of the high barrier to inversion or rotation at a doubly bonded nitrogen.[9] We conclude that it is the presence of the ring or, more specifically, the s-cis/s-trans equilibrium about the C(6)–C(7) bond that is responsible for the observed changes the cis form being favored in methanol and at low temperatures in isopentane.

Twist of this bond makes the chromophore inherently chiral. In addition the asymmetric carbon atom serves as a chiral anchor to distinguish between the twists of opposite chirality, and circular dichroism is observed. Our data indicate, moreover, that it is mainly the s-cis form that gives rise to the CD spectra[10] due

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(2) For a summary of X-ray data, see, e.g.: Noack, K.; Thomson, A. J. *Helv. Chim. Acta* **1979**, *62*, 1902.

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(5) (*S*)-*N*-(1-Methylpropyl)-β-cyclocitrylideneamine (**1**), (*S*)-*N*-(2-hydroxy-1-methyl-ethyl)-β-cyclocitrylideneamine (**2**).

(6) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246.

(7) Moscowitz, A.; Wellman, K.; Djerassi, C. *J. Am. Chem. Soc.* **1963**, *85*, 3515.

(8) The calculated rotatory strength of the dominant conformer is −3.6, of the other +10.6 × 10^{-39} cgs (linearity 0.998).

(9) A large-scale CI treatment of allylideneimine gives, for the C=N double bond, a barrier to planar inversion of 128 kJ/mol and to rotation of 245 kJ/mol: Bonacic-Koutecky, V.; Persico, M. *J. Am. Chem. Soc.* **1983**, *105*, 3388.

(10) For the allylideneimine chromophore of **1** twisted by 40° from s-cis, we calculate for P helicity a rotatory strength of +2.2 × 10^{-39} cgs for the $n\pi^*$ transition and 1.4 × 10^{-39} cgs for the $\pi\pi^*$ transition in the CNDO approximation. It is tempting, moreover, to speculate that the different absolute values of rotatory strengths which we obtain by the linearity test correspond to conformations that differ not only in their sense of helicity, but also in the degree of twist.

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