dimethylphenylsilyl enol ether (**12**) and benzaldehyde (0.5 M each, benzene) showed no evidence of reaction after 200 h at 150 °C. In contrast, silacyclobutane analog **13**[5] reacts with benzaldehyde even at 27 °C, albeit slowly ($t_{1/2} \approx 4$ days, 0.8 M each, benzene), to form efficiently a mixture of syn and anti aldol addition products (12:1, respectively).[6] At 100 °C, complete conversion is attained within 34 h, with a slight erosion in syn selectivity (7:1, 84% yield).[7] Both *E*- and *Z*-rich mixtures of 3-pentanone phenylsilacyclobutane enol ethers react with benzaldehyde at 100 °C to form predominantly the syn aldol adduct (4 days, 66:34 $E{:}Z \rightarrow 7.6{:}1$ syn:anti, 95%; 15:85 $E{:}Z \rightarrow 2.8{:}1$ syn:anti, 86%),[8] indicating that both isomers are syn-selective, although the *E* isomer is more so. Interestingly, in the examples described, the methylsilacyclobutane derivative[9] is found to react at roughly half the rate of the corresponding phenylsilacyclobutane derivative, suggesting an electronic factor for further study. At present, the useful range of substrates with ketone silacyclobutane enol ethers appears to be limited to reactive aldehydes; reaction of **13** with isobutyraldehyde, for example, is found to be impractically slow (ca. one-tenth the rate of reaction with benzaldehyde).

Noncatalyzed aldol addition reactions of *O*-silacyclobutane ketene acetals are also dramatically accelerated versus their acyclic counterparts and may represent the most useful demonstration of the silacyclobutane-mediated aldol strategy. For example, the reaction of *O*-trimethylsilyl ketene acetal **14** with benzaldehyde is reported to require heating at 150 °C (neat, 18 h) for completion and affords the addition product **15** in 81% yield.[1] As a control, **14** was heated with benzaldehyde in benzene solution (0.2 M each, 150 °C), forming less than 25% of the aldol product **15** after 24 h as well as several unidentified byproducts. In marked contrast, methylsilacyclobutane derivative **16**[10] reacted completely and cleanly with benzaldehyde within 4 h at 27 °C (0.2 M each, benzene) to afford the adduct **17** quantitatively. This derivative also undergoes smooth addition with less reactive carbonyl substrates such as isobutyraldehyde (0.2 M, benzene, 1 day, 60 °C, 80%) and acetone (excess, benzene, 3 days, 65 °C, 85%). (*E*)-*O*-Methylsilacyclobutane ketene acetal **18**[10] reacted efficiently with benzaldehyde at 23 °C to afford the syn adduct **19** with good stereocontrol (19:1 syn:anti, quantitative). Though the reactions described were performed with distilled silyl ketene acetals in benzene solution, preliminary experiments have shown that aldol reactions of silacyclobutane ketene acetals prepared in situ in tetrahydrofuran are also feasible. In a process that is almost certainly mechanistically distinct, but nevertheless of interest, each of these silacyclobutane-accelerated aldol reactions is found to be catalyzed by potassium *tert*-butoxide and, presumably, by other nucleophiles as well.[11]

As a working hypothesis, it is suggested that silacyclobutane-mediated aldol reactions proceed by way of a pentavalent (tbp or square pyramidal) organosilicon species where a boatlike transition state is preferred (**1**, **13**, **18**), though a chairlike transition state is readily accessible and, in some cases (**7**, (*Z*)-silyl enol ether from 3-pentanone), may dominate.[2] The preliminary studies described herein suggest a general strategy[3] for the development of new bond-forming processes, both stoichiometric and catalytic, wherein a potential transition state involving hypervalent silicon is made energetically accessible by the simple expedient of incorporation of the silicon atom within a four-membered ring.

Acknowledgment. Generous financial assistance from the National Science Foundation and American Cyanamid Company and NSF predoctoral fellowship support for S.E.K. and H.C. are gratefully acknowledged.

Supplementary Material Available: ^{1}H and ^{13}C NMR and IR spectra of each new compound and X-ray coordinates for compound **6** (48 pages). Ordering information is given on any current masthead page.

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[5] Prepared in 92% yield (distilled) by reaction of 1-chloro-1-phenylsilacyclobutane (Auner, N.; Grobe, J. *J. Organomet. Chem.* **1980**, *188*, 25) with the lithium enolate of cyclohexanone.

[6] It is noteworthy that this stereoselectivity is opposite that of the $TiCl_4$-induced reaction (Mukaiyama aldol reaction: Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503).

[7] Yields are determined by integration of ^{1}H NMR spectra employing an internal standard.

[8] Prepared in 81% yield (distilled) by trapping of the kinetic mixture of lithium enolates formed from 3-pentanone and lithium diisopropylamide (LDA) with 1-chloro-1-phenylsilacyclobutane (ref 5). The *Z*-rich mixture arose adventitiously by isomerization of this mixture during a distillation, presumably catalyzed by a basic impurity.

[9] 1-Chloro-1-methylsilacyclobutane was prepared from commercially available (3-chloropropyl)dichloromethylsilane by a modification (Baker, K. V.; Brown, J. M.; Hughes, N.; Skarnulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698) of the literature procedure: Damrauer, R.; Davis, R. A.; Burke, M. T.; Karn, R. A.; Goodman, G. T. *J. Organomet. Chem.* **1972**, *43*, 121.

[10] Prepared by kinetic trapping of the lithium enolate (LDA) with 1-chloro-1-methylsilacyclobutane (ref 9) with purification by Kugelrohr distillation (70–85% yield). In the case of **18**, approximately 40% of the C-silylated product is present as a contaminant; this compound is inert under the reaction conditions.

[11] Reactions described as "noncatalyzed" were performed with distilled reagents in neutral glassware and followed reproducible, bimolecular kinetics.

Bicyclic Ring Size Effect on β- vs α-Deprotonation of Diazenium Dications

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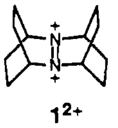
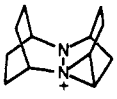
Sesquibicyclic diazenium dication $\mathbf{1}^{2+}$ is a rather strong CH acid which is deprotonated slowly by chloride and more rapidly by pyridine at a carbon β to nitrogen to give the thermally labile *N*-aminoaziridinium cation **2**.[1] We report here that expanding one of the dimethylene bridges of $\mathbf{1}^{2+}$ to three and four carbons greatly increases acidity and causes a switch from β proton loss to α and that these changes may be understood using AM1 semiempirical MO calculations.[2]



$\mathbf{1}^{2+}$



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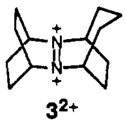
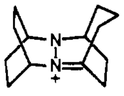


$\mathbf{3}^{2+}$



4

$\mathbf{3}^{2+}$ is isolable at room temperature[3] but is far more acidic than $\mathbf{1}^{2+}$. In contrast to $\mathbf{1}^{2+}$, reaction of $\mathbf{3}^{2+}$ with water is rapid, although it produces substantial amounts of $\mathbf{3}^{\bullet +}$, making NMR characterization of the initial products difficult. Basic workup gives 2,3-diazabicyclo[2.2.2]oct-2-ene and 1,4-cycloheptanedione in low yield, but no 6,7-diazabicyclo[3.2.2]non-6-ene. These products are most easily explained by hydrolysis of the α-deprotonation product, *N*-aminoimmonium cation **4**. We were surprised to see evidence for α-deprotonation of $\mathbf{3}^{2+}$ because we expected only a rather small weakening of its C_α—H bonds. The H—C_α,N(p) dihedral angle θ is calculated to be 77.0°, and if bond weakening followed a $\cos^2\theta$ relationship (as the hyperconjugative contribution to ESR splitting constants does), its C_α—H bond would only be weakened 5% as much as that for a perfectly aligned hydrazine dication C_α—H bond. However, AM1 calculations predict that significant $N^+{=}C_\alpha$ bonding is present for α-deprotonation product **4**, as summarized in Table I. The N^+C_α bond length for **4** corresponds to 92% of the change from $\mathbf{1}^{2+}$-H_α (which as expected has essentially no double bonding, as indicated by its pyramidal atoms and large twist angle) to the unstrained acyclic model, and α-deprotonation of $\mathbf{3}^{2+}$ is estimated to be about 30 kcal/mol more

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[1] Nelsen, S. F.; Wang, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5905.

[2] (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Structures were optimized using the substantially improved programs VAMP 4.30 or 4.40 (on a Stardent 3000 computer) or SCAMPIBM 4.30 (on an IBM 6000), made available to us by their author, T. Clark, Universität Erlangen–Nürnberg.

[3] $\mathbf{3}^{2+}(PF_6^-)_2$ was isolated in 97% yield by oxidation with $NOPF_6$ in acetonitrile (see supplementary material).

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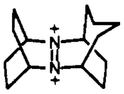
Table I. Results of AM1 Calculations on α-Deprotonated Hydrazine Dications

	species			
	$\mathbf{1}^{2+}$-H_α	$\mathbf{3}^{2+}$-H_α(**4**)	$\mathbf{5}^{2+}$-H_α(**6**)	$R_2NRN^+{=}CR_2$[a]
$d(N^+C_\alpha)$, Å	1.435	1.343	1.335	1.334
$f(\Delta d)$[b]	≡0	0.92	0.99_4	≡1.0
N^+C_α twist, deg	79.0	38.2	26.5	2.9
α_{av} at N^+, C_α, deg	115.4, 115.1	119.3, 117.9	119.9, 119.3	120.0, 120.0
$\Delta\Delta H_f(\beta\text{-}\alpha)$,[c] kcal/mol	−28.9	−4.7[d]	+15.9[e]	
rel $\Delta\Delta H_f(\alpha)$ vs neutral,[f] kcal/mol	58.1	26.0	5.9	[≡0]
rel $\Delta\Delta H_f(\alpha)$ vs cation,[g] kcal/mol	66.5	36.2	18.7	[≡0]

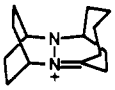
[a] R = CH_3. [b] Fractional change in $d(N^+C_\alpha)$ between $\mathbf{1}^{2+}$-H_α and the acyclic model. [c] $\Delta H_f(X^{2+}\text{-}H_\beta) - \Delta H_f(X^{2+}\text{-}H_\alpha)$, for the most stable β- and α-deprotonation products (which are those derived by proton loss from the largest ring). [d] Products derived by deprotonation at the $(CH_2)_2$ bridges are destabilized by 5.3, 6.6, and 6.8 kcal/mol. [e] Products derived by deprotonation at the $(CH_2)_2$ bridges are destabilized by 1.8, 4.8, and 4.9 kcal/mol. [f] $[\Delta H_f(X^{2+}\text{-}H_\alpha) - \Delta H_f(X^0)]$, minus this quantity for the acyclic model.[4] [g] $[\Delta H_f(X^{2+}\text{-}H_\alpha) - \Delta H_f(X^{\bullet+})]$, minus this quantity for the acyclic model.[4]

facile than for $\mathbf{2}^{2+}$,[4] despite **4** having a calculated twist of 38° at the $N^+{=}C_\alpha$ bond. For $\mathbf{1}^{2+}$, where the α-deprotonation product is prevented from attaining significant $N^+{=}C$ bonding, the observed β-deprotonation product is calculated to be thermodynamically more favorable than the α-deprotonation product by 28.8 kcal/mol. The most stable of the four β-deprotonation products of $\mathbf{3}^{2+}$, that derived by deprotonation of the trimethylene bridge, is calculated to be 4.7 kcal/mol thermodynamically more stable than the α-deprotonation product, but the products of these irreversible deprotonations will be determined by kinetics, not thermodynamics of deprotonation.[5]

We have been unable to detect **4** spectroscopically, possibly because of its high reactivity with nucleophiles. It may also be noted in the table that AM1 predicts α-deprotonation of the next higher homologue, $\mathbf{5}^{2+}$ (θ, 64°; $\cos^2\theta$, 0.19), to be more facile than that of $\mathbf{3}^{2+}$ by about 18 kcal/mol and predicts the product **6** to have a 26.5° twist at the $N^+{=}C_\alpha$ bond but little other distortion relative to the acyclic model. $\mathbf{5}^{2+}$ ought to be even more acidic than $\mathbf{3}^{2+}$ and **6** (which contains a *trans*-cyclooctene structure) to be isolable. Neutral **5** was prepared by addition of 1,3-cyclohexadiene to protonated 7,8-diazabicyclo[4.2.2]dec-7-ene followed by hydrogenation and deprotonation.[6] In contrast to $\mathbf{1}^{2+}$ and $\mathbf{3}^{2+}$, dication $\mathbf{5}^{2+}$ (bridgehead signals: ^1H NMR δ 6.03 and 5.91; ^{13}C NMR δ 82.5 and 81.6)[6] decomposes slowly in CD_3CN even at −38 °C to produce cation **6**, which was isolated as the hexafluorophosphate salt in 83% yield after an ether quench. **6**-PF_6 shows three bridgehead ^1H NMR signals at δ 4.47, 3.79, and 3.61, an olefinic ^{13}C NMR C_q at 175.6 and bridgehead CH at 66.6, 55.7, and 53.9, weak IR absorptions at 1608 and 1571 cm^{-1}, and UV bands at 298 (ϵ 4360) and 210 (ϵ 3700).[6] The spectroscopic effects of twisting at neutral N=C bonds have received considerable study from the extensive matrix isolation work reported on bridgehead imines generated from bicyclic bridgehead azides.[7] We believe **6** to be the first twisted $N^+{=}C$ species to be reported. Electrochemical measurements of the kinetics of deprotonation of tetraalkyldiazenium dications and the use of their α-deprotonation products for the preparation of substituted hydrazines will be reported in due course.



$\mathbf{5}^{2+}$



6

Acknowledgment. We thank the National Institutes of Health for financial support of this work under GM-29549, the National Science Foundation for grants supporting the spectroscopic and computational equipment, and Timothy Clark for the computer programs employed.

Supplementary Material Available: Experimental procedures for the preparation of $\mathbf{3}^{2+}(PF_6^-)_2$ and $\mathbf{6}^+PF_6^-$ and a listing of NMR spectral data for $\mathbf{5}^{2+}(PF_6^-)_2$ determined from mixtures with **6** (4 pages). Ordering information is given on any current masthead page.

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(4) Meaningful comparisons of heats of formation for compounds of different empirical formulas and strain are always a problem. The last two rows of the table tabulate the difference in ΔH_f for the α-deprotonated dication and the neutral compound and the radical cation, respectively, with the proper quantity for the acyclic model subtracted, which gives an indication of the effects imposed by the polycyclic structure. Neither set of numbers provides a perfect comparison because of significant differences in bonding at the nitrogens between the different compounds. We note that the differences between the entries for $\mathbf{1}^{2+}$-H_α and $\mathbf{3}^{2+}$-H_α are 32.1 and 30.3, respectively, while those between $\mathbf{3}^{2+}$-H_α and $\mathbf{5}^{2+}$-H_α are 20.1 and 17.5, respectively, which are rather similar, despite the differences in the magnitudes of the numbers depending upon whether comparisons were made with the neutral hydrazines or their radical cations.

(5) A referee suggested that examination of charges at the protons or s-orbital coefficients in the LUMO might reflect the large changes in α-proton kinetic acidities. Neither does. Higher charge is calculated at the bridgehead hydrogens of the [222] rings of both $\mathbf{3}^{2+}$ and $\mathbf{5}^{2+}$ than is calculated at the larger ring, in contradiction to the experimental site of α-deprotonation. The LUMOs are π^*(NN) and have vanishingly small coefficients at the bridgehead hydrogens. The structural changes undergone upon deprotonation are apparently too large to make the dication a good enough model for the deprotonation transition state for such approximations to work.

(6) See supplementary material.

(7) For a recent review, see: Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067.

The Redox Chemistry of $(n\text{-}Bu_4N)_2[Os_2Cl_8]$: Low-Temperature Spectroelectrochemical Characterization of $[Os_2Cl_8]^-$ and Voltammetric Evidence for $[Os_2Cl_8]^0$

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The nature of metal–metal-bonded systems is of particular and enduring interest.[1] Face-to-face complexes of form $[M_2X_8]^{n-}$ (M = Cr, Mo, W, Tc, Re, Os; X = Cl, Br) allow comparisons of the unsupported M–M multiple bond according to periodic trends and as a function of the varying electronic occupancy of the binuclear $\sigma\pi\delta\delta^*\pi^*\sigma^*$ orbital manifold. The maximal, quadruple bond occurs for eight-electron (8e) systems, typified by $[Re_2Cl_8]^{2-}$. So far, $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ represent the only octahalide isolated and structurally characterized in two oxidation states.[2] However, $[Re_2Cl_8]^{3-}$, which is more reactive than $[Tc_2Cl_8]^{3-}$, was recently characterized in solution by generation from $[Re_2Cl_8]^{2-}$ in an

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* To whom correspondence should be addressed.

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(2) (a) Cotton, F. A.; Daniels, L.; Davison, A.; Orvig, C. *Inorg. Chem.* **1981**, *20*, 3051. (b) Cotton, F. A.; Bratton, W. K. *J. Am. Chem. Soc.* **1965**, *87*, 921.

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