F430 Model Chemistry. Evidence for Alkyl- and Hydrido-Nickel Intermediates in the Reactions of the Nickel(I) Octaethylisobacteriochlorin Anion

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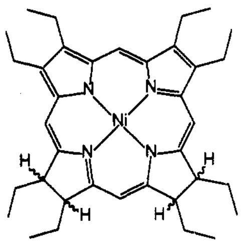
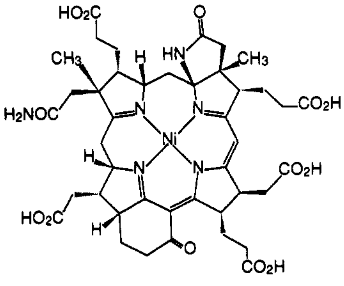
The reactions of $Ni^I(OEiBC)^-$ with alkyl (isomeric propyl, butyl, and hexyl) and aryl halides were investigated in acetonitrile, dimethylformamide, and tetrahydrofuran solutions. The principal products result from reduction or dehydrohalogenation of the alkyl or aryl halide. Alkene formation is favored by more polar solvents and by secondary vs primary substitution of the alkyl halide. Isomerization of alkenes occurs during the reaction, which strongly implies the intermediacy of hydrido–nickel and alkyl–nickel intermediates. Coupling processes, which produce significant quantities of ethane from methyl iodide, become insignificant as the length or steric bulk of the alkyl group increases. No coupling products are observed for aryl or benzyl halides. The current observations provide strong support for the nonradical nickel-based mechanism previously proposed and suggest that the dehydrohalogenation processes in this system involve β-hydride elimination.

The mechanisms by which the nickel(I) octaethylisobacteriochlorin anion, $Ni^I(OEiBC)^-$, reacts with electrophiles are of interest because of their relevance to the reactivity of the nickel(I) form of the hydrocorphinoid compound F430.[1–3] F430 is the nickel-containing prosthetic group of methyl coenzyme M reductase, which catalyzes the reductive cleavage of the thioether-cofactor methyl coenzyme M in the final step of methanogenesis[4] and may catalyze the reductive dehalogenation of chlorinated hydrocarbons by methanogenic bacteria.[5] F430 and isobacteriochlorins are the only tetrapyrrole compounds for which nickel(I) complexes have been isolated.[6–8]



Ni(OEiBC)



F430

All available evidence shows that the reaction of $Ni^I(OEiBC)^-$ with alkyl halides follows second-order kinetics.[1,3] The rate constants are substantial and decrease with increasing bulk of the substrate alkyl group. This suggests both that $Ni^I(OEiBC)^-$ is an extremely reactive nucleophile and that alkyl–nickel intermediates are formed in the initial step of these reactions. The nature of the product-forming steps that follow in the mechanism is not as well established. Reaction with ethyl iodide or tosylate yields ethane, ethylene, and butane.[2] These products could result from the disproportionation and combination of ethyl free radicals, which in turn could form by homolysis of the alkyl–nickel intermediate. However, the solvent dependence of the product distribution and other evidence establish that free-radical processes are at most minor contributors to the mechanism. We proposed that a competition between proton donor and excess alkyl halide for reaction with a common alkyl–nickel intermediate determined the relative yields of the reduction and coupling products, ethane and butane, respectively. The dehydrohalogenation product, ethylene, forms either by β-hydride elimination from an alkyl–nickel complex or by an E_2 elimination of HX in which $Ni^I(OEiBC)^-$ functions as a base. Hydrido–nickel complexes are invoked in both of these mechanisms and were also proposed as intermediates in the formation of H_2 that results from the reaction of $Ni^I(OEiBC)^-$ with proton donors.[2]

In this paper we extend our investigations of the reactivity of $Ni^I(OEiBC)^-$ with electrophiles to include reactions with phenyl, benzyl, cyclopropylcarbinyl, and the isomeric propyl, butyl, and hexyl halides. Our results establish that coupling processes become less important as the steric bulk of the alkyl group increases and that the $Ni^I(OEiBC)^-$ reaction system isomerizes terminal alkenes to internal alkenes. These observations strongly support the intermediacy of alkyl- and hydrido–nickel complexes and our proposed mechanism.

Experimental Section

General Methods. Ni(OEiBC) was prepared by literature methods.[6] The purification of solvents and reagents, the treatment of glassware, and the precautions employed in manipulating compounds were described previously.[2] Alkyl and aryl halide substrates and the alkane, alkene, and arene products that were expected to be produced from them were purchased from Aldrich or ChemService and were the best grade available. Gaseous C_3 and C_4 products were purchased from Scott Specialty Gases, Inc., as pure compounds or analyzed gas mixtures in nitrogen. The methylcyclopropane used as a GC standard was generated in a mixture with 1-butene by reaction of 0.037 M cyclopropylcarbinyl bromide in neat tri-*n*-butyltin hydride (3.8 M).[9] All alkyl and aryl halide substrates were distilled immediately before use. Primary alkyl halides purified in

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this manner typically were better than 99.9% pure by GC analysis, whereas secondary and tertiary halides were typically 99.5% pure.

Reactions and Product Analyses. Procedures for the sodium mercury amalgam reduction of Ni(OEiBC), reaction of $Ni^I(OEiBC)^-$ with substrates, and sampling and GC analysis of head-space gases were reported previously.[2] In order to minimize the introduction of adventitious "products" (see below), the ratio of substrate to nickel(I) was decreased relative to that employed in earier investigations. In addition, each experiment was accompanied by a simultaneous blank experiment. The blank was identical in all respects save only that Ni(OEiBC) was omitted. The solvent that was used in the blank experiment was from the same batch of pretreated solvent used to prepare the $Ni^I(OEiBC)^-$ solution. The amounts of products detected in the blank experiments were negligible compared to that produced in the nickel(I)-dependent reaction, with the exception of the cases of secondary, tertiary, and phenyethyl halides in DMF. Significant quantities of alkenes were formed in these cases, presumably as a result of elimination catalyzed by base produced during the reduction of Ni(OEiBC) by reaction of amalgam with the residual water in dried DMF. The quantity of products observed in the nickel(I)-dependent reactions were corrected by subtraction of the quantity observed in blank experiments.

To prevent loss on standing, head-space gases were sampled first with the valved injection system described previously.[2] Microliter syringes were then used to sample and inject the solution. Products were identified by comparison of their retention times to those of individual pure compounds and mixtures of known composition. The mixtures were also used to ensure that the separation method could reliably resolve the expected products.

Propane, propene, hexane, and 2,3-dimethylbutane, the products from propyl halides, were separated on a 6-ft Poropak Q column (50–160 °C ramp). An 8-ft 0.19% picric acid on Graphpac-GC column (30 °C) was used to separate 1-butene and methylcyclopropane, the products from cyclopropylcarbinyl bromide, and to separate butane, the isomeric butenes, isobutane, and isobutylene, the products from butyl halides. Hexane and the isomeric hexenes from the hexyl halides were separated on a 30-ft 23% AT-1700 on Chromasorb P-AW (90 °C, 30 mL/min flow). The later two columns were unable to resolve the coupling products octane and dodecane from excess alkyl halide or solvent. These products were analyzed in separate experiments on a 6-ft OV-17 column (40–250 °C). A 6-ft OV-101 column (50–190 °C) was used to separate the benzene, toluene, styrene, biphenyl, and bibenzyl products from phenyl and benzyl halides. All columns were thoroughly conditioned prior to use and regenerated after each run by holding the oven at a temperature slightly below the column maximum until the solvent and alkyl halide eluted from the column.

Results

The reaction of $Ni^I(OEiBC)^-$ with methyl and ethyl halides proceeds by competing reduction, coupling, and dehydrohalogenation paths.[2] The mass balance of the reaction, which has a stoichiometry of 2:1 Ni(I):R–X, is essentially complete in THF.

Analysis of the products afforded by the substrates considered here is more challenging than analysis of the products derived from methyl and ethyl halides. One problem is introduction of adventitious "products" in the substrate. Unlike methyl and ethyl halides, which have volatile decomposition products, GC analyses of undistilled alkyl halides or distilled alkyl halides that had been permitted to stand showed that they contained several major impurities at greater than percent levels. Identifiable impurities included the corresponding alkane, the alkenes derived by dehydrohalogenation, and the alkanes produced by coupling two molecules of the alkyl halide. Because alkyl halide is typically added in 100–200-fold molar excess relative to $Ni^I(OEiBC)^-$, the use of impure substrates directly introduces "products" in amounts comparable to or greater than that produced in the reaction. Blank experiments showed that this was not a significant problem for purified substrates. A second problem is the distribution of products. The products from methyl and ethyl halides are located predominantly in the head space of the reaction vessel. The products formed in this study were expected to distribute between the head space and the solution. Moreover, the widely different volatilities and solubilities of the expected products in particular reactions (for example, butene vs octane) raised the possibility that the distributions of the individual products could be quite different. To obtain a complete picture, both phases were analyzed for products. The actual products were such that differential distribution was not a significant problem. However, the errors associated with determining the number of moles of products in both phases plus the uncertainties introduced by corrections for the blank experiments led to relatively large errors in determining the absolute quantities of products produced. We did not attempt to determine the mass balance as a consequence. Rather, we determined and report only the relative number of moles of products formed, which is known much more precisely. The information obtained in this case is quite informative.

Table I. Products of the Reactions of $Ni^I(OEiBC)^-$ with Alkyl and Aryl Halides

		relative yield,[a] %		
reactant	product	CH_3CN	THF	DMF
1-iodopropane	propane	72	87	25
	propene	28	13	75
	hexane	*b*		
1-bromopropane	propane		96	42
	propene		4	58
2-iodopropane	propane	55	70	7
	propene	45	30	93
	2,3-dimethylbutane	*b*		
2-bromopropane	propane		72	12
	propene		28	88
1-bromobutane	butane		67	33
	1-butene		10	64
	cis-2-butene		9	1
	trans-2-butene		14	2
2-bromobutane	butane		tr[c]	4
	1-butene		tr[c]	16
	cis-2-butene		35	17
	trans-2-butene		65	63
1-bromo-2-methylpropane	isobutane		29	30
	isobutylene		71	70
2-bromo-2-methylpropane	isobutane		15	3
	isobutylene		85	97
1-bromohexane	hexane		100	81
	1-hexene			19
	cis-2-hexene			tr[c]
	trans-2-hexene			tr[c]
2-bromohexane	hexane		3	10
	1-hexene		85	24
	cis-2-hexene		4	13
	trans-2-hexene		8	53
	trans-3-hexene			tr[c]
3-bromohexane	hexane			10
	1-hexene			0
	cis-2-hexene			9
	trans-2-hexene			47
	trans-3-hexene			34
iodobenzene	benzene			100
4-bromotoluene	toluene		100	100
benzyl bromide	toluene		100	100
(1-bromoethyl)benzene	styrene		100	
cyclopropylcarbinyl bromide[d]	methylcyclopropane			5
	1-butene		100	95

[a] Relative yields of products determined by GC analysis of the solution phase of reaction mixture. Product distributions in the head-space gases were similar, although slightly enriched in the more volatile products. [b] Product was a minor component (<10%) of the head-space gases but was not detected in solution phase. [c] Peak observed, but too small and broad to integrate reliably. [d] Reduction with neat butyl tin hydride gave 6:94 methylcyclopropane:1-butene.

Table I presents the relative yield of products in the solution phase from the reactions of $Ni^I(OEiBC)^-$ with phenyl, benzyl, cyclopropylcarbinyl, and the isomeric propyl, butyl, and hexyl halides in acetonitrile, THF, and DMF solutions. The reactivities of $Ni^I(OEiBC)^-$ in these solvents are typical of the extremes of behavior observed in different solvents.[2] The relative yields of products in the head-space gases are similar to those reported in Table I, differing at most by slight enrichment in the more volatile

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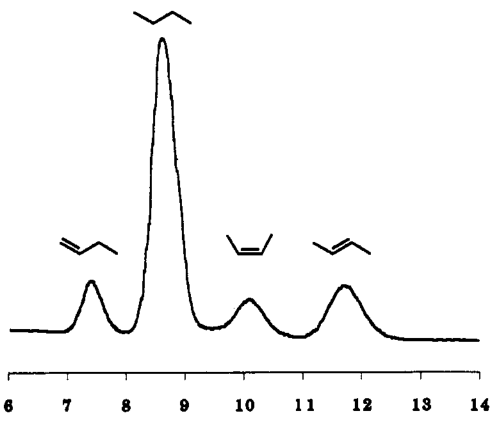


Figure 1. Gas chromatogram of the products of the reaction of 1-bromobutane with $Ni^I(OEiBC)^-$ in THF.

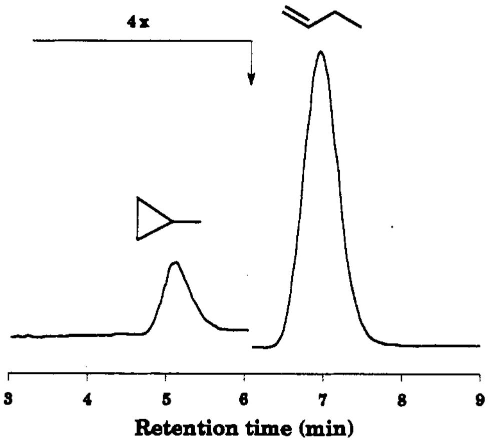


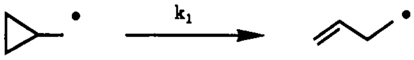
Figure 2. Gas chromatogram of the products of the reaction of cyclopropylcarbinyl bromide with $Ni^I(OEiBC)^-$ in DMF. The vertical scale is decreased by a factor of 4 at $t = 6.1$ min.

products. The identity and yields of products that we report here for several substrates do not agree with those reported by others.[3]

A striking feature of the data in Table I is the nearly complete absence of products derived from coupling of the alkyl or aryl halides. Small amounts of the coupling product hexane or 2,3-dimethylbutane were observed in the head space when 1- or 2-iodopropane, respectively, were reacted with $Ni^I(OEiBC)^-$ in acetonitrile solution. None was detected in the solution phase of these reactions, which implies that very little of the coupling product was formed. No coupling products were observed when these substrates were reacted with $Ni^I(OEiBC)^-$ in THF or DMF. Furthermore, no coupling products were produced for any other substrate investigated here, including several like benzyl bromide which afford reasonably stable free radicals. In combination with our earlier data,[2] the current results establish that the coupling pathway becomes unimportant as the length or steric bulk of the alkyl group increases.

The predominant product formed in the reaction of primary alkyl halides with $Ni^I(OEiBC)^-$ in THF is the alkane produced by direct reduction. Alkene formation by dehydrohalogenation becomes increasingly significant for secondary and tertiary alkyl halides. Alkenes are the major product for all alkyl halides in the more polar solvent DMF. This is consistent with the observed solvent dependence of the formation of ethylene from ethyl iodide.[2] Interestingly, the alkenes formed are not simply those that can be obtained by direct elimination of hydrogens β to the halogen. As illustrated in Figure 1, the reaction of 1-bromobutane and $Ni^I(OEiBC)^-$ affords the internal alkenes *cis*- and *trans*-2-butene in quantitites greater than that of the direct elimination product 1-butene. Control experiments show that $Ni^I(OEiBC)^-$ itself does not isomerize alkenes.

Figure 2 shows the results of the reaction of $Ni^I(OEiBC)^-$ with cyclopropylcarbinyl bromide in DMF. This substrate is frequently used as a free radical clock because the rearrangement of the cyclopropylcarbinyl radical to the 1-butenyl radical, eq 1, which



(1)

has $k_1 = 1.0 \times 10^8\ s^{-1}$ at 25 °C, is one of the fastest known radical skeletal rearrangements.[10] The direct reduction product methylcyclopropane accounts for 5% of the product, which is only slightly less than that afforded by reduction with neat tri-*n*-butyltin hydride.[9] In contrast, only 1-butene is observed when the reaction of this substrate with $Ni^I(OEiBC)^-$ is carried out in THF.

Discussion

The nickel-based mechanism outlined in eqs 2–8 is consistent with all of our previous observations about the reactions of $Ni^I(OEiBC)^-$ with alkyl halides.[1,2] The nucleophilic attack of $Ni^I(OEiBC)^-$ on R–X, eq 2, is second order and rate limiting. The reduction of the initial alkyl–nickel intermediate by a second equivalent of $Ni^I(OEiBC)^-$ explains the 2:1 Ni(I):R–X stoichiometry of the overall reaction and is in accord with the observation that electrocatalytic reduction of alkyl halides is mediated by Ni(OEiBC) at the potential of the Ni(II)/Ni(I) couple. Furthermore, the kinetics of the reduction of the 17-e^- neutrally charged alkyl–nickel complex by the 17-e^- anionic Ni(I) complex should be rapid. The product-forming reactions follow the rate-determining step of the mechanism. The relative yields of the reduction and coupling products depend on a competition between a proton donor and excess alkyl halide for the common alkyl–nickel intermediate, $R\text{–}Ni^{II}(OEiBC)^-$, eqs 4 and 5, respectively. Consistent with this, simultaneous addition of proton donors and methyl iodide to $Ni^I(OEiBC)^-$ completely suppresses the formation of ethane. The formal dehydrohalogenation of alkyl halides to alkenes can occur by β-hydride elimination from the alkyl–nickel intermediates, eqs 6 and 7, orby an E_2 elimination of HX in which $Ni^I(OEiBC)^-$ functions as a base, eq 8. Both of these mechanisms require the formation of hydrido–nickel complexes, which we also proposed as intermediates in the production of H_2 from $Ni^I(OEiBC)^-$ and proton donors.[2]

$$Ni^I(OEiBC)^- + R\text{–}X \rightarrow R\text{–}Ni^{III}(OEiBC) + X^- \quad (2)$$

$$R\text{–}Ni^{III}(OEiBC) + Ni^I(OEiBC)^- \rightarrow R\text{–}Ni^{II}(OEiBC)^- + Ni^{II}(OEiBC) \quad (3)$$

$$R\text{–}Ni^{II}(OEiBC)^- + HA \rightarrow R\text{–}H + Ni^{II}(OEiBC) + A^- \quad (4)$$

$$R\text{–}Ni^{II}(OEiBC)^- + R\text{–}X \rightarrow R\text{–}R + Ni^{II}(OEiBC) + X^- \quad (5)$$

$$R\text{–}Ni^{II}(OEiBC)^- \rightarrow H\text{–}Ni^{II}(OEiBC)^- + R_{-H} \quad (6)$$

$$R\text{–}Ni^{III}(OEiBC) \rightarrow H\text{–}Ni^{III}(OEiBC) + R_{-H} \quad (7)$$

$$Ni^I(OEiBC)^- + R\text{–}X \rightarrow H\text{–}Ni^{III}(OEiBC) + R_{-H} + X^- \quad (8)$$

An alternative mechanistic scheme, eqs 9–13 plus eq 4, requires the intermediacy of free radicals. An important feature of this scheme is that coupling and dehydrohalogenation products arise only from the respective combination, eq 10, and disproportionation, eq 11, of the free radicals. In contrast, direct reduction products result from free radicals by (1) hydrogen atom transfer

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[10] (a) Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275. (b) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687.

$$\text{R–Ni}^{\text{III}}(\text{OEiBC}) \rightarrow \text{Ni}^{\text{II}}(\text{OEiBC}) + \text{R}^{\bullet} \tag{9}$$

$$2\text{R}^{\bullet} \xrightarrow{k_{10}} \text{R–R} \tag{10}$$

$$2\text{R}^{\bullet} \xrightarrow{k_{11}} \text{R–H} + \text{R}_{-\text{H}} \tag{11}$$

$$\text{R}^{\bullet} + \text{HS} \xrightarrow{k_{12}} \text{R–H} + \text{S}^{\bullet} \tag{12}$$

$$\text{R}^{\bullet} + \text{Ni}^{\text{I}}(\text{OEiBC})^{-} \xrightarrow{k_{13}} \text{R–Ni}^{\text{II}}(\text{OEiBC})^{-} \tag{13}$$

$$\text{Ni}^{\text{I}}(\text{OEiBC})^{-} + \text{R–X} \rightarrow \text{Ni}^{\text{II}}(\text{OEiBC}) + \text{R}^{\bullet} + \text{X}^{-} \tag{14}$$

from solvent or other donor, eq 12, (2) disproportionation of free radicals, eq 11, and (3) colligation, eq 13, followed by protonation of the resulting R–$Ni^{II}(OEiBC)^-$, eq 4. The absence of hydrido–nickel complexes in this scheme is also noteworthy. Helvenston and Castro favor a mechanism of this type and propose an unprecedented S_N2-NBF (no bond formed) process, eq 14.[3] The latter invokes a three-electron attack of $Ni^I(OEiBC)^-$ on alkyl halide that has the sensitivity to steric factors of an S_N2 process but that leads to concerted production of free radicals without the intermediacy of an alkyl–nickel complex.[11]

Certain evidence from earlier studies is not consistent with a major role for the free radical mechanism.[1,2] The cessation of coupling processes on addition of proton donors (as opposed to hydrogen atom donors) cannot be rationalized directly. The marked solvent dependence of the ratio of ethylene to butane produced from ethyl–X is inconsistent with the involvement of free radicals. The ratio of the rate constants for disproportionation and combination of free radicals, k_{11}/k_{10}, is not strongly affected by the reaction medium.[12] Finally, to the extent that product formation occurs by eqs 10–12, the stoichiometry of the reaction will approach 1:1 rather than the experimentally determined 2:1. Note that the sum of eqs 9, 13, and 4 represents the same net chemical change as the sum of eqs 3 and 4.

The decrease in the importance of the coupling pathway with increasing length of the alkyl group that we report here provides strong support for the nickel-based mechanism and is incompatible with the free radical mechanism. The rate of eq 5 should decrease as the steric bulk of the R group increases. Thus, as we observe, coupling should be disfavored relative to reduction as the R group gets larger. In contrast, the proportion of coupling should be independent of the size of the R group if a free radical mechanism operates. The ratio k_{11}/k_{10} is virtually identical for primary ethyl, propyl, and butyl radicals.[12b] Furthermore, the decrease in coupling cannot be attributed to increases in the rates of competing processes. The rate constant for the hydrogen transfer reaction, k_{12}, with both tri-*n*-butyltin hydride[13] and thiophenol[14] is insensitive to the radical structure. Colligation rate constants, k_{13}, for several Cr[15] and Co[15,16] complexes decrease by at most a factor of 3 as $R^{\bullet}$ varies over the series CH_3, primary, and secondary. Two different isomers of $Ni(cyclam)^{2+}$ show a much greater decrease in k_{13} over this series.[17] However, this would result in an increase in the proportion of free radicals involved in self-reactions, which in turn would give a net increase in coupling products.

The observation of alkene rearrangement during the reaction of $Ni^I(OEiBC)^-$ with alkyl halides provides considerable mechanistic insight. Alkene formation by radical disproportionation, eq 11, or by E_2 elimination, eq 8, can only introduce a C=C bond between the halogen-bearing carbon and an adjacent carbon. No facile mechanism for alkene isomerization exists for these pathways. On the other hand, alkene isomerization is a characteristic reaction of transition metal hydride complexes.[18] Insertion of the alkene into the metal hydride bond affords an alkyl–metal complex. If insertion occurs in a manner such that a terminal alkene produces a secondary alkyl–metal complex, β-hydride elimination of the adjacent 3-H can afford the 2-alkene. Thus, production of *cis*- and *trans*-2-butene from 1-bromobutane provides compelling evidence for the existence of both alkyl- and hydrido–nickel intermediates and for the reversibility of eqs 6 and/or 7. It also appears to rule out E_2 elimination, eq 8, as the sole pathway for alkene formation. Further support for the last conclusion can be found in the distribution of alkenes produced from 2-bromobutane. The distribution does not match that which would be expected on the basis of the statistical and steric availability of adjacent hydrogens to a base.

The reaction of cyclopropylcarbinyl bromide with $Ni^I(OEiBC)^-$ in DMF was reported to afford 1-butene as the sole product.[3] This result was presented as evidence of free radical intermediates. We reexamined the reaction and found that it affords 5% methylcyclopropane and 95% 1-butene in DMF. No methylcyclopropane was detected when the reaction was run in THF. Newcomb and Curran discussed the dangers of employing the rearrangements of cyclopropylcarbinyl halides as qualitative mechanistic probes for radical reactions and suggested that the radical ring opening be used only as a clock in reactions *known* to proceed via radical intermediates.[19] The difficulty is that these halides can rearrange to butenyl products in processes that involve radical, anionic,[20] and cationic[21] intermediates as well as in processes that lack free intermediates.[22] Thus, the predominant formation of 1-butene by itself does not necessarily imply a radical mechanism. In the case of the reaction with $Ni^I(OEiBC)^-$ in DMF, the assumption that the observed product distribution is solely the result of free radical processes leads to difficulties. The observed distribution and reasonable estimates of the concen-

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(11) See footnote 22 of ref 3.

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(23) If one assumes that only free radical processes operate, then the rate constant k_1 for cyclopropylmethyl radical ring opening, eq 1, is roughly 19 times larger than the sum of the pseudo-first-order rate constants for colligation, eq 13, and hydrogen atom transfer, eq 12; i.e. $k_1 = 19(k_{13}[\text{Ni(I)}] + k_{12}[\text{HS}])$. Hydrogen atom transfer from DMF does not compete with ring opening of the radical. H–Ni(OEiBC) is a more efficient donor. The initial concentration of $Ni^I(OEiBC)^-$ in the experiment was 2×10^{-4} M. Half of this material would be consumed in the production of radicals, giving an approximate initial concentration of Ni(I) of 10^{-4} M for the colligation reaction. The concentration of H–Ni(OEiBC) would be much smaller. Given $k_1 = 1.0 \times 10^8$ s^{-1}, a lower estimate of the second-order rate constants for the cyclopropylmethyl radical would be roughly 5×10^{10} M^{-1} s^{-1}! The rate constant for colligation of the sterically similar radical $(CH_3)_2CHCH_2^{\bullet}$ to $Ni(cyclam)^{2+}$ is 3.40×10^7 for the α-isomer and $< 2 \times 10^5$ for the β-isomer.[17] Colligation of the sterically less demanding $CH_3^{\bullet}$ radical occurs with a rate constant of about 1×10^9 M^{-1} s^{-1} to both isomers of $Ni(cyclam)^{2+}$ and to Ni[tetrakis(4-sulfonatophenyl)porphyrin].[17,24] Co and Cr complexes, whose colligation rate constants are relatively insensitive to steric effects, have rate constants for CH_3 of (1–4) $\times 10^8$ M^{-1} s^{-1}.[15,16]

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trations of intermediate species would then require that the rate constant for colligation of the cyclopropylmethyl radical by $Ni^{I}(OEiBC)^{-}$, eq 13, be larger then diffusion control and be several orders of magnitude larger than known colligation rate constants.[23] Moreover, the rate constant is sufficiently large that a major portion of radicals produced by homolysis of $R–Ni^{III}(OEiBC)$, eq 9, would be scavenged by colligation with $Ni^{I}(OEiBC)^{-}$, eq 13, and would not form products via free radical equations, eqs 10–12. Overall, the discussion suggests that non free radical processes must play some role in the reactions of cyclopropylcarbinyl bromide. This conclusion is consistent with other results of our investigations.

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