stems *from* a balance between an attempt to maximize bonding between the two bridgehead carbons and the tendency toward a planar CH_3^+ geometry. An inward tilt of the bridgehead hydrogen improves the orbital alignment which promotes bonding at smaller α as the dominant effect. However, at larger bridgehead carbon separations, the energy balance will change in favor of a planar geometric configuration surrounding $C_{(1)}$. The increase in both α and β is bound to decrease the hyperconjugative interaction that lengthens r_2, and, therefore, eventually, with increasing α, r_2 begins to shorten.

Much more surprising, however, is the affect of α on the motion of the substituent at the bridgehead where the radical center develops ($C_{(2)}$). Following the variation in α as it increases, this angle (γ) first decreases and then, at around $\alpha = 153°$ ($r = 2.0$ Å), rises steeply *overshooting the planar geometry* ($\gamma = 180°$) by ca. 16.7°. The value of γ then goes down again approaching planarity from the opposite direction (this process is described in Scheme I). The maximum overshoot angle ($\gamma = 197°$) is obtained at α around 160°. With use of the 3-21G optimized geometry for the radical cation at $\alpha = 160°$ but in the higher level 6-31G* basis, the hydrogen atom tilt inward was followed from $\gamma = 197°$ to $\gamma = 165°$ in several steps. The total energy was found to rise monotonically by 2.5 kcal/mol, showing the basis set independence of the second oscillation.

To the best of our knowledge, a double oscillation such as that exhibited by the second bridgehead hydrogen has never been reported before. The first oscillation of the latter hydrogen is similar to that calculated for the hydrogen on $C_{(1)}$ and stems probably from the same origin. The cause of the second oscillation, however, is less clear. We note that the "overshoot" in γ takes place when the covalent interaction across the ring has been practically nullified, and the localization of the positive charge on $C_{(1)}$ has, by and large, been completed. On this basis one could suspect that the pyramidalization results from an interaction between the positive charge and the radical center. Such a pyramidalization may be due to polarization of the SOMO toward the positive charge and/or to the repulsion between the latter and the partly positively charged hydrogen atom.

In order to examine the hypothesis that this overshoot effect is caused by the neighboring positive charge, a model system was studied. It consisted of a unit positive charge located 1.5 Å away from the carbon atom along the symmetry axis of a planar methyl radical. Optimization of the methyl fragment at the 3-21G level[5] (UHF) showed indeed a symmetric pyramidalization of 6.85° (which in terms of the angle γ in our case is equivalent to 200.4°). A symmetric pyramidalization of 5.6° (196.65° in terms of γ) was obtained by using the 6-31G* basis set.[8] Finally, the system of Me• with Na^+ replacing the positive charge was fully geometry optimized by using the 6-31G* basis set[8] for the Me fragment and CEP-31G[9] basis and core potential for Na (UHF). The equilibrium geometry has a C–Na distance of 2.73 Å and a symmetric pyramidalization angle of 7.8°.

The aforementioned ab initio predicted effect of a positive charge on the geometry of a radical center is amenable to experimental verification. The best probe would probably be the determination of the ESR coupling constants of the substituents around the radical center in a caged or folded structure in which the radical center is located close to a positively charged group such as the quaternary ammonio substituent embedded in the molecular framework.

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Registry No. Bicyclobutane radical cation, 85915-57-7; methyl radical, 2229-07-4; sodium ion, 17341-25-2.

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Ethylene Formation in the Reduction of 1,4-Dihaloalkanes with a Nickel(I) Macrocycle

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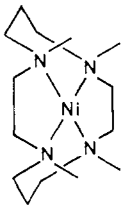
The nickel tetraaza macrocycle[1-5] $Ni(tmc)^+$ reacts with 1,4-dihaloalkanes (halide = Br, I) to produce ethylene, eq 1. No

$$X{-}(CH_2)_4{-}X + 2Ni(tmc)^+ \rightarrow 2XNi(tmc)^+ + 2C_2H_4 \qquad (1)$$

cyclobutane or butenes were observed by VPC under any conditions, although suitable controls were performed to show that they would have survived the reaction conditions. 1-Bromobutane and minor amounts of *n*-butane (2–10%) result only when a deficient quantity of $Ni(tmc)^+$ is used. With excess $Ni(tmc)^+$, however, both byproducts are largely eliminated, and ethylene is formed in >90% yield.



R,S,R,S-[Ni(tmc)$^+$]

The reactions proceed by way of an organometallic intermediate, which is inferred to be $(tmc)Ni(CH_2)_3CH_2X^+$, because it hydrolyzes[6] to the 1-halobutane upon standing or when H_3O^+ is added. The unimolecular rate constants for hydrolysis at pH 12 are 1.3×10^{-2} and 2.7×10^{-2} s^{-1}, for X = Br and I, respectively. These values lie in the same narrow range spanned by values for the hydrolysis of other $RNi(tmc)^+$ complexes,[6] $(0.8–2.7) \times 10^{-2}$ s^{-1}. The organometallic complex can be detected spectrophotometrically (λ_{max} 405 nm, ϵ 2×10^3 M^{-1} cm^{-1}) under suitable reaction conditions. It resembles known organonickel complexes spectrophotometrically and chemically.[3,4] With excess alkyl halide the organonickel complex yields 1-bromobutane; this in turn gives minor amounts of *n*-butane from the *n*-butylnickel complex formed from it. Addition of $Ni(tmc)^+$ to this organometallic complex causes its "immediate" decomposition, accompanied by ethylene formation, eq 2. This reaction is catalytic, requiring but a trace of excess $Ni(tmc)^+$.

$$(tmc)Ni(CH_2)_3CH_2X^+ \xrightarrow{Ni(tmc)^+} XNi(tmc)^+ + 2C_2H_4 \qquad (2)$$
$$(X = Br, I)$$

The methyl-substituted 1,4-dibromobutane $BrCH(CH_3)(CH_2)_2CH_2Br$ yields equal amounts of the analogous alkenes, ethylene and propene; no methylcyclobutane is observed. Some pentane and 1-pentene are formed from the 1-pentyl radical. Other 1,4-disubstituted compounds $Br(CH_2)_4Y$ (Y = Cl, OH, OTs) do not yield ethylene but yield organonickel complexes that hydrolyze exclusively to $CH_3(CH_2)_3Y$ (Table I). The alkene dihalide 1,4-dibromo-but-2-ene gives only 1,3-butadiene, without a detectable organonickel intermediate. The reactions shown in Scheme I are consistent with these observations.

Ethylene formation by reduction of 1,4-dihaloalkanes is rare, the usual products of single electron transfer being butane (e.g., from reaction of Cr^{2+} [7] and $Co(CN)_5^{3-}$ [8]). Stable dimetallic

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[1] The complex depicted is 1*R*,4*S*,8*R*,11*S*-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), which we abbreviate as *R,S,R,S*-[Ni(tmc)$^+$] or, when it is not confusing, simple as $Ni(tmc)^+$. Convenient electrochemical, photochemical, and chemical methods have been reported[2-4] for the preparation of the highly air-sensitive solutions of the nickel(I) reagent from the nickel(II) salt, which is very stable and readily prepared.[5]

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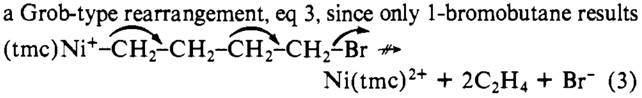
Table I. Reactions[a] of $(tmc)Ni(CH_2)_4Y^+$ Ions with $Ni(tmc)^+$ and with H_2O

$R-Ni(tmc)^+$, R =	with $Ni(tmc)^+$ product	with $Ni(tmc)^+$ k/M^{-1} s^{-1} [b]	hydrolysis product	hydrolysis k_{hyd}/s^{-1} [c]
$-(CH_2)_4I$	C_2H_4		$I(CH_2)_3CH_3$	2.7×10^{-2}
$-(CH_2)_4Br$	C_2H_4	1.6×10^3	$Br(CH_2)_3CH_3$	1.3×10^{-2}
$-(CH_2)_4Cl$		$(\leq 10^1)$	$Cl(CH_2)_3CH_3$	0.8×10^{-2}
$-(CH_2)_4OH$	nr	$<10^{-2}$	$HO(CH_2)_3CH_3$	0.8×10^{-2}
$-(CH_2)_4OTs$	nr	$<10^{-2}$	$TsO(CH_2)_3CH_3$	0.8×10^{-2}
$-CH(CH_3)-(CH_2)_3Br$ [e]	*d*		$[Br(CH_2)_4CH_3]$ [e]	

[a] At 25.0 °C and 0.010 M NaOH. [b] Compare with $k = 1.5 \times 10^3$ M^{-1} s^{-1} for 1-bromobutane and $k = 2.2$ M^{-1} s^{-1} for 1-chloropropane. [c] Cf. k_{hyd} for $RNi(tmc)^+$ complexes (R = alkyl); the rate constants[6] lie in the range (0.8–2.7) × 10^{-2} s^{-1}. [d] Equal quantities of ethylene and propene, along with some *n*-pentane and 1-pentene from disproportionation of the 1-pentyl radical that results from reaction of the hydrolysis product (1-bromopentane) with $Ni(tmc)^+$ (see Scheme I). [e] Assumed from relative rates of 2° and 1° RBr's; smaller amounts of $(tmc)NiCH_2(CH_2)_2CH(Br)CH_3$ may be formed, hydrolyzing to 2-bromopentane.

complexes ($LM-(CH_2)_4-ML$; M = Co,[9-11] Rh;[12] L = N_4 macrocycle) are also observed, especially in reactions that proceed by nucleophilic (i.e., two-electron) pathways, and cyclobutane is formed in the reactions with *tert*-butyllithium.[13,14] Ethylene does result from reduction of 1,4-dibromobutane with lithium. A Grob-type rearrangement of $Br-(CH_2)_4-Li$ has been suggested.[15] In the case of $(tmc)Ni(CH_2)_3CH_2Br^+$, however, one can discount a Grob-type rearrangement, eq 3, since only 1-bromobutane results



$$(tmc)Ni^+-CH_2-CH_2-CH_2-CH_2-Br \not\rightarrow Ni(tmc)^{2+} + 2C_2H_4 + Br^- \quad (3)$$

from nickel–carbon bond hydrolysis, whereas ethylene requires the addition of $Ni(tmc)^+$ in at least trace quantities. A tetramethylene diradical, known[16] to undergo competitive cyclization and fragmentation, is also ruled out since no cyclobutane was observed here.

We suggest instead that ethylene formation is initiated by a second electron-transfer step, namely, the reaction between $Ni(tmc)^+$ and $(tmc)Ni(CH_2)_3CH_2Br^+$, eq 4.[17] This is supported

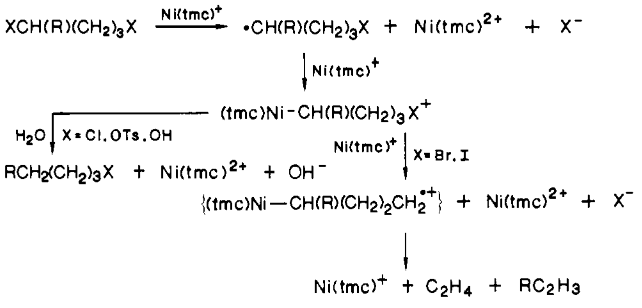
$$Ni(tmc)^+ + (tmc)Ni(CH_2)_3CH_2Br^+ \rightarrow BrNi(tmc)^+ + (tmc)Ni(CH_2)_3CH_2^{\bullet+} \quad (4)$$

by the similarity of the directly measured k_4 with rate constants for analogous bromine atom abstraction reactions[4] between $Ni(tmc)^+$ and bromoalkanes (Table II). It may be that a metallacyclopentane intermediate then intervenes and that ethylene is formed from it.

$$(tmc)Ni(CH_2)_3CH_2^{\bullet+} \rightarrow c\text{-}\{(tmc)Ni(CH_2)_4{}^+\} \rightarrow Ni(tmc)^+ + 2C_2H_4 \quad (5)$$

There is considerable precedent for metallacycle formation,[15,18,19]

Scheme I[a]



[a] R = H, CH_3.

Table II. Rate Constants[a,b] for Halogen–Atom Abstraction Reactions between $Ni(tmc)^+$ and Substituted Halobutanes

halobutane	$10^{-3}k$/ M^{-1} s^{-1}	proposed $RNi(tmc)^+$ int., R =
$Br(CH_2)_4Br$	4.5[b,c]	$Br(CH_2)_4^-$
$CH_3CH(Br)(CH_2)_3Br$	4.3[d]	none
$Br(CH_2)_4Cl$	3.6[c]	$Cl(CH_2)_4^-$
$Br(CH_2)_4OTs$	*e*	$TsO(CH_2)_4^-$
$Br(CH_2)_4OH$	*e*	$HO(CH_2)_4^-$
$[M(CH_2)_4Br]^+$	1.6[c,f]	

[a] At 25.0 °C and 0.010 M NaOH. [b] Value is $k/2$, corrected statistically for comparison purposes. [c] Compare $k = 1.5 \times 10^3$ M^{-1} s^{-1} for 1-bromobutane. [d] Compare $k = 2.8 \times 10^3$ M^{-1} s^{-1} for 2-bromopropane. [e] Not determined. [f] M = $Ni(tmc)^+$.

although this macrocyclic system is sufficiently sterically crowded about nickel that we must also consider an internal electron-transfer reaction with concerted C=C bond formation and Ni–C bond breaking, that avoids a cyclic intermediate. The subtle distinction requires the use of structurally rigid dihalides that will not permit metallacycle formation, as being planned at this time.

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Holes in the Oxygen (2p) Valence Bands and the Concomitant Formation of Peroxide-like Species in Metal Oxides: Their Role in Metallicity and Superconductivity[†]

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Presence of electron holes in the valence bands of binary as well as complex copper chalcogenides has been recognized for sometime.[1-3] Holes in the valence bands of these compounds are induced by the presence of $Cu^{1+}(3d^{10})$ ions, giving rise to interesting structural distortions and electronic properties. Presence of such holes also explains[4] the instability of Fe_2S_3 with respect to FeS and FeS_2; here, electrons of S^{2-} origin create holes in the

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