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

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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^{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.

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

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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Table I. Concentration Ratio Effect on the Reactions of $Ni(tmc)^+$ with CH_3I and C_2H_5I[a]

$10^4[RX]_0$	$10^4[Ni(tmc)^+]_0$	$[RX]_0/[Ni(tmc)^+]_0$	$[I^-]_\infty$[b]$/\Delta[Ni(tmc)^+]$	k/s^{-1}[c]	prod[e]
		CH_3I			
0.85	3.4	0.25	0.50	4.0×10^{-3}	CH_4
1.71	3.2	0.53	0.47	4.1×10^{-3}	CH_4
10.7	3.2	3.34	0.50	4.3×10^{-3}	CH_4
		C_2H_5I			
0.70	2.6	0.27	0.50	4.6×10^{-3}	C_2H_6 (100)
15.0	4.0	3.75	1.0	0.078	C_2H_6 (25) C_2H_4 (25) C_4H_{10} (50)
15.0	4.0	3.75	0.50[d]	very fast	C_2H_6 (100)

[a] In 0.03 M NaOH, 0.1 M ionic strength. [b] Ratio of the free iodide produced and $Ni(tmc)^+$ consumed in reaction. [c] Rate constant for decomposition of $RNi(tmc)^+$ at 25 °C. [d] Solution was acidified as soon as $C_2H_5Ni(tmc)^+$ formation was complete. [e] Values in parentheses are in %.

reduction of $Ni(tmc)^{2+}$ at −1.3 V vs. SCE[25,28] or photochemically.[25] Ethyl radical precursors, $[(NH_3)_5CoOOCC_2H_5](ClO_4)_2$[29,30] and $C_2H_5C(CH_3)_2OOH$[31] were prepared by literature procedures. Alkyl halides (Aldrich, Fisher) and diethyl ketone (Eastman) were distilled prior to use.

Spectral and kinetic data were obtained by use of Cary 219 and Perkin-Elmer Lambda Array 3840 spectrophotometers. The reactions of $RNi(tmc)^+$ with R′X were initiated by injection of R′X into a spectrophotometric cell containing a solution of freshly-generated $RNi(tmc)^+$.[25] The progress of the reaction was monitored at the absorption maximum of the organonickel complex near 400 nm[25] or at the 228-nm maximum of iodide ion. Kinetic data followed pseudo-first-order kinetics; rate constants were evaluated by standard procedures.

Organic products were analyzed gas chromatographicaly by direct injection of spent-reaction solutions onto the GC column and by GCMS in some cases.[32] Free iodide ion was determined spectrophotometrically ($\epsilon_{228} = 1.46 \times 10^4$ M^{-1} cm^{-1}) after the reaction solutions had been acidified to 1 M $HClO_4$.

All the experiments were done strictly anaerobically under an argon, nitrogen, or helium atmosphere by using syringe/septa techniques. The ionic strength was kept constant at 0.10 M (NaOH + $LiClO_4$).

The disproportionation/combination ratio was determined for ethyl radicals produced thermally or photochemically. A 275-W sun lamp and a Rayonet UV reactor containing low-pressure mercury lamps were used as light sources for the photochemical generation of radicals.

Results

The alkylnickel complexes, prepared in solution according to eq 1, show reduced kinetic stability when excess alkyl halide is

$$2Ni(tmc)^+ + RX \rightarrow RNi(tmc)^+ + Ni(tmc)^{2+} + X^- \quad (1)$$

used in the preparation. The only exception seems to be $CH_3Ni(tmc)^+$, which does not react with alkyl halides. Table I illustrates the point for the methyl and ethyl complexes. Irrespective of the reagent in excess, the overall stoichiometry of the reaction with CH_3I, $[Ni(tmc)^+]/[CH_3I]$, is 2:1, as confirmed by spectrophotometric titrations and the free iodide analysis. Similarly, the decomposition of $CH_3Ni(tmc)^+$ produces CH_4 with $k \sim 4 \times 10^{-3}$ s^{-1} under all conditions. The reaction of $Ni(tmc)^+$ with CH_3I is thus fully described by eq 1 and 2.

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

The overall stoichiometry of the reaction of $Ni(tmc)^+$ with C_2H_5I, on the other hand, changes depending on excess reagent. At stoichiometric concentrations, and also with $Ni(tmc)^+$ in excess over C_2H_5I, eq 1 occurs and is followed by the hydrolysis of $C_2H_5Ni(tmc)^+$.[25]

$$C_2H_5Ni(tmc)^+ + H_2O \rightarrow C_2H_6 + Ni(tmc)^{2+} + OH^- \quad (3)$$

Free iodide produced in the reaction with excess C_2H_5I was analyzed at different stages of the reaction. Acidification of the reaction solution immediately after the formation of $C_2H_5Ni(tmc)^+$ caused rapid acidolysis of the organonickel complex.

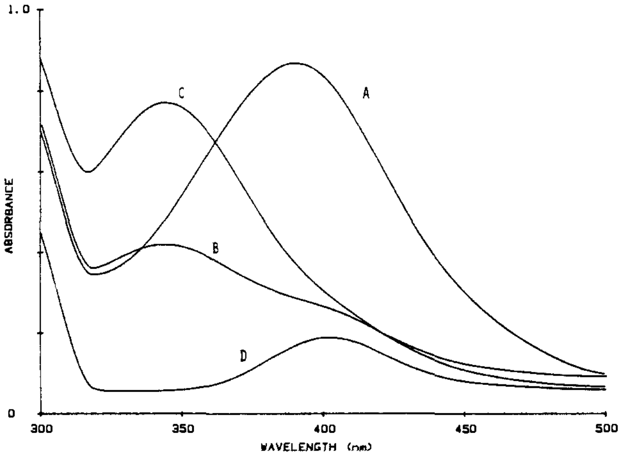

Figure 1. The reaction of 6×10^{-4} M $Ni(tmc)^+$ with a small excess of C_2H_5I (4×10^{-4} M) at 25 °C and pH 12 produces 3×10^{-4} M $C_2H_5Ni(tmc)^+$ (A). Addition of excess CH_3I (0.01 M) to solution A yields 1.5×10^{-4} M $CH_3Ni(tmc)^+$ + 1.5×10^{-4} M $Ni(tmc)^{2+}$ (B). A direct reaction of 6×10^{-4} M $Ni(tmc)^+$ with CH_3I produces 3×10^{-4} M $CH_3Ni(tmc)^+$ (C). All solutions contained $\sim 1 \times 10^{-3}$ M $Ni(tmc)^{2+}$ (D).

$$C_2H_5Ni(tmc)^+ + H^+ \rightarrow C_2H_6 + Ni(tmc)^{2+} \quad (4)$$

Under these conditions the ratio of the iodide produced and $Ni(tmc)^+$ consumed in the reaction, $[I^-]_\infty/[Ni(tmc)^+]$, is 0.50, as required by eq 1 and 4. When both formation and decomposition of $C_2H_5Ni(tmc)^+$ were allowed to proceed to completion in the presence of excess C_2H_5I, however, the consumption ratio changed to 1.0. The reaction produced ethane, ethylene, and butane in a 1:1:2 ratio. The decomposition rate constant of $C_2H_5Ni(tmc)^+$ ($k = 8.0 \times 10^{-2}$ s^{-1}) was significantly higher than hydrolysis at the same pH ($k = 4.6 \times 10^{-3}$ s^{-1}). The reaction of $Ni(tmc)^+$ with excess C_2H_5I is thus well described by eq 1 and 5.

$$C_2H_5Ni(tmc)^+ + C_2H_5I \rightarrow Ni(tmc)^{2+} + I^- + (C_2H_6 + C_2H_4 + C_4H_{10}) \quad (5)$$

Other alkyl halides also react with $C_2H_5Ni(tmc)^+$ and with other primary alkylnickel complexes generated in solution from $Ni(tmc)^+$ and equivalent amounts of RI, RBr, or $RC(CH_3)_2OOH$. The reaction of $C_2H_5Ni(tmc)^+$ with CH_3I causes the 390-nm maximum of $C_2H_5Ni(tmc)^+$ to disappear with the concomitant formation of a peak at 346 nm, characteristic of $CH_3Ni(tmc)^+$, eq 6 (Figure 1). Subsequently, $CH_3Ni(tmc)^+$ slowly decomposes with $k \sim 4 \times 10^{-3}$ s^{-1}.

$$C_2H_5Ni(tmc)^+ \xrightarrow{CH_3I} 0.5CH_3Ni(tmc)^+ + 0.5Ni(tmc)^{2+} \quad (6)$$

The reaction of $C_2H_5Ni(tmc)^+$ with $C_6H_5CH_2Cl$ is accompanied by the formation of a transient red color, consistent with $C_6H_5CH_2Ni(tmc)^+$, which is known[25] to be a short-lived species. Reactions of primary alkyl halides R′X with alkylnickel complexes

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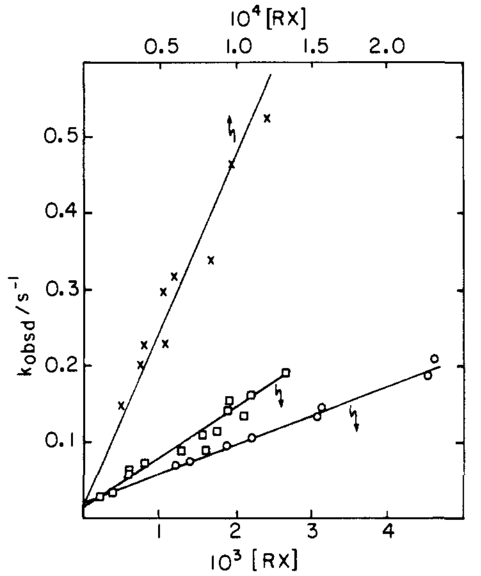


Figure 2. Kinetic data for the reactions of $C_2H_5Ni(tmc)^+$ with CH_3I (○), C_2H_5I (□), and $2\text{-}C_3H_7I$(X) at 25 °C, $[OH^-] = (0.6\text{–}33) \times 10^{-3}$ M, $\mu = 0.10$ M ($NaOH + LiClO_4$). The slopes of these lines define the apparent second-order rate constant k_{obsd} of eq 8.

$RNi(tmc)^+$ ($R \neq CH_3$) presumably also involve the formation of $R'Ni(tmc)^+$, although this could not be detected spectrophotometrically owing to the spectral similarity of all the primary alkylnickel complexes. These reactions were shown by GC product analysis to lead to a complex mix of alkanes and alkenes. All the products possible from (cross and homo) coupling and disproportionation of R and R′, as described in eq 7, were observed.

$$R'X + RNi(tmc)^+ \rightarrow 0.5R'Ni(tmc)^+ + 0.5Ni(tmc)^{2+} + \text{hydrocarbon products} \quad (7)$$

The reactions of $C_2H_5Ni(tmc)^+$ with $2\text{-}C_3H_7Br$ and $2\text{-}C_3H_7I$ seem to produce no intermediate organonickel complex, consistent with our previous finding[25] that $(CH_3)_2CHNi(tmc)^+$ does not readily form from $(CH_3)_2\dot{C}H + Ni(tmc)^+$.

Kinetics. Reactions of alkyl halides with $RNi(tmc)^+$ were studied under pseudo-first-order conditions by using a large excess of the alkyl halide. First-order plots were linear to at least 80% completion for reactions of CH_3I, C_2H_5I, C_2H_5Br, $1\text{-}C_3H_7I$, $1\text{-}C_3H_7Br$, and $2\text{-}C_3H_7Br$. Reactions of $2\text{-}C_3H_7I$ were quite fast ($t_{1/2} = 1.5\text{–}5.5$ s), and the kinetic parameters were evaluated from the last 25–60% of the reaction, assuming a pseudo-first-order rate law. Nothing in the results indicated that a different treatment was warranted. Pseudo-first-order rate constants varied linearly with [R′X] in all cases (although with a relatively large scatter, Figure 2),[33] yielding the rate law of eq 8. The values of k_{obsd} are summarized in Table II. Both $C_2H_5Ni(tmc)^+$ and $C_3H_7Ni(tmc)^+$ react with alkyl halides following the trend R′I > R′Br and secondary R′X > primary > methyl.

$$-\frac{d[RNi(tmc)^+]}{dt} = k_{obsd}[R'X][RNi(tmc)^+] \quad (8)$$

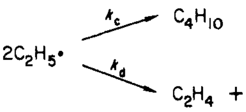
The organic products of all the reactions (Table III) cover the whole range of alkanes and alkenes that are the disproportionation and dimerization products of R and R′, including mixed dimers. Owing to the gaseous nature of most of the products and their low solubility in water, the recovery was usually only ~40–80%. Nevertheless, the product distribution in Table III is believed to represent all of the reactions fairly well since analyses of solution and gas samples gave identical results, except in reactions producing $C_6H_5(CH_2)_2CH_3$ and $(C_6H_5CH_2)_2$.

Table II. Summary of the Kinetic Data for the Reactions of $RNi(tmc)^+$ with $R'X$[a]

$RNi(tmc)^+$	$R'X$	$k_{obsd}/M^{-1}\,s^{-1}$ [b]
$C_2H_5Ni(tmc)^+$	CH_3I	38.1 (13)
	C_2H_5I	63.1 (45)
	$2\text{-}C_3H_7I$	4680 (190)
	C_2H_5Br	18.0 (22)
	$2\text{-}C_3H_7Br$	498 (64)
$1\text{-}C_3H_7Ni(tmc)^+$	CH_3I	27.0 (15)
	$1\text{-}C_3H_7I$	47.0 (27)
	$2\text{-}C_3H_7I$	3380 (320)

[a] 25 °C, $[OH^-] = (0.6\text{–}33) \times 10^{-3}$ M, $\mu = 0.10$ M. [b] Rate constant as defined in eq 8. Standard deviations of the last digits are given in parentheses. In the reactions of CH_3I, $k_{obsd} = 2k_{13}$. In all other cases $k_{obsd} = k_{13}$, see text.

Determination of k_d/k_c for Ethyl Radicals. Involvement of free radicals in the reactions of alkylnickel complexes with alkyl halides would require that the product distribution be identical with that determined independently for a particular radical. The disproportionation/combination ratio (k_d/k_c) for primary alkyl radicals has been reported for a number of solvents,[34] but no data were available for aqueous solutions.[35] The ratio k_d/k_c was thus



$$2C_2H_5\cdot \begin{cases} \xrightarrow{k_c} C_4H_{10} \\ \xrightarrow{k_d} C_2H_4 + C_2H_6 \end{cases} \quad (9)$$

determined for ethyl radicals prepared by several independent methods: reduction of ethyl iodide by $(CH_3)_2CO^{-}$;[36,37] photolysis of diethyl ketone[34] and $(NH_3)_5CoO_2CC_2H_5^{2+}$;[30] and reduction of $C_2H_5C(CH_3)_2OOH$ by $V(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{2+}$. All the methods are in good agreement yielding $k_d/k_c = 0.35 \pm 0.04$. This value, the highest ever reported for ethyl radicals, is not unexpected in view of the high dielectric constant and internal pressure of water.[34,38,39]

Exchange Reactions of Alkyl Radicals with Alkyl Halides. Careful analysis of the data in Table III shows that a larger proportion of the products is derived from the alkyl halide than from the alkylnickel complex itself. Also, C_2H_5I was produced in the reactions of $C_2H_5Ni(tmc)^+$ with alkyl halides.[40] Mass spectral analysis of butane produced in the reaction of $C_2D_5Ni(tmc)^+$ with a large excess of C_2H_5I unequivocally identified C_4H_{10} as the major product (83%), with but minor contributions from $C_4H_5D_5$ (15%) and C_4D_{10} (2%). C_2D_5I was also produced. The clear implication of all these findings is that there is an effective exchange reaction between the alkyl halides and alkyl groups originally bound to nickel. An attractive possibility is the alkyl radical/alkyl halide exchange reaction (eq 10).

$$C_2H_5\cdot + (CH_3)_2CHI \rightarrow (CH_3)_2CH\cdot + C_2H_5I \quad (10)$$

However, the rate constants measured for these exchange reactions in aprotic solvents are too slow to account for the observations in this work. For example, from the available data,[41,42] we estimate

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[33] Occasionally an experimental point would deviate from the calculated value by as much as 50%. This might be caused by the presence of trace amounts of oxygen or partial (<10%) isomerization of the Ni(*R,R,S,S*-tmc)$^+$ to another isomer Ni(*R,S,R,S*-tmc)$^+$, a process identified previously,[25] despite the precautions taken in the preparations and handling of solutions.

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Table III. Products of Reactions of $RNi(tmc)^+$ with Excess Alkyl Halides[a]

R	R′X (mM)	prod (rel. amt)
C_2H_5[b]	CH_3I (8.5)	CH_4 (3.7), C_2H_6 (1.0), C_2H_4 (0.66), C_4H_{10} (1.0)
	C_2H_5I (4.0)	C_2H_6 (1.0), C_2H_4 (0.93), C_4H_{10} (1.8)
	1-C_3H_7I (1.8)	C_2H_6 (1.0), C_2H_4 (1.3), C_4H_{10} (0.63), C_3H_8 (1.3), C_3H_6 (1.3), $CH_3(CH_2)_4CH_3$[c], C_2H_5I[c]
	2-C_3H_7I (1.2)	C_2H_6 (1.0), C_2H_4 (1.1), C_4H_{10} (0.56), C_3H_8 (4.1), C_3H_6 (4.0), $CH_3CH_2CH(CH_3)_2$ (1.8), $(CH_3)_2CHCH(CH_3)_2$ (1.5), C_2H_5I (3.9)
	$C_6H_5CH_2Cl$ (1.5)	C_2H_6 (1.0), C_2H_4 (1.0), C_4H_{10} (1.5), $C_6H_5CH_2CH_2CH_3$ (5.2), $(C_6H_5CH_2)_2$ (5.2)
1-C_3H_7[d]	1-PrI (1.8)	C_3H_8 (1.0), C_3H_6 (0.87), C_6H_{14} (3.1)
CH_2-c-C_5H_9[e]	$Br(CH_2)_4CH{=}CH_2$ (0.5)	C_{12} dimers (linear and cyclized isomers), no disproportionation products

[a] ~25 °C, $[OH^-] = 1 \times 10^{-2}$ M. [b] Prepared in situ from $Ni(tmc)^+$ (6×10^{-4} M) and C_2H_5I (3×10^{-4} M). [c] Not separated by GC. [d] Prepared in situ from 5×10^{-4} M $Ni(tmc)^+$. [e] Prepared in situ from 6.5×10^{-4} M $Ni(tmc)^+$.

$k_{10} \leqslant 2 \times 10^4$ M^{-1} s^{-1} in toluene at 25 °C. The data in this work would require $k_{10} \sim 10^6$ M^{-1} s^{-1} at 25 °C in water. We, therefore, determined the approximate value of k_{10} in aqueous solution at room temperature. Ethyl radicals were generated from $V(H_2O)_6^{2+}$ and $C_2H_5C(CH_3)_2OOH$, eq 11, in a solution containing excess

$$V(H_2O)_6^{2+} + C_2H_5C(CH_3)_2OOH \xrightarrow{H^+} V(H_2O)_6^{3+} + C_2H_5\cdot + (CH_3)_2CO \quad (11)$$

$(CH_3)_2CHI$. From the amounts of C_2- and C_3-products[43] (predominantly alkanes formed by the reduction of $C_2H_5\cdot$ and $(CH_3)_2CH\cdot$ by $V(H_2O)_6^{2+}$), the known rate constant for the dimerization of ethyl radicals,[44] and the independently estimated value of $k_{12} \sim 6 \times 10^5$ M^{-1} s^{-1}, we calculate $k_{10} \sim 6 \times 10^5$ M^{-1} s^{-1}, in good agreement with the value estimated from the product analysis of the ethylnickel reaction. A detailed study of the kinetics of the exchange reactions between alkyl radicals and alkyl halides in aqueous solution is in progress.

$$V(H_2O)_6^{2+} + C_2H_5\cdot \xrightarrow{H^+} V(H_2O)_6^{3+} + C_2H_6 \quad (12)$$

Radical trapping experiments were thwarted by the high reactivity of alkylnickel complexes toward the standard radical traps. Reagents which would similarly trap any $Ni(tmc)^+$ produced also reacted directly with $RNi(tmc)^+$.

Discussion

A satisfactory mechanism for the reactions of $RNi(tmc)^+$ complexes with alkyl halides must account for the following observations: (a) reactions occur with a 1:1 stoichiometry, eq 5; (b) mixtures of disproportionation and combination products are formed in all of the reactions; (c) most of the products are derived from excess alkyl iodide R′I; (d) variable amounts of RX are produced depending on the nature of R and R′X; (e) $R'Ni(tmc)^+$ species are intermediates in the reactions of $RNi(tmc)^+$ and R′X; (f) all reactions follow a mixed second-order rate law; and (g) the reactivity order follows the trends RI > RBr > RCl and methyl < primary < secondary. Similarly, in the $RNi(tmc)^+$ series, the reactivity is R = $CH_3 \ll C_2H_5$, 1-C_3H_7. All these observations can be accommodated by the mechanism of eq 13–17.

$$RNi(tmc)^+ + R'X \rightarrow \{RNi(tmc)^{2+}, R'X^-\} \quad (13)$$

$$\{RNi(tmc)^{2+}, R'X^-\} \rightarrow R\cdot + R'\cdot + Ni(tmc)^{2+} + X^- \quad (14)$$

$$R'\cdot + RNi(tmc)^+ \rightleftarrows R'Ni(tmc)^+ + R\cdot \quad (15)$$

$$R\cdot + R'X \rightleftarrows RX + R'\cdot \quad (16)$$

$$R\cdot,R'\cdot \rightarrow (RH, R(-H), R'H, R'(-H), R_2, R'_2, RR') \quad (17)$$

The standard reduction potentials of alkylnickel complexes have not been determined. However, they are potent reductants[25] and quite likely capable of reducing alkyl halides in one-electron processes. The reduction may take place by electron transfer as shown in eq 13 or by a halogen atom transfer, eq 18. In both

$$RNi(tmc)^+ + R'X \rightarrow RNi(tmc)(X)^+ + R'\cdot \quad (18)$$

cases an organonickel(III) intermediate is postulated, which then rapidly eliminates a carbon-centered radical. A distinction between electron- and atom-transfer mechanisms is not likely to be easily resolved, as discussed earlier.[25] Although they are 18-electron species, the alkylnickel complexes are probably paramagnetic, as recently found for $CH_3Ni(tmc)^+$.[45] Atom transfer thus becomes a reasonable possibility. The reactivity order (Table II) is similar to that found for the reactions of $Ni(tmc)^+$ with alkyl halides[25] and thus consistent with both reactivity modes. A one-electron, inner-sphere reduction of aryl halides by arylnickel(II) complexes has been invoked as a chain initiation reaction in the biaryl synthesis with nickel.[21b]

Alkyl radicals are produced homolytically from $R'X^{-}$[46] and $RNi(tmc)^{2+}$, eq 14. The latter is expected to undergo homolysis quite rapidly owing to its d^7 electronic structure. The radical capture by $RNi(tmc)^+$ is apparently a highly efficient process as demonstrated by the quantitative formation of $CH_3Ni(tmc)^+$ according to eq 6. The exchange reaction 16, which would affect the stoichiometry of eq 6, is unimportant in the case of CH_3I, as expected on thermodynamic grounds.

The proposed product-forming reaction, eq 17, is the self reaction of alkyl radicals. The product distribution should, therefore, match that determined independently. From the data in Table III one calculates $[C_2H_4]/[C_4H_{10}] = 0.52$ for R = R′ = C_2H_5 and $[C_3H_6]/[C_6H_{14}] = 0.28$ for R = R′ = 1-C_3H_7. The value k_d/k_c for $C_3H_7\cdot$ has not been determined directly, but it is probably very close to that for $C_2H_5\cdot$ (0.35). Both values determined in the nickel reactions (0.52 and 0.28) are in the correct range for free-radical self reactions. The low recovery of the products is probably responsible for the relatively large experimental error. The quantitative analysis becomes increasingly difficult when R $\neq$ R′ because of the contributions from homo- and cross-disproportionation and homo- and cross-combination and the alkyl radical/alkyl halide exchange reactions. Qualitatively the products are analogous to those derived from systems with R = R′.[47]

The exchange reaction 10 is greatly accelerated in water ($k \sim 6 \times 10^5$ M^{-1} s^{-1}) compared to aprotic solvents ($k \sim 2 \times 10^4$ M^{-1} s^{-1} in toluene). This is undoubtedly a result of a highly polar transition state,[41,42,48-50] although the magnitude of the effect might not have been predicted. The good agreement between the values of k_{10} obtained in the $V(H_2O)_6^{2+}/C_2H_5C(CH_3)_2OOH$ reaction

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(42) Ingold, K. U. In "Free Radicals"; J. Kochi, Ed.; Wiley: New York, 1973.

(43) The contribution from the competing reaction

$$V(H_2O)_6^{2+} + C_2H_5C(CH_3)_2OOH \xrightarrow{H^+} V(H_2O)_6^{3+} + CH_3\cdot + CH_3COC_2H_5$$

was insignificant enough that it was ignored in the calculations.

(44) (a) Stevens, G. C.; Clarke, R. M.; Hart, E. J. *J. Phys. Chem.* **1972**, *76*, 3863. (b) Hickel, B. *J. Phys. Chem.* **1975**, *79*, 1054.

(45) D'Aniello, M. J.; Barefield, E. K. *J. Am. Chem. Soc.* **1976**, *98*, 1610.

(46) Eberson, L. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 533.

(47) The oxidation of $C_2H_5Ni(tmc)^+$ by $Co(NH_3)_6^{3+}$ produces $Ni(tmc)^{2+}$ and a mixture of ethane, ethylene, and butane, with *R* = 0.27. An initial electron transfer step seems inevitable in this system, which provides additional support for the transient formation of $RNi(tmc)^{2+}$ in reactions which ultimately yield $Ni(tmc)^{2+}$ and free radical products.

(48) Danen, W. C.; Saunders, D. G. *J. Am. Chem. Soc.* **1969**, *91*, 5924.

(49) Danen, W. C.; Winter, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 716.

(50) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917.

and that predicted by the mechanism of eq 13–17 strongly supports the proposed mechanism.

In an alternative scheme the organonickel(III) complex reacts directly with the radical R·′ (eq 19). Not only is it very unlikely

$$\mathrm{RNi(tmc)^{2+} + R\cdot' \rightarrow \{RR' + RH + R(-H) + R'H + R'(-H)\} + Ni(tmc)^{2+}} \quad (19)$$

that a reaction between a radical and an organometallic intermediate gives the same product distribution as the self reaction of free radicals, but this scheme also requires that R and R′ be equally distributed among the products. The only radical/alkyl halide exchange reaction allowed would be a nonproductive self-exchange reaction of R·′ and R′X (eq 16), since the alkyl group R never passes through a free radical stage.

Similarly, a mechanism that would account for the facile formation of R′Ni(tmc)$^+$ by the involvement of Ni(tmc)$^+$, eq 20–21, cannot account for the stoichiometry of reaction 7 or the distribution of organic products.

$$\mathrm{R\cdot' + RNi(tmc)^+ \rightarrow RR' + Ni(tmc)^+} \quad (20)$$

$$\mathrm{Ni(tmc)^+ + 0.5\ R'X \rightarrow 0.5\ Ni(tmc)^{2+} + 0.5\ R'Ni(tmc)^+ + 0.5\ X^-} \quad (21)$$

An implication of the mechanism in eq 13–17 is that $k_{obsd} = 2k_{13}$ for reactions with CH_3I, but $k_{obsd} = k_{13}$ in all other cases, since the loss of a second mol of RNi(tmc)$^+$ in the rapid step 15 takes place only with CH_3I. Reaction 15 is kinetically unimportant for R = R′ (self-exchange reaction) and presumably also when R′ = 2-C_3H_7 (no 2-C_3H_7Ni(tmc)$^+$ formation takes place).[25]

Mechanistic differences between the present work and related biaryl formation from ArNiBr$(PEt_3)_2$ and ArBr[21b] can most likely be traced to the coordination properties of macrocycles. In the radical chain mechanism proposed by Tsou and Kochi,[21b] biaryl is formed by reductive elimination from a metastable organonickel(III) species, eq 22. Effective blocking of all four cis

$$\mathrm{(Ar)_2Ni^{III}X \rightarrow ArAr + Ni^{I}X} \quad (22)$$

positions by the macrocyclic ligand rules out the formation of the cis-dialkylnickel complex, *cis*-(R)$_2$Ni(tmc)$^+$. A trans isomer, on the other hand, could be formed (and is probably an intermediate in the exchange reaction 15), but its stereochemistry rules out successful dialkyl and/or alkane/alkene elimination.

Organonickel(III) complexes were proposed as reaction intermediates in an earlier study of the electrochemical reduction of alkyl halides catalyzed by macrocyclic nickel complexes in acetonitrile.[13] The mechanism of the organonickel(III) formation by a one-step oxidative addition of alkyl halides to nickel(I) as well as the proposed product forming steps are, however, inconsistent with our observations.

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Kinetics and Mechanism of Nitrile Hydration Catalyzed by Unhindered Hydridobis(phosphine)platinum(II) Complexes. Regioselective Hydration of Acrylonitrile

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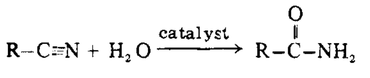
Abstract: The reaction between *trans*-PtHCl$(PR_3)_2$ (R = Me and Et) and 1 equiv of NaOH in 50–50 water/acetonitrile solutions yields a species that catalyzes the hydrolysis of acetonitrile to acetamide at rates of 178 and 70 mol/(mol of catalyst h) for the R = Me and Et derivatives, respectively, at 80 °C. These catalysts remain active for days and give as many as 6000 turnovers. The PMe_3 derivative catalyzes hydrolysis of acrylonitrile but exhibits low regioselectivity between the olefin and nitrile functionalities at 80 °C; at 25 °C, it hydrates 21 mol of acetonitrile/(mol of catalyst h) and regioselectively (97%) hydrates 6.1 mol of acrylonitrile/(mol of catalyst h) to acrylamide. The catalytic intermediates, $[PtH(H_2O)(PEt_3)_2]^+$, $[PtH(N{\equiv}CCH_3)(PEt_3)_2]^+$, and PtH(NHC(O)Me)$(PEt_3)_2$, have been intercepted and spectroscopically characterized and their interconversions demonstrated. Except at low hydroxide concentrations, the rates of catalysis were independent of hydroxide concentration, and proton transfer from solvating water to coordinated *N*-carboxamido, rather than nucleophilic attack of hydroxide on coordinated nitrile, limits the rate. Rate constants of ~8 and ~20 s^{-1} were determined for the proton-transfer process for the PEt_3 and PMe_3 systems, respectively. A kinetic isotope effect of 3.4 was observed in reactions using D_2O. Adjusting the catalytic solutions to pH 8.5 resulted in a linear hydroxide dependence, and rate constants of $4.9 \pm 0.3 \times 10^3$ and $7.0 \pm 0.4 \times 10^3$ M^{-1} s^{-1} were measured for nucleophilic attack of hydroxide on coordinated acetonitrile for the PEt_3 and PMe_3 systems, respectively. Deuterium labeling experiments using *trans*-PtDCl$(PMe_3)_2$ to catalyze acrylonitrile hydration showed that olefin hydration proceeds through a coordinated olefin intermediate and, unlike nitrile hydration, involves a reductive elimination step in the catalytic cycle.

Carboxamides (RC(O)NH$_2$) are generally prepared by hydration of the corresponding nitriles with strong acid or base catalysts[1] (eq 1). These reactions are slow and appreciable hydrolysis of the product carboxamide to the carboxylic acid,[1] as well as the hydrolysis of other functional groups present, occurs faster than nitrile hydration. Increasing use of acrylamide polymers in paper and surfactant production, wastewater treatment, and oil recovery has resulted in acrylamide becoming a major industrial chemical.[2] Difficulties[2] in the conventional



$$\mathrm{R{-}C{\equiv}N + H_2O \xrightarrow{catalyst} R{-}\overset{O}{\overset{\|}{C}}{-}NH_2} \quad (1)$$

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[1] (a) Compagnon, P. L.; Miocque, M. *Ann. Chim.* **1970**, *5*, 11–37. (b) Hegedus, L. S.; Nade, L. G. "Compendium of Organic Synthetic Methods"; Wiley: New York, 1977.

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