J. Am. Chem. Soc. **1986**, *108*, 713–719

samples of CuTPP in frozen solution and polycrystalline ZnTPP gave the same H||z ENDOR spectrum as CuTCP. Therefore, the discrepancy is not due to a difference in sample composition. Second, the study by Brown and Hoffman[13] established that the three components of the proton hyperfine tensor have the same sign. By contrast, in [CuTCP]$_2$ A_x^H, $A_y^H > 0$ and $A_z^H < 0$. An analysis of the ENDOR spectra from phenyl-deuterated CuTPP in frozen toluene-d_8–CDCl$_3$, on the other hand, leads to the conclusion that A_x^H, A_y^H, $A_z^H > 0$. Figure 6 shows spectra obtained with z, z', and xy field settings (cf. Figure 1a). Computer-calculated spectra are given by the dotted lines. Computer simulations of the xy spectrum established unequivocally that A_x^H and A_y^H must have the same sign. With the z' setting, the ENDOR spectrum contains contributions from the H||z orientation as well as from molecules oriented so that H lies on a cone making an angle of approximately 50° with the molecular z axis. The shape of this spectrum is sensitive to the relative signs of all three hyperfine components. It was found that only a calculation based on the assumption that the three components have the same sign gives a result that fits the experimental spectrum. It is hard to conceive of a mechanism that would cause the A_z^H value of the pyrrole protons to change sign upon going from CuTCP to [CuTCP]$_2$. The possibility that the hyperfine shifted peaks in the z^- and z^+ spectra are not due to the pyrrole protons cannot be excluded and this seems to offer the most satisfactory explanation for the results.

Table I shows that, except for the A_z^H data, the results obtained in this study closely match those reported for CuTPP.[13] Apparently the introduction of the crown ether groups does not perturb the electronic structure of the Cu porphyrin core. The single crystal measurements show that the three ^{14}N hyperfine tensor components must have the same sign. The same conclusion is reached with regards to the proton hyperfine tensor components. The theoretical analysis presented by Brown and Hoffman[13] is based on the assumption that the hyperfine coupling components are all positive. The ENDOR study of [CuTCP]$_2$ provides evidence that this is correct. It is noteworthy that the ENDOR study of phenyl-deuterated CuTPP demonstrates that information on *relative* signs can be derived from spectra of samples in powders or frozen solution as well.

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Kinetics and Mechanism of the Alkylnickel Formation in One-Electron Reductions of Alkyl Halides and Hydroperoxides by a Macrocyclic Nickel(I) Complex

Andreja Bakac* and James H. Espenson*

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received July 8, 1985*

Abstract: The nickel(I) macrocycle Ni(1*R*,4*R*,8*S*,11*S*-tmc)$^+$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) reacts readily with primary alkyl halides in alkaline aqueous solutions, yielding alkylnickel(II) complexes, RNi(tmc)$^+$. The reaction is proposed to occur in two steps, the first and rate-limiting being one-electron transfer from Ni(tmc)$^+$ to RX, either by halogen atom transfer or outer-sphere electron transfer, to yield an alkyl radical R·. The latter is captured by Ni(tmc)$^+$ in a second and more rapid reaction. This mechanism is supported by the nature of the alkylnickel complexes produced, by the reactivity order within a series of alkyl halides (methyl < primary < secondary), and by the trapping of the carbon-centered radical $CH_2CH(CH_2)_3CH_2\cdot$ in competition with its cyclization. Free radicals are also involved in the formation of alkylnickel complexes in reactions of Ni(tmc)$^+$ with alkyl hydroperoxides. No organonickel formation is observed in reactions with benzyl bromide, whereas benzyl chloride yields the short-lived PhCH$_2$Ni(tmc)$^+$. The steady-state concentration of benzyl radicals in the faster PhCH$_2$Br reactions is too high to allow significant coupling with Ni(tmc)$^+$ in competition with the radical self-reaction. With 2-propyl halides the alkylnickel complex is also not formed because radical coupling occurs in preference to the Ni–C bond formation owing to steric reasons.

Reactions of alkyl halides with reduced metal ions are among the most convenient synthetic routes for the preparation of organotransition-metal complexes. The great interest in these reactions lies additionally in the variety of mechanisms involved in the metal–carbon bond formation. A distinction among a halogen atom transfer,[1-6] electron transfer,[7] or oxidative addition[8-13] is usually possible on the basis of the reactivity order within a series of alkyl halides, detailed product analysis, trapping of radical intermediates, and stereochemistry around the α-carbon.

The rich chemistry of nickel and its importance in catalytic processes have prompted a number of studies of the reduction of alkyl halides by nickel complexes. These reactions are generally characterized by a multiplicity of reaction pathways and a diversity

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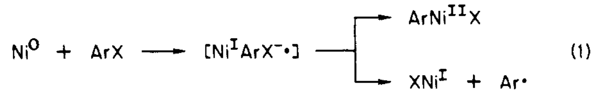
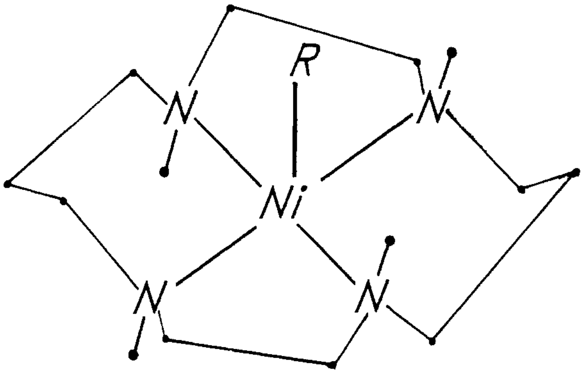
of products.[14,15] For example, the reaction between aryl halides and $Ni(PEt_3)_4$ produces nickel(I) in addition to the expected oxidative addition product ArNiX.[16] In the proposed mechanism both arise from a single intermediate (eq 1). Related oxidative



$$Ni^0 + ArX \longrightarrow [Ni^IArX^{-}\cdot] \longrightarrow \begin{cases} ArNi^{II}X \\ XNi^I + Ar\cdot \end{cases} \quad (1)$$

additions to nickel(0) complexes yield nickel(II) products,[17] mixtures of nickel(I) and nickel(II),[18-21] or nickel(I) alone.[18,22] The organonickel(II) products can react further with alkyl/aryl halides in coupling or disproportionation reactions.[16,23,24]



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

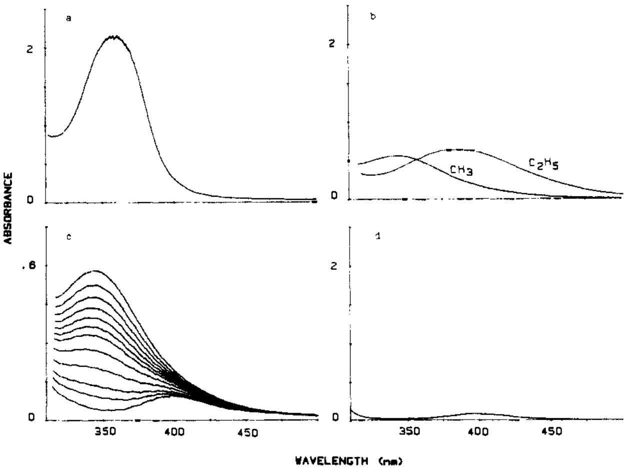
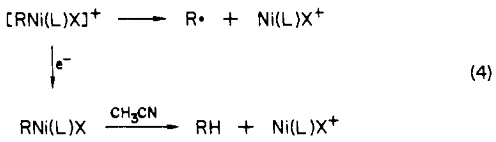


Figure 1. Spectral changes in the reactions of $Ni(tmc)^+$ with alkyl halides: (a) 5.5×10^{-4} M $Ni(tmc)^+$; (b) $CH_3Ni(tmc)^+$ and $C_2H_5Ni(tmc)^+$ formed upon addition of excess CH_3I or C_2H_5I, respectively, to a; (c) Decomposition of $CH_3Ni(tmc)^+$ formed in b. Repetitive scans were taken over a period of 5 min; (d) 5.5×10^{-4} M $Ni(tmc)^{2+}$. All solutions contained 0.2 M $(CH_3)_2CO$, 1 M $(CH_3)_2CHOH$, and 0.01 M NaOH.

Our interest in the area arose from reports[25-29] that nickel(II) macrocycles including $Ni(R,R,S,S\text{-tmc})^{2+}$ (henceforth $Ni(tmc)^{2+}$),[30,31] first synthesized by Barefield and co-workers,[32] catalyze the electrochemical reduction of alkyl halides in acetonitrile and because a long-lived nickel(I) complex can be prepared.[31] In the proposed mechanism for electrocatalysis[25-29] nickel(II) is first reduced to nickel(I), which then undergoes oxidative addition with alkyl halide yielding an organonickel(III) complex, eq 2–3. The latter then rapidly yields products derived from the radical or carbanion, as in eq 4.

$$NiL^{2+} \xrightarrow{e^-} NiL^+ \quad (2)$$

$$NiL^+ + RX \longrightarrow [RNi(L)X]^+ \quad (3)$$



$$[RNi(L)X]^+ \longrightarrow R\cdot + Ni(L)X^+$$
$$\Big\downarrow e^- \quad (4)$$
$$RNi(L)X \xrightarrow{CH_3CN} RH + Ni(L)X^+$$

Interest in the chemistry of macrocyclic complexes of nickel has been enhanced further by the recent discovery of Factor F430, a cofactor of methanogenic bacteria. It is the first nickel-containing tetrapyrrole found in living organisms.[33] Interestingly, all methanogenic bacteria investigated to date incorporate nickel during growth and synthesize Factor F430.[33b]

In this work we have examined reactions of directly prepared $Ni(tmc)^+$ with several alkyl halides in aqueous solution. The strongly reducing potential, $E° = -0.90$ V, and reasonable stability of this nickel(I) complex in alkaline aqueous solutions[31] make it an ideal candidate for such a study. The electrocatalytic properties of $Ni(tmc)^{2+}$ in CH_3CN[26] and the ready availability of the nickel(I) complex have provided us with a unique opportunity to examine directly the chemistry of the proposed reactive species in the catalytic cycle. We find that under our experimental conditions $Ni(tmc)^+$ reacts with alkyl halides by a *one-electron mechanism* yielding alkylnickel(II) complexes, $RNi(tmc)^+$.

Experimental Section

$Ni(tmc)(ClO_4)_2$ was prepared according to the published procedure.[32] The complex was reduced to $Ni(tmc)^+$ electrochemically[31] at −1.3 V vs.

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(30) (a) We are thankful to a referee for pointing out the discrepancies in the nomenclature sometimes adopted for this and related compounds. The complex used in this work, (1*R*,4*R*,8*S*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), which we abbreviate as $Ni(R,R,S,S\text{-tmc})^{2+}$ or simply as $Ni(tmc)^{2+}$, has been known in the literature as *trans*-III-$Ni(tmc)^{2+}$ or *R*,*S*,*S*,*R*-$Ni(tmc)^{2+}$. In the latter name there is a mismatch in the numbering of nitrogens and the designators of their chirality. (b) The complex $Ni(R,R,S,S\text{-tmc})^{2+}$ is one of several isomers, which include the form $Ni(R,S,R,S\text{-tmc})^{2+}$. There is no interconversion of the two nickel(II) complexes in aqueous solution over extended periods of time. The nickel(I) complexes, on the other hand, are much less stable toward isomerization such that aqueous solutions of pure $Ni(R,R,S,S\text{-tmc})^+$ or pure $Ni(R,S,R,S\text{-tmc})^+$ isomerize to a mixture with an approximate ratio of 3:1 of the two isomers, respectively, in several hours at room temperature. Similar observations relating to transformations of $Ni(R,R,S,S\text{-tmc})^+$ have been reported by others,[32] although they were not attributed to this particular isomerization. Investigations of the chemistry of the $Ni(R,S,R,S\text{-tmc})^+$ will be reported separately (Ram, M. S.; Bakac, A.; Espenson, J. H., to be published).

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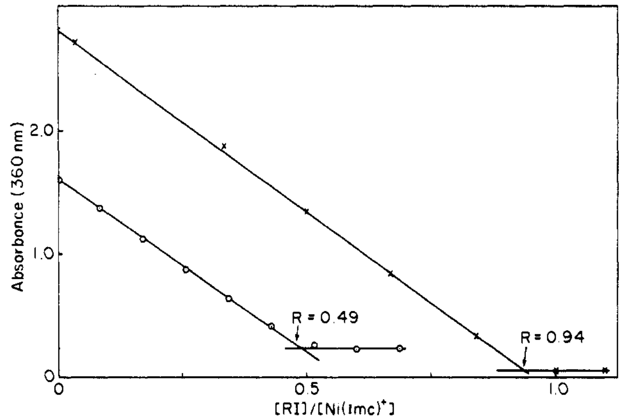

Figure 2. Spectrophotometric titrations of Ni(tmc)$^+$ with 1-C_4H_9I (circles) and 2-C_3H_7I (crosses).

SCE. The reduction was usually carried out to only ~50% completion to avoid contamination with oxygen which presented some problems if electrolysis was prolonged. (A reaction between Ni(tmc)$^+$ and oxygen at low oxygen levels not only reduces the yield of Ni(tmc)$^+$ but also produces some unidentified yellow product(s), most likely oxo- and/or peroxonickel species, which interfere with the chemistry of Ni(tmc)$^+$. Complicated reactions of macrocyclic nickel(I) complexes with low concentrations of oxygen have been reported earlier.[27,34]) Electrochemically prepared stock solutions containing (0.5–1) × 10^{-3} M Ni(tmc)$^+$ were kept at 0 °C and used within several hours of preparation to ensure isomeric purity.[30b]

In other experiments Ni(tmc)$^+$ was prepared photochemically. The method[35] is based on the photochemistry of acetone and the strongly reducing properties of $(CH_3)_2CO^{-}\cdot$. Typically an air-free solution of Ni(tmc)$^{2+}$ in 0.1 M acetone and 1 M 2-propanol at pH 11–12 was irradiated for 60–90 s in a Rayonet UV-reactor. The reduction was quantitative, but the presence of 2-propanol limited the usefulness of these solutions. Ni(tmc)$^+$ prepared by Zn/Hg reduction of Ni(tmc)$^{2+}$ suffered from similar problems owing to the presence of Zn(II) in solution; among other factors, Zn(II) appears to dealkylate the RNi(tmc)$^+$ complexes.

All the experiments were carried out in an atmosphere of Cr^{2+}-scrubbed argon, nitrogen, or helium in alkaline solutions owing to the extreme sensitivity of Ni(tmc)$^+$ and RNi(tmc)$^+$ to oxygen and H^+. Alkyl halides were distilled prior to use. Spectral and kinetic data were obtained by use of Cary 219 and Perkin-Elmer Lambda Array 3840 spectrophotometers. A Canterbury SF 3A stopped-flow spectrophotometer was used for kinetic measurements on faster reactions.

Organic products were analyzed by gas chromatography and in some cases by GC/MS.[36] Quantitative determination of the free iodide ions produced in reactions of Ni(tmc)$^+$ with alkyl iodides was done spectrophotometrically (ϵ_{228} = 1.46 × 10^4 M^{-1} cm^{-1}) after the reaction solutions had been acidified to 1 M $HClO_4$.[37] Formaldehyde produced in the Ni(tmc)$^+$-catalyzed decomposition of *tert*-butyl hydroperoxide was determined by the chromotropic acid method.[38] Since *tert*-butylhydroperoxide interferes with this analysis, the reaction was carried out such that Ni(tmc)$^+$ was present even at the end of experiments in which several catalytic turnovers had occurred. The amount of unreacted Ni(tmc)$^+$ in these experiments was determined spectrophotometrically at λ 360 nm.

Results

Table I. Spectral Data for Some RNi(tmc)$^+$ Complexes[a]

R	λ_{max}	10^{-3} ϵ/M^{-1} cm^{-1}
CH_3	346	2.44
C_2H_5	390	2.40
C_3H_7	388	2.51
$CH_2CH(CH_2)_3CH_2$ + c-$C_5H_9CH_2$[b]	420	1.90

[a] In (1–100) × 10^{-3} M NaOH. [b] ~1:9 mixture of the two isomers.

Table II. Yields of CH_2O in the Methanol-Promoted Catalytic Decomposition of $(CH_3)_3COOH$ in the Presence of Excess Ni(tmc)$^+$ [a]

[Ni(tmc)$^+$][b]	[$(CH_3)_3COOH$][b]	[$(CN_3)_3COOH$]$_{xs}$[c]	[CH_2O]
3.88	15.6	13.7	15.1
4.96	21.8	19.3	18.5
8.10	31.2	27.2	29.1

[a] All concentrations in 10^{-5} M. Experiments were run so as to preserve an excess of Ni(tmc)$^+$ during the catalyzed decomposition of the hydroperoxide. [b] Amount reacted. [c] Amount of hydroperoxide used in excess of the ideal stoichiometry of eq 10.

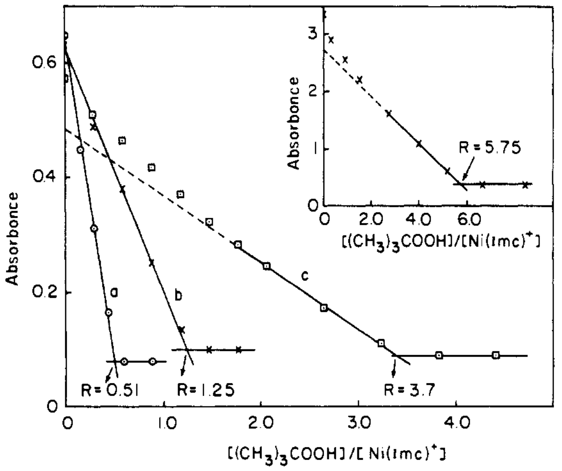

Figure 3. Spectrophotometric titrations of Ni(tmc)$^+$ with $(CH_3)_3COOH$ in (a) H_2O; (b) 4 M CH_3OH; (c) 16 M CH_3OH. Conditions: pH 11.8 (NaOH), μ = 0.15 M ($LiClO_4$), [Ni(tmc)$^+$]$_0$ = 7.5 × 10^{-5} M, λ 360 nm (2 cm cell). Inset: titration in 8.3 M 2-C_3H_7OH, [Ni(tmc)$^+$]$_0$ = 3.9 × 10^{-4} M.

Stoichiometry. Upon addition to excess CH_3I to a solution of Ni(tmc)$^+$ the band at λ 360 nm (ϵ = 4.0 × 10^3 M^{-1} cm^{-1}) rapidly disappears, to be replaced by a less intense band at λ 346 nm. A subsequent slower reaction produces the much weaker absorptions of Ni(tmc)$^{2+}$ (λ_{max} 400 nm). These changes are illustrated in Figure 1. At low levels of CH_3I the two stages of the reaction occur simultaneously. The stoichiometry of the overall reaction, eq 5, was determined by a spectrophotometric titration

$$2Ni(tmc)^+ + CH_3I + H_2O \rightarrow 2Ni(tmc)^{2+} + I^- + CH_4 + OH^- \quad (5)$$

and by iodide and methane analyses. On the basis of these data and those presented later we formulate the sequence of reactions between Ni(tmc)$^+$ and CH_3I as follows

$$Ni(tmc)^+ + CH_3I \xrightarrow{k_1} Ni(tmc)^{2+} + I^- + \cdot CH_3 \quad (6)$$

$$Ni(tmc)^+ + \cdot CH_3 \rightarrow CH_3Ni(tmc)^+ \quad (7)$$

$$\text{overall:} \quad 2Ni(tmc)^+ + CH_3I = CH_3Ni(tmc)^+ + Ni(tmc)^{2+} + I^- \quad (8)$$

This is later followed by

$$CH_3Ni(tmc)^+ + H_2O \rightarrow CH_4 + Ni(tmc)^{2+} + OH^- \quad (9)$$

Higher straight chain alkyl halides react with Ni(tmc)$^+$ in analogous reactions. The results of a spectrophotometric titration of Ni(tmc)$^+$ with *n*-C_4H_9I are shown in Figure 2. Spectral data for some RNi(tmc)$^+$ complexes are summarized in Table I.

The oxidation of Ni(tmc)$^+$ with *tert*-butylhydroperoxide also produces $CH_3Ni(tmc)^+$, as confirmed by the appearance of an absorption maximum in the UV spectrum at 346 nm and by the decomposition rate of the product which is within the experimental error identical with that measured in CH_3I experiments (3.8 × 10^{-3} s^{-1} vs. 4.1 × 10^{-3} s^{-1} at 25 °C in solutions containing (0.8–1.5) × 10^{-4} M $CH_3Ni(tmc)^+$ and 0.033 M NaOH at 0.1 M ionic strength). Spectrophotometric titrations, Figure 3, in purely

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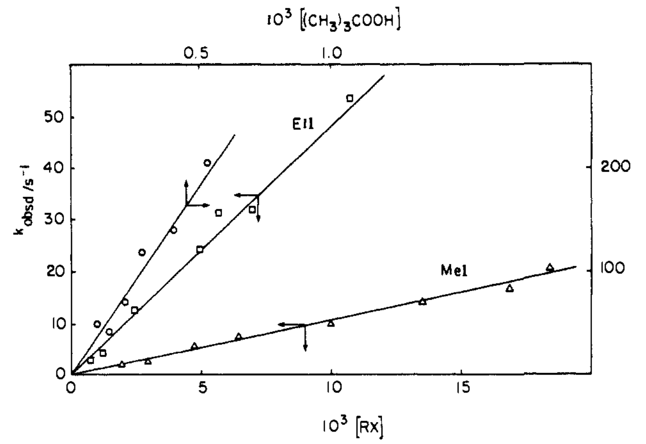


Figure 4. Kinetic data for the reactions of Ni(tmc)$^+$ with CH_3I (△), C_2H_5I (□), and $(CH_3)_3COOH$ (○) at 25 °C, μ = 0.50 M, $[Ni(tmc)^+]_0$ = (1.2–9.2) × 10^{-5} M, [OH$^-$] = (10–175) × 10^{-3} M.

aqueous solutions yielded a ratio $R = [(CH_3)_3COOH]/[Ni(tmc)^+]$ of 0.51, consistent with the stoichiometry of eq 10. Also presented

$$2Ni(tmc)^+ + (CH_3)_3COOH \rightarrow Ni(tmc)^{2+} + CH_3Ni(tmc)^+ + (CH_3)_2CO + OH^- \quad (10)$$

in Figure 2 are the results of the spectrophotometric titrations in aqueous alcoholic solutions. Upon addition of methanol or ethanol, the stoichiometric ratio R increases from its value in H_2O (0.51) to 3.7 in 16 M CH_3OH and 5.75 in 8.3 M $(CH_3)_2CHOH$. In addition, the titration plots become significantly nonlinear in alcohol-containing solutions. The yields of formaldehyde produced in aqueous methanolic solutions, Table II, are within the experimental error identical with the amount of $(CH_3)_3COOH$ used in excess over the ideal 2:1 stoichiometry of eq 10. The yields of $CH_3Ni(tmc)^+$ are comparable to those obtained in purely aqueous solutions, i.e., the reaction eventually sacrifices the Ni(tmc)$^+$ "catalyst", which is lost to alkylnickel formation. The reaction stoichiometry in CH_3OH/H_2O is given in eq 11.

$$2Ni(tmc)^+ + (1 + n)(CH_3)_3COOH + nCH_3OH \rightarrow CH_3Ni(tmc)^+ + Ni(tmc)^{2+} + (CH_3)_2CO + OH^- + n(CH_3)_3COH + nCH_2O + nH_2O \quad (11)$$

The reactions of both $PhCH_2Cl$ and $PhCH_2Br$ with Ni(tmc)$^+$ are too fast to be measured by the stopped-flow technique. That with $PhCH_2Br$ takes place with an approximate 1:1 stoichiometry and produces no identifiable organonickel species. The cloudiness caused by the precipitation of bibenzyl made it impossible to determine the stoichiometry precisely.

The reaction of Ni(tmc)$^+$ with $PhCH_2Cl$ is concentration dependent. At higher concentrations of Ni(tmc)$^+$ (≥3 × 10^{-4} M) and less than stoichiometric quantities of $PhCH_2Cl$, Ni(tmc)$^+$ and $PhCH_2Cl$ are consumed in a 2:1 stoichiometric ratio. The reaction produces a red intermediate with a short lifetime ($t_{1/2}$ ~ 0.8 s at 25 °C), which we presume to be $PhCH_2Ni(tmc)^+$. At low initial $[Ni(tmc)^+]$ (≤5 × 10^{-5} M), and in the presence of an excess of $PhCH_2Cl$ the stoichiometry is approximately 1:1. No organonickel is produced under those conditions, and $(PhCH_2)_2$ is the sole organic product.

The reaction of $(CH_3)_2CHI$ with Ni(tmc)$^+$ takes place with a 1:1 stoichiometry, Figure 2, and produces no detectable alkylnickel intermediates, eq 12. The products are the C_3 and C_6

$$(CH_3)_2CHI + Ni(tmc)^+ \rightarrow Ni(tmc)^{2+} + I^- + \{C_3H_6 + C_3H_8 + (CH_3)_2CHCH(CH_3)_2\} \quad (12)$$

hydrocarbons which can result from several sources, including the self-reaction of 2-propyl radicals. The same stoichiometry and hydrocarbon products were obtained with $(CH_3)_2CHBr$ and $(CH_3)_2CH(CH_3)_2OOH$.

Kinetics of the Alkylnickel Formation. The kinetic studies were conducted in the presence of a large excess of sufficiently soluble alkyl halides (CH_3I, C_2H_5I, C_2H_5Br, 1-C_3H_7I, 2-C_3H_7I, 1-C_4H_9I) or $(CH_3)_3COOH$. Under these conditions all the reactions showed good pseudo-first-order kinetics. Plots of k_{obsd} vs. concentration of the reagent in excess were linear with zero intercepts (Figure 4), consistent with the rate expression of eq 13. The results for

$$-\frac{d[Ni(tmc)^+]}{dt} = 2k[Ni(tmc)^+][RX] \quad (13)$$

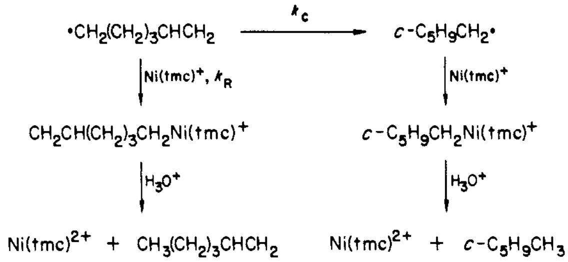
alkyl halide reactions are summarized in Table III. The value of k for $(CH_3)_3COOH$ is 1.78 × 10^5 M^{-1} s^{-1}. Stock solutions of $Br(CH_2)_4CHCH_2$ and 1-$C_6H_{13}Cl$ were made up in methanol owing to their low solubility in water. Kinetic solutions thus contained 0.02–0.82 M CH_3OH. Both halides reacted according to the rate law of eq 13, although the formation and decomposition of c-$C_5H_9CH_2Ni(tmc)^+$/$CH_2CH(CH_2)_4Ni(tmc)^+$ took place on similar time scales necessitating the use of a consecutive kinetics treatment. Activation parameters for the reaction of Ni(tmc)$^+$ with $Br(CH_2)_4CHCH_2$ have values $\Delta H^\ddagger$ = 50.0 ± 0.3 kJ/mol and $\Delta S^\ddagger$ = −15.4 ± 0.9 J/mol K.

Table III. Kinetics of Reduction of Alkyl Halides by Ni(tmc)$^{+a}$

R	10^{-3} k/M^{-1} s^{-1}, X = I	Br	Cl
CH_3	0.540 (8)		
C_2H_5	2.40 (7)	0.39 (1)	
1-C_3H_7	1.94 (2)		
1-C_4H_9	2.80 (2)	1.0 (3)	
2-C_3H_7	18.0 (4)		
$CH_2CH(CH_2)_3CH_2$		1.52 (1)^b	
		0.938 (4)^c	
		0.610 (9)^d	
		0.393 (5)^e	
1-C_6H_{13}			≤0.002^f

^{a} Conditions as in Figure 4. Number of runs averaged is given in parentheses. ^{b} t = 20 °C. ^{c} 15 °C. ^{d} 9.7 °C. ^{e} 3.9 °C. ^{f} Some decomposition/autoxidation of Ni(tmc)$^+$ took place on the time scale of the reaction.

Scheme I



Radical Capture by Ni(tmc)$^+$. One-electron reduction of 6-bromo-1-hexene produces 1-hexenyl radical, which undergoes cyclization to cyclopentylmethyl radical[39] with a rate constant of 2.2 × 10^5 s^{-1} at 25 °C.[39b] Further reduction of the two radicals produces 1-hexene and methylcyclopentane, respectively. In several instances[2,5,40] this cyclization reaction has provided support for the proposed one-electron reduction mechanism. In addition, the hydrocarbon product analysis allows one to use this as a radical clock and thus estimate the rate constant for the capture of the 1-hexenyl radical by Ni(tmc)$^+$ according to Scheme I. The reaction of Ni(tmc)$^+$ with $Br(CH_2)_4CHCH_2$ produces the organonickel species c-$C_5H_9CH_2Ni(tmc)^+$ and $CH_2CH(CH_2)_3CH_2Ni(tmc)^+$ which immediately hydrolyze to the respective hydrocarbons upon acidification. The distribution of hydrocarbon products is determined by the magnitude of the rate constants k_c and k_R and the concentration of Ni(tmc)$^+$. In all the experiments c-$C_5H_9CH_3$ accounted for ≥85% of the total hydrocarbon. The rate constant k_R was calculated from the

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(39) (a) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355. (b) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *Ibid.* **1981**, *103*, 7739.

(40) Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7145.

expression[41] of eq 14. The values at two different temperatures are $k_R = 6 \times 10^7$ M^{-1} s^{-1} (25 °C, $k_c = 2.2 \times 10^5$ s^{-1} [39b]) and 4 $\times$ 10^7 M^{-1} s^{-1} (0 °C, $k_c = 9 \times 10^4$ s^{-1} [39b]).

$$\frac{k_R}{k_c} = \frac{1}{[\mathrm{Ni(tmc)}^+]_0}\left(e^{2k_R[\mathrm{c\text{-}C_5H_9CH_3}]_\infty/k_c} - 1\right) \qquad (14)$$

Decomposition of Alkylnickel Complexes. In the absence of excess alkyl halide[37] the $\mathrm{RNi(tmc)^+}$ complexes decompose in alkaline solutions according to

$$\mathrm{RNi(tmc)^+ + H_2O \rightarrow RH + Ni(tmc)^{2+} + OH^-} \qquad (15)$$

The decomposition takes place on time scales from ≤ 1 min up to ~15 min at 25 °C depending on the reaction conditions and the nature of the group R. The results of a cursory study of the decomposition of $\mathrm{CH_3Ni(tmc)^+}$ indicate that the rate is pH independent in the pH range 11–13. On the other hand, trace amounts of the oxo/peroxonickel species, which are formed when traces of O_2 enter the systems, have a strongly accelerating effect on the decomposition rate. Owing to that, the decomposition rates generally increased with the age of the $\mathrm{Ni(tmc)^+}$ stock solution.

High initial concentrations of $\mathrm{Ni(tmc)^+}$ and/or $\mathrm{CH_3Ni(tmc)^+}$ in photochemically prepared solutions apparently stabilize $\mathrm{CH_3Ni(tmc)^+}$. The half-life for the $\mathrm{CH_3Ni(tmc)^+}$ decomposition in such solutions containing ~3 × 10^{-4} M $\mathrm{CH_3Ni(tmc)^+}$ and (1–3) × 10^{-3} M $\mathrm{Ni(tmc)^{2+}}$ is typically 500–1000 s, approximately 5 times longer than in the absence of a large excess of $\mathrm{Ni(tmc)^{2+}}$. This chemistry was not pursued further.

Upon acidification solutions of $\mathrm{RNi(tmc)^+}$ decompose instantaneously according to eq 16.

$$\mathrm{RNi(tmc)^+ + H^+ \rightarrow RH + Ni(tmc)^{2+}} \qquad (16)$$

A possibility that there is a homolytic component (i.e., the reversal of eq 7) in the decomposition of organonickel complexes was investigated for $\mathrm{C_2H_5Ni(tmc)^+}$. Under hydrolysis conditions, pH 11–13, homolysis (eq 17) is at best a minor pathway, as

$$\mathrm{C_2H_5Ni(tmc)^+ \rightarrow C_2H_5\cdot + Ni(tmc)^+} \qquad (17)$$

evidenced by the lack of any measurable amounts of $\mathrm{Ni(tmc)^+}$ among the products. Moreover, addition of $\mathrm{Ni(tmc)^+}$ to solutions of $\mathrm{C_2H_5Ni(tmc)^+}$ had no effect on the decomposition rate, consistent with the rate of eq 17 being much lower than that of eq 15. All attempts to promote homolysis by adding reagents which are known to react with $\mathrm{C_2H_5\cdot}$ and/or $\mathrm{Ni(tmc)^+}$ and would thereby shift the equilibrium in eq 17 to the right, failed owing to rapid direct reactions between $\mathrm{C_2H_5Ni(tmc)^+}$ and such potential scavengers as nitroxides, $\mathrm{Co(NH_3)_5F^{2+}}$, N_2O, $\mathrm{CH_3NO_2}$, H_2O_2, etc. Preliminary observations[30] indicate that the organonickel complexes in the (*R*,*S*,*R*,*S*) series are less reactive toward these and other reagents.

Discussion

Several lines of evidence strongly support our assignment of a one-electron mechanism to the reduction of alkyl halides by $\mathrm{Ni(tmc)^+}$, eq 6–9. The overall 2:1 stoichiometry in the organonickel formation step (RX = primary alkyl halide and benzyl chloride) identifies these complexes as organonickel(II) species. The reactivity order of $\mathrm{Ni(tmc)^+}$ toward alkyl halides is CH_3 < primary < secondary; it is apparently governed by the stability of the free radical (and possibly the standard reduction potential[42] of alkyl halides), similar to the other one-electron reductions,[1–6] Table IV. A reverse reactivity order is expected for two-electron processes owing to the dominant influence of steric effects in these reactions. This is exemplified by the data for $\mathrm{Co(dmgH)_2(PBu_3)^-}$ in Table IV.

The reduction of $\mathrm{(CH_3)_3COOH}$ in purely aqueous solutions yields $\mathrm{CH_3Ni(tmc)^+}$, eq 10. The occurrence of two one-electron steps in the reaction is confirmed by the overall stoichiometry and the nature of the products. It receives further support from the effect of alcohols on the stoichiometry. Radical participation in catalytic oxidations of alcohols by H_2O_2 and hydroperoxides has been well documented.[43] The $\mathrm{Ni(tmc)^+}$-catalyzed oxidation of alcohols by $\mathrm{(CH_3)_3COOH}$ can be easily accounted for by the following set of reactions taking methanol as example.

Table IV. Rate Constants (M^{-1} s^{-1}) for the Reduction of Alkyl Halides by Some Metal Complexes at 25 °C

RX	$\mathrm{Ni(tmc)^+}$ [a]	$\mathrm{Co(CN)_5{}^{3-}}$ [b]	Cr(15-ane)$^{2+}$ [c]	Co-$\mathrm{(dmgH)_2}$-$\mathrm{(PBu_3)^-}$ [d]
$\mathrm{CH_3I}$	540	0.01	0.046	2300
$\mathrm{C_2H_5I}$	2400	0.059	0.413	
1-$\mathrm{C_3H_7I}$	1940	0.043		
2-$\mathrm{C_3H_7I}$	1.80 × 10^4	1.20	4.93	3
$\mathrm{PhCH_2Cl}$	(~10^7)[e]	4.9 × 10^{-4}	323	440
$\mathrm{PhCH_2Br}$	(>10^8)[e]	2.33	1.91 × 10^4	

[a] This work. [b] Reference 3; in 80% aqueous $\mathrm{CH_3OH}$. [c] Reference 5; in 50% aqueous $\mathrm{(CH_3)_3COH}$. [d] Reference 8; in $\mathrm{CH_3OH}$. [e] Estimated values, see text.

$$\mathrm{Ni(tmc)^+ + (CH_3)_3COOH \rightarrow Ni(tmc)^{2+} + OH^- + (CH_3)_3CO\cdot} \qquad (18)$$

$$\mathrm{(CH_3)_3CO\cdot \rightarrow CH_3\cdot + (CH_3)_2CO} \qquad (19)$$

$$\mathrm{CH_3\cdot + Ni(tmc)^+ \rightarrow CH_3Ni(tmc)^+} \qquad (7)$$

$$\mathrm{(CH_3)_3CO\cdot + CH_3OH + OH^- \rightarrow CH_2O^-\cdot + (CH_3)_3COH + H_2O} \qquad (20)$$

$$\mathrm{CH_2O^-\cdot + Ni(tmc)^{2+} \rightarrow Ni(tmc)^+ + CH_2O} \qquad (21)$$

The length of the catalytic chain depends on the relative importance of reactions 19 and 20. The initial curvature of the titration plots in aqueous alcohols (Figure 3) is probably caused by reaction 22, which seems to be important only at the highest concentrations of $\mathrm{Ni(tmc)^+}$ used in this work.

$$\mathrm{Ni(tmc)^+ + (CH_3)_3CO\cdot + H_2O \rightarrow Ni(tmc)^{2+} + (CH_3)_3COH + OH^-} \qquad (22)$$

The $\mathrm{CH_3Ni(tmc)^+}$ complex has been synthesized earlier from $\mathrm{Ni(tmc)(CF_3SO_3)_2}$ and $\mathrm{(CH_3)_2Mg}$ and isolated as the trifluoromethanesulfonate salt.[44] The formal oxidation state of the nickel in this complex is thus undoubtedly 2+.

The 1:1 stoichiometry observed in the reactions of 2-propyl halides with $\mathrm{Ni(tmc)^+}$ and the failure to detect $\mathrm{(CH_3)_2CHNi(tmc)^+}$ could be explained by a change from a one-electron mechanism for the methyl and primary alkyl halides to a two-electron process for the secondary alkyl halides. The importance of steric effects in displacement reactions, however, makes this mechanistic change-over highly unlikely. Moreover, the observed reactivity order in Table III (methyl < primary < secondary) is as expected for a series of alkyl halides reacting by a one-electron mechanism. The overall stoichiometry is thus most likely determined by the course of events following the rate-determining step (rds), i.e.,

$$\mathrm{Ni(tmc)^+ + (CH_3)_2CHX \xrightarrow{rds} Ni(tmc)^{2+} + X^- + (CH_3)_2CH\cdot} \qquad (23)$$

$$\mathrm{2(CH_3)_2CH\cdot \rightarrow (C_3H_6 + C_3H_8 + C_6H_{14})} \qquad (24)$$

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(41) Note that these experiments utilized an excess of the alkyl halide over $\mathrm{Ni(tmc)^+}$, making the simpler expression of ref 5 inadequate in the present case.

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(44) D'Aniello, M. J., Jr.; Barefield, E. K. *J. Am. Chem. Soc.* **1976**, *98*, 1610. The maximum position in the UV spectrum at λ 346 nm obtained in this work matches well with λ_{max} 352 nm reported in this reference, although the value of the molar absorptivity has not been reported. The decomposition kinetics measured in this work ($t_{1/2}$ ~ 3 min) are somewhat faster than reported in ref 44 ($t_{1/2}$ ~ 15 min). This could be due to the presence of catalytic amounts of O_2 in stock solutions of $\mathrm{Ni(tmc)^+}$ as described in the text.

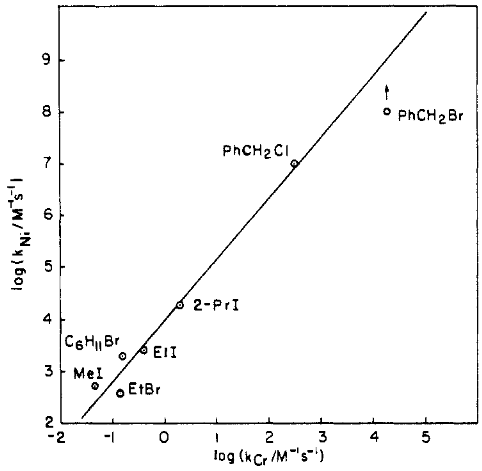


Figure 5. Correlation between the rate constants for the reduction of alkyl halides by $Ni(tmc)^+$ and $Cr(15\text{-}aneN_4)^{2+}$. Values of k_{Ni} for $PhCH_2Cl$ and $PhCH_2Br$ (lower limit) are estimates.

The failure of 2-propyl radicals to react with $Ni(tmc)^+$ can be traced to the steric crowding around the α-carbon. Indeed, molecular models show that methyl and methylene groups bound to the four macrocyclic nitrogens severely limit the acceptable bulk around the α-carbon of the incoming radical. Apparently only methyl and primary alkyls meet these requirements.[45]

The formation of bibenzyl in the reactions of $Ni(tmc)^+$ with benzyl bromide and benzyl chloride as well as the formation of benzylnickel under a limited set of conditions in the reaction with benzyl chloride strongly imply the intermediacy of benzyl radicals in both. The preferential formation of $(PhCH_2)_2$ over $PhCH_2Ni(tmc)^+$ in the reaction of $PhCH_2Br$ is probably closely linked to the very high rate of reaction 25, which makes the

$$PhCH_2Br + Ni(tmc)^+ \rightarrow PhCH_2\cdot + Ni(tmc)^{2+} + Br^- \qquad (25)$$

steady-state concentration of benzyl radicals quite high.[46] At high $[PhCH_2\cdot]$ reaction 26 is the dominant pathway for the disappearance of $PhCH_2\cdot$ and $PhCH_2Ni(tmc)^+$ formation, eq 27,

$$2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph \qquad (26)$$

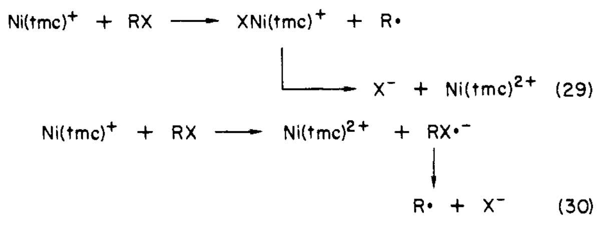
$$PhCH_2\cdot + Ni(tmc)^+ \rightarrow PhCH_2Ni(tmc)^+ \qquad (27)$$

is ruled out on kinetic grounds. Since no $PhCH_2Ni(tmc)^+$ was observed in the reaction of 5×10^{-4} M $Ni(tmc)^+$ and 2.5×10^{-4} M $PhCH_2Br$, one can estimate $k_{25} \geq 10^8$ M^{-1} s^{-1}, taking $k_{26} = 2.7 \times 10^9$ M^{-1} s^{-1} [47] and $k_{27} \sim 10^8$ M^{-1} s^{-1}. Similarly, from the limiting conditions for the $PhCH_2Ni(tmc)^+$ formation in the $PhCH_2Cl$ reaction, we calculate $k_{28} \sim 10^7$ M^{-1} s^{-1}. The formation

$$PhCH_2Cl + Ni(tmc)^+ \rightarrow Ni(tmc)^{2+} + PhCH_2\cdot + Cl \qquad (28)$$

of $c\text{-}C_5H_9CH_3$ in the $Br(CH_2)_4CHCH_2$ reaction provides additional support[48] for the one-electron mechanism in the alkyl halide reductions by $Ni(tmc)^+$. It also allows us to estimate the rate constant for the reaction of $Ni(tmc)^+$ with $\cdot CH_2(CH_2)_3CHCH_2$. The value $k_R = 6 \times 10^7$ M^{-1} s^{-1} is in the general range observed for the metal ion–radical coupling reactions.[49]

With the question of one-electron vs. two-electron reduction of alkyl halides by $Ni(tmc)^+$ settled, we turn to the characterization of the reaction mechanism in more detail. The distinction to be made is that between atom transfer, eq 29, and outer-sphere electron transfer, eq 30, in the rate determining step. The formation of substitutionally inert halometal(III) complexes in reactions of Cr(II) and Co(II)[1-6] with alkyl halides provides a reliable proof for the proposed atom transfer. Ni^{II}(tmc) complexes, on the other hand, are substitutionally extremely labile,[50] and other means must be sought to establish the reaction mechanism. The reactivity pattern in the $Ni(tmc)^+$ reduction of alkyl halides closely resembles that of $Cr(15\text{-}aneN_4)^{2+}$, Figure 5. Qualitatively, reactions of Cr^{2+} exhibit the same reactivity order.[51] A similar trend is also observed in reactions of $Co(CN)_5{}^{3-}$ with aliphatic halides. It is thus tempting to suggest that all four metal complexes react by the same atom-transfer mechanism. However, lack of available data for a demonstrably outer-sphere reduction of alkyl halides by a transition metal complex[52] makes this assignment somewhat speculative. Also, the relatively slow reactions of $Co(CN)_5{}^{3-}$ with benzyl halides are at present difficult to explain on that basis. Note that the carbon–halogen bond energies[53] (presumably crucial in determining the kinetics of atom transfer reactions) within the series of alkyl halides and their standard reduction potentials[42] (i.e., the driving force in outer-sphere electron-transfer reactions) follow similar trends. The expected effect on the reaction is thus qualitatively similar irrespective of the mechanism. For the present time, therefore, a decision between eq 29 and 30 seems unwarranted.



$$Ni(tmc)^+ + RX \longrightarrow XNi(tmc)^+ + R\cdot \;\; \llcorner\!\rightarrow X^- + Ni(tmc)^{2+} \qquad (29)$$

$$Ni(tmc)^+ + RX \longrightarrow Ni(tmc)^{2+} + RX\cdot^- \;\; \downarrow\; R\cdot + X^- \qquad (30)$$

Electrocatalytic reductions of alkyl halides in CH_3CN in the presence of macrocyclic nickel(II) complexes, including $Ni(R,R,S,S\text{-}tmc)^{2+}$, were proposed to take place through formation of alkylnickel(III) intermediates produced in oxidative addition reactions between $Ni(tmc)^+$ and alkyl halides.[25-29] Our results, on the other hand, unequivocally show that $Ni(tmc)^+$ reacts with alkyl and benzyl halides in aqueous alkaline solutions in one-electron processes. Possibly, the mechanism in CH_3CN is different from that in H_2O. Alternatively, a different mechanism can be proposed for the reactions in CH_3CN in light of our results on formation of organonickel complexes and their reactivity toward alkyl halides.

$$Ni^{II}L \xrightarrow{e^-} Ni^{I}L$$

$$2Ni^{I}L + RX \rightarrow Ni^{II}L + X^- + RNi^{II}L$$

$$RNi^{II}L + RX \rightarrow Ni^{II}L + 2R\cdot + X^-$$

$$2R\cdot \rightarrow (R_2 + R(-H) + RH)$$

$$RNi^{II}L \xrightarrow{CH_3CN} Ni^{II}L + RH + CH_2CN^-$$

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(45) This is not to say that the reaction $Ni(tmc)^+ + \cdot CH(CH_3)_2 \rightarrow (CH_3)_2CHNi(tmc)^+$ cannot take place at all but only that it is slower than the radical self-reactions under the conditions employed.

(46) A very rapid reaction between $PhCH_2Ni(tmc)^+$ and benzyl halides[37] may provide an alternative explanation of the reaction stoichiometry and products. However, the necessary condition that the rate constant for $PhCH_2X + PhCH_2Ni(tmc)^+ \rightarrow 2PhCH_2\cdot + Ni(tmc)^{2+} + X^-$ be as high or higher than k_{25} and k_{28} makes this explanation less appealing.

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(48) It is known that cyclization can occur by a pathway other than formation of a free radical [Garst, J. F.; Hines, A. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6443 and references therein]. A possibility that $CH_2CH(CH_2)_3CH_2Ni(tmc)^+$ undergoes intramolecular cyclization is presently under investigation.

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(51) Aqueous Cr^{2+} does not react with simple alkyl halides at measurable rates, whereas the reactions with benzyl chloride, bromide, and iodide at 27 °C have rate constants[1] of 3.2×10^{-3}, 0.41, and 1.8 M^{-1} s^{-1}, respectively. Cr^{2+} thus reacts with benzyl halides many orders of magnitude more rapidly than with aliphatic halides, similarly to $Cr(15\text{-}aneN_4)^{2+}$ and $Ni(tmc)^+$.

(52) The occurrence of an outer-sphere electron-transfer reaction between some Co(II) complexes and substituted benzyl halides has been demonstrated.[7] No data exist, however, for simple alkyl halides.

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Mechanistic Investigation of Carbon–Carbon Bond Formation in the Reduction of Alkyl Halides by Organonickel Complexes in Aqueous Solution

Andreja Bakac* and James H. Espenson*

Contribution from the Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011.

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Abstract: The macrocyclic alkylnickel(II) complexes, RNi(tmc)$^+$ (R = C_2H_5, C_3H_7, and CH_2-c-C_5H_9; tmc = (1*R*,4*R*,8*S*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), react with alkyl halides R′X (R′ = CH_3, C_2H_5, 1-C_3H_7, 2-C_3H_7, and $PhCH_2$) in alkaline aqueous solutions, yielding combination and disproportionation products of R and R′. The reactivity of R′X increases in the order methyl < primary < secondary and Cl < Br < I. In the case R = R′ = C_2H_5, the product distribution compares with that determined independently for ethyl radicals in aqueous solution. The proposed one-electron reduction of alkyl halide by the alkylnickel complexes in the rate-determining step produces an organonickel(III) complex and the alkyl halide radical anion. Both products rapidly eliminate ethyl radicals whose self-reactions yield the final products. Alkyl halide/alkyl radical exchange reactions effectively compete with radical self-reactions. The rate constant for the reaction $C_2H_5\cdot + 2\text{-}C_3H_7I \rightarrow 2\text{-}C_3H_7\cdot + C_2H_5I$ in aqueous solution was determined by competition with $V(H_2O)_6^{2+}$. The value $k_{2\text{-PrI}} \sim 6 \times 10^5\ M^{-1}\ s^{-1}$ is significantly higher than in aprotic solvents.

Low valent transition-metal complexes play crucial roles as catalysts in the carbon–carbon bond-forming reactions of alkyl/aryl halides. The cross-coupling reactions of alkyl lithium and Grignard reagents with alkyl halides,[1-7] the catalytic electrochemical reduction of alkyl halides,[8-14] and catalyzed coupling of alkyl/aryl halides[15-19] have all been proposed to involve organometallic intermediates. This has prompted several mechanistic investigations of the formation and reactivity of the proposed intermediates[7,19-23] and related organometallic complexes[24] toward alkyl and aryl halides. Prominent among the complexes investigated are a number of organonickel complexes, $RNiL_2X$,[15-18,20-23] which effectively couple with alkyl and aryl halides, and a series of macrocyclic nickel complexes which catalyze the electrochemical reduction of alkyl halides.[11-14]

We have recently studied the kinetics of the reduction of alkyl halides by a univalent macrocyclic nickel complex, Ni$^{\text{I}}$(*R*,*R*,*S*,*S*-tmc)$^+$[25,26] (hereafter Ni(tmc)$^+$), in aqueous solution. The lifetimes of the organonickel complexes produced in these reactions were significantly shorter in the presence of excess alkyl halide. This and the formation of coupled products, alkanes and alkenes, indicated the occurrence of a direct reaction between alkyl halides and alkylnickel complexes. Here we report the results of a complete kinetic and mechanistic study of these reactions.

$$\mathrm{RNi(tmc)^+ + RX \rightarrow Ni(tmc)^{2+} + (R_2 + RH + R(-H)) + X^-}$$

Experimental Section

Ni(tmc)$(ClO_4)_2$ was prepared according to the published procedure.[27] Alkaline aqueous solutions of Ni(tmc)$^+$ were prepared by electrochemical

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(26) As pointed out earlier,[25a] there are discrepancies in the adopted nomenclature for this compound in the literature. The nickel(II) complex has been known as *trans*-III-Ni(tmc)$^{2+}$ and (*R*,*S*,*S*,*R*)-Ni(tmc)$^{2+}$. In the latter name the numbering of nitrogens for the purpose of naming the ligand differs from that used in assigning the chirality.

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