can be seen in these figures, both malonate moieties bind to three different calcium ions. The geometries of the hydrogen benzylmalonate ions are comparable with those of the free acid[27] and those found in both the barium complex[12] and the methylguanidinium salt[28] of this ion. As is usually the case in substituted malonate structures, in molecule B the two carboxyl groups are nearly orthogonal. The dihedral angle between the planes O(1b)–C(1b)–O(2b) and O(3b)–C(3b)–O(4b) is 92°, the group at C(1b) being 14° out of the central atom plane [C(1b)–C(2b)–C(3b)] while that at C(3b) forms an angle of 82° with this plane. In molecule A, however, the two carboxyl groups are almost coplanar, the dihedral angle between them being only 5°. This result is very surprising, but it is noteworthy that in the methylguanidinium salt of the related hydrogen ethylmalonate ion, the corresponding dihedral angle of 21° is also relatively small.[28] The present value of 5° is, however, the smallest such angle reported to date. The approximate coplanarity of the carboxyl groups of molecule A is clearly seen in both Figures 1 and 3.

The present structural study, in conjunction with previous related work, serves to underscore our contention that a major reason for the presence of Gla rather than Glu in calcium-binding proteins is the ability of Gla to provide extra carboxylate moieties that are used to form extensive polymeric arrays linking several calcium centers to each other. This aggregation, along with the extraordinary flexibility of calcium in adapting to a wide variety of binding sites, clearly allows the protein to discriminate between calcium and magnesium since the stereochemical requirements of magnesium are very rigid[10] and this precludes the formation of polymeric networks involving magnesium.

Registry No. $Ca(bzmalH)_2$, 114058-41-2.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (U_{ij}) (3 pages); a table of observed and calculated structure amplitudes (12 pages). Ordering information is given on any current masthead page.

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Cyclopentane Formation in the Reduction of 1,5-Dihaloalkanes with a Nickel(I) Macrocycle

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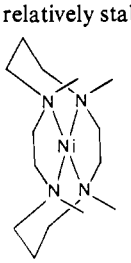
Alkyl halides are known[1,2] to react with the nickel(I) macrocycle[3] $Ni(tmc)^+$ to yield a relatively stable organometallic entity.



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

With 1,5-dihalopentanes, $X(CH_2)_5X$ (X = Br, I), however, cyclopentane is produced in nearly quantitative yield. We report here how this rare[4–7] transformation occurs, since mechanistic precedents are few indeed, and synthetic applications of this easily accessible[8] nickel reagent may be considerable.

Table I. Rate Constants[a] for Reactions of Bromoalkyl Compounds with $Ni(tmc)^+$

dihalide	$10^{-3}k/M^{-1}\ s^{-1}$	monohalide	$10^{-3}K/M^{-1}\ s^{-1}$
$Br(CH_2)_4Br$	4.5[b]	$(tmc)Ni(CH_2)_4Br^+$	1.6
$Br(CH_2)_5Br$	4.2[b]	$(tmc)Ni(CH_2)_5Br^+$	3.2
$Br(CH_2)_4Cl$	3.6	1-bromobutane	1.5
		1-bromopentane	1.0

[a] 25.0 °C, 0.020 M NaOH, μ = 0.10 M. [b] Statistically corrected; values are $k/2$.

The reaction between $Ni(tmc)^+$ and $X(CH_2)_5X$ (eq 1) actually occurs in steps. Initially, the reaction proceeds by the accepted[1,2]

$$2Ni(tmc)^+ + X(CH_2)_5X \rightarrow 2XNi(tmc)^+ + c\text{-}C_5H_{10} \quad (1)$$

atom-transfer (i.e., inner-sphere electron-transfer) mechanism, first to yield $X(CH_2)_4CH_2^\bullet$ and thence (when this radical reacts with a second $Ni(tmc)^+$) the organometallic complex $(tmc)Ni(CH_2)_4CH_2X^+$. Cyclopentane is formed by the $Ni(tmc)^+$-catalyzed decomposition of $(tmc)Ni(CH_2)_5X^+$ (eq 2).

$$(tmc)Ni(CH_2)_5X^+ \xrightarrow{Ni(tmc)^+} XNi(tmc)^+ + c\text{-}C_5H_{10} \quad (2)$$

The following observations pertain to the reaction of 1,5-dibromopentane and related compounds: (1) Spectrophotometric titrations established that $Ni(tmc)^+$ and $Br(CH_2)_5Br$ react in a 2:1 ratio, the same as when monohaloalkanes react with $Ni(tmc)^+$. (2) Cyclopentane is the major product (80–98% by vapor-phase chromatography), accompanied by minor (2–20%) but variable amounts of 1-bromopentane, 5-bromo-1-pentene, and *n*-pentane, depending on the reaction conditions. The highest yields of cyclopentane are observed when excess $Ni(tmc)^+$ is used. (3) 1-Bromopentane and 5-bromo-1-pentene are completely absent when the nickel(I) reagent is used in excess. (4) With even the slightest excess of $Ni(tmc)^+$, the characteristic absorption spectrum of an organonickel complex was not seen. (5) With excess 1,5-dibromopentane, however, the visible absorption spectrum of an organonickel complex[6,7] was observed. This intermediate shows an absorption maximum at 405 nm ($\epsilon \sim 2 \times 10^3\ M^{-1}\ cm^{-1}$). It was identified as $(tmc)Ni(CH_2)_5Br^+$, because it hydrolyzes[9] to 1-bromopentane upon standing or when H_3O^+ is added. The unimolecular rate constant for hydrolysis is $1.7 \times 10^{-2}\ s^{-1}$, which lies in the same narrow range found for almost all other $RNi(tmc)^+$ complexes.[9] (6) Addition of $Ni(tmc)^+$ to the organometallic intermediate causes its "immediate" decomposition, accompanied by cyclopentane formation. This reaction is catalytic, requiring but a trace of excess $Ni(tmc)^+$. (7) The rate constants for the reaction of $Ni(tmc)^+$ with $Br(CH_2)_4Br$, $Br(CH_2)_5Br$, $Br(CH_2)_4Cl$, $Br(CH_2)_4OH$, $Br(CH_2)_4OTs$, and $(tmc)Ni(CH_2)_4Br^+$ are all very similar and are close to those for primary monobromoalkanes, as the values[10] given in Table I show. This provides additional evidence upon which we base our conclusion that the initial reaction of $Ni(tmc)^+$ with $X(CH_2)_5X$, like that

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(2) Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 3267.
(3) The complex[4] 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 not confusing, simply as $Ni(tmc)^+$.
(4) Radical-induced reactions of 1,5-diiodopentane with peroxides form cyclopentane in only 4–8% yields: Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 4059.
(5) An unsuccessful attempt to observed ϵ-elimination has been reported: Trahanovsky, W. S.; Doyle, M. P. *J. Org. Chem.* **1967**, *32*, 146.
(6) Cyclopentane results in reactions of 1,5-dihaloalkanes with sodium naphthalenide (Garst, J. F.; Barbas, J. T. *J. Am Chem. Soc.* **1974**, *96*, 3329) and with *tert*-butyllithium (Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098).
(7) The reaction of $Co(CN)_5^{3-}$ with 1,5-diiodopentane yields 1-pentane (94%) and *cis*-2-pentene (6%); no cyclopentane is formed: Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.
(8) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435.
(9) Ram, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4115.
(10) At 25.0 °C and 0.010 M NaOH. Values cited for the dibromides are $k/2$, corrected statistically for comparison purposes.

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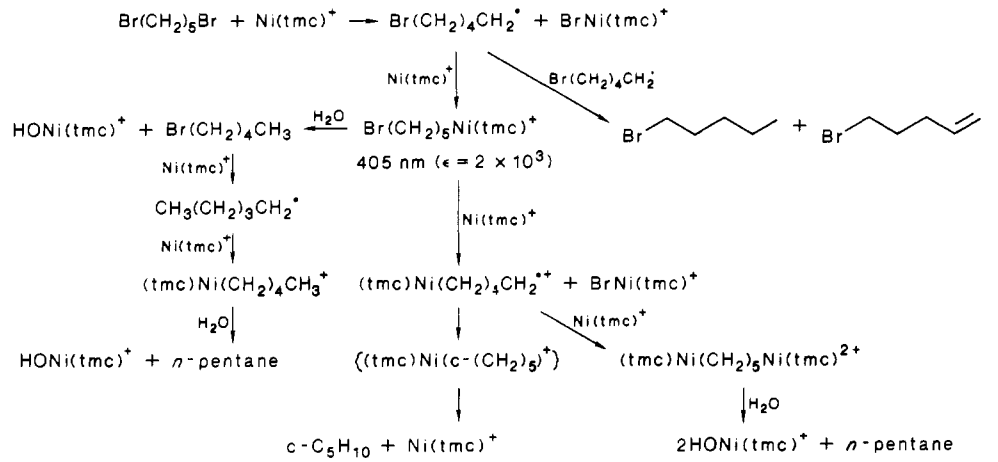
Scheme I



with RX, proceeds by an electron-transfer reaction via the radical $X(CH_2)_4CH_2^{\bullet}$.

The reactions shown in Scheme I are consistent with all of the observations cited. The byproduct 1-bromopentane forms from hydrolysis when the halide is in excess, and *n*-pentane results from hydrolysis of the *n*-pentylnickel complex. These products do not appear when $Ni(tmc)^+$ is employed in excess. Similarly, 5-bromo-1-pentene, presumed to arise along with 1-bromopentane from disproportionation of 5-bromo-1-pentyl radical, is not observed when excess $Ni(tmc)^+$ is used. That is so because with excess $Ni(tmc)^+$ the preferred reaction is capture of the radical, followed by $Ni(tmc)^+$-catalyzed decomposition of the organometallic species so formed. The similarity of all of the rate constants for bromine atom abstraction permits all of the possible products to accumulate, although their distribution naturally depends on the concentration of the reagent in excess and the order of addition. *Cyclopentane formation is essentially quantitative when Ni(tmc)$^+$ is held in large stoichiometric and local excess.*

The similarity of the rate constant for $Ni(tmc)^+$ with $Br(CH_2)_5Br$ and $CH_3(CH_2)_4Br$ constitutes one line of evidence that the initial step in both is the same reaction, Br atom abstraction. This reaction produces the organometallic intermediate $(tmc)Ni(CH_2)_4CH_2Br^+$ by a faster reaction, radical capture. The organometallic intermediate leads to cyclopentane; this reaction also starts by the reaction of the organonickel complex with a $Ni(tmc)^+$, to yield a terminal radical, $(tmc)Ni(CH_2)_4CH_2^{\bullet+}$. This species, the precursor of cyclopentane, may then form a metallacyclohexane that undergoes reductive elimination to form cyclopentane and regenerate the $Ni(tmc)^+$ catalyst, as shown in Scheme I.

Whether the putative metallacycle is an intermediate or activated complex, cannot, however, be ascertained from these data. The rate at which the intermediate $(tmc)Ni(CH_2)_4CH_2^{\bullet+}$ reacts, whether by metallacycle formation or otherwise, must greatly exceed the rate of its capture by $Ni(tmc)^+$ to form a straight-chain dimetallic alkane. Since the rate constants for the capture of other aliphatic radicals by $Ni(tmc)^+$ are $\sim 10^7$–10^8 M^{-1} s^{-1},[6,7] we estimate the unimolecular rate constant by which $(tmc)Ni(CH_2)_4CH_2^{\bullet+}$ yields cyclopentane to be $>10^5$ s^{-1}.

The reaction between the Ni(0)–bipyridyl complex and $Br(CH_2)_5Br$ produces cyclopentane in good yield (83%).[11] This reaction is suggested to proceed by an organonickel intermediate, although it is not known whether it is a metallacycle[12,13] or a dimetallic[14] complex. This reaction[11] is not fully analogous to our observations, however, since it requires an aprotic solvent (THF, ether, acetone, etc.), yielding only *n*-pentane in protic solvents like methanol and ethanol.

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