deuterating 1,2-pdta on Co(III), removing the ligand, and then complexing it to Cr(III), we have been able to completely assign the $^2$H NMR spectrum of [Cr(1,2-pdta-$\alpha$-$d_8$)]$^-$.

The different rates of exchange of the four chemically distinct R glycinate protons of [Co(1,2-pdta)]$^-$ have been well documented.[19,24] The order of exchange was found to be $R_A > R_A' > R_B' > R_B$. The G rings do not normally exchange. In this study, [Co(1,2-pdta)]$^-$ was deuterated to the extent that the $R_A$ resonances at 3.4 and 4.1 ppm in the $^1$H NMR spectrum began to diminish. We anticipated that the remaining protons at $R_A'$, $R_B'$, and $R_B$ had also partially exchanged at this point since the integration showed that one total deuteron had been incorporated. As noted earlier, the 1,2-pdta ligand is stereospecific.[1] Therefore, preferential $^2$H substitution of 1,2-pdta on one metal ion permits specific assignments to be made after the 1,2-pdta is transferred to a new metal ion. The R resonances can be assigned for [Cr(1,2-pdta)]$^-$, as shown in Figure 4, by noting the relative enrichment obtained on Co(III). In addition, transfer of the ligand from one metal ion to another leads to racemization around the nitrogen atoms. This places labels in the G positions as well as the R positions in the same proportion. Thus, the area under the $G_A$ resonance should be equal to the combined areas of the $R_A$ and $R_A'$ resonances, and the area under the $G_B$ resonances should be equal to the combined areas of the $R_B$ and $R_B'$ resonances. This, indeed, was the result obtained from a curve-fitting analysis of the resonances observed.

**Summary.** Deuteron NMR spectroscopy was used to establish the stereochemistry of a series of Cr(III)–edda complexes. As with most Co(III) complexes, edda was found to favor the sym-cis configuration on Cr(III). In the two instances where an unsym-cis isomer was isolated, the isomer was obtained in small quantities and found to be unstable relative to the sym-cis isomer, as evidenced by $^2$H NMR spectroscopy.[9] Preferential deuteration of a sym-cis isomer permitted definitive specific assignments to be made to the geminal deuterons on the glycinate chelate rings. Although specific assignments could not be made for the unsym-cis isomers, efforts to this end led to the complete assignment of all the resonances previously reported for the Cr(III) complex of the related ligand 1,2-pdta.

**Acknowledgment.** We wish to acknowledge W. D. Wheeler, S. Kaizaki, and N. Koine for their useful input. Acknowledgment is also made to the USDA (Grant 82-CRCR-1-1005) and National Institutes of Health (Grant GM 23081) for partial support of this study. The Nicolet NT-200WB was acquired with the assistance of the Boeing Corp.

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# Free-Radical Pathways to Alkyl Complexes of a Nickel Tetraaza Macrocycle

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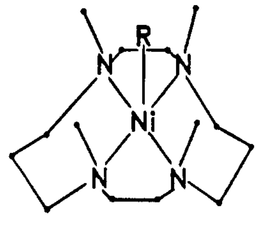
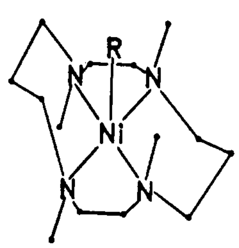
The cationic nickel(I) macrocycle (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), abbreviated *R*,*S*,*R*,*S*-[Ni(tmc)]$^+$, reacts in aqueous, alkaline solutions on the stopped-flow time scale with alkyl halides to form a new series of organonickel complexes. Kinetic data were obtained for a large number of alkyl halides. The trends in the rate constants are benzyl > allyl > secondary > primary > methyl > cyclopropyl, and RI > RBr > RCl. These trends suggest that carbon-centered free radicals R• are produced by a bimolecular reaction between Ni(tmc)$^+$ and RX and are then captured by a second Ni(tmc)$^+$. Further evidence for free-radical involvement comes from cyclization of the radical produced from 6-bromo-1-hexene, from the yields of products in those instances where dimerization of the free radical competes with its capture by Ni(tmc)$^+$, and from the nonreactivity of alkyl tosylates. The organonickel complexes slowly hydrolyze in unimolecular processes to yield hydrocarbon and the nickel(II) complex *R*,*S*,*R*,*S*-[Ni(tmc)]$^{2+}$. The organonickel complexes do not undergo unimolecular homolysis but react with Co(II) macrocycles with a 1:2 stoichiometry to form cobalt–carbon bonds. This reaction most likely occurs not by homolytic displacement but by electron transfer followed by radical capture.

## Introduction

Despite an extensive chemistry of organonickel complexes,[1] efforts directed toward alkyls of nickel macrocycles have been relatively limited. Some success was realized[2] in the preparation by Grignard routes of several alkylnickel complexes containing the "tetramethylcyclam" or "tmc" macrocycle. In the series of compounds reported,[2] the chirality at the nitrogen donors defines the stereochemistry[3] as *R*,*R*,*S*,*S*; we abbreviate the formulas of the organometallic compounds as *R*,*R*,*S*,*S*-[RNi(tmc)]$^+$. An alternative route to them, the reaction of alkyl halides with the nickel(I) macrocycle, was shown to proceed by a free-radical mechanism.[4] Previous studies of organonickel macrocycles, both preparative[2] and mechanistic,[4] have concentrated on that isomer. We consider here the nickel(I) complex *R*,*S*,*R*,*S*-[Ni(tmc)]$^+$, the isomer with "four methyls up", which is the other reasonably stable and well-characterized stereoisomer[5,6] in the Ni(tmc) series.



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



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

Interest in this area derives in part from observations that have identified nickel macrocycles as catalysts for the electrochemical

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(1) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1974; Vol. I, Chapter IV and references therein.

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

(3) The complex used here is (1*R*,4*S*,8*R*,11*S*)-(1,4,8,11-tetramethyl-1,4,8,11-tetrazacyclotetradecane)nickel(I), which we abbreviate as *R*,*S*,*R*,*S*-[Ni(tmc)]$^+$ or (when it is not confusing) simply as Ni(tmc)$^+$. It has also been referred to in the literature as the trans-I isomer. This complex is an isomer of that we studied previously,[4] *R*,*R*,*S*,*S*-[Ni(tmc)]$^+$, also known as the trans-III form. The nickel(II) complexes do not interconvert in aqueous solution over extended periods of time (weeks or longer), but in the nickel(I) state, a mixture of the two, in an approximate 3:1 ratio in favor of *R*,*S*,*R*,*S*, results when either stands several hours at room temperature.

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reduction of alkyl halides in acetonitrile.[7-11] The nickel(I) complex is clearly involved in the electrochemical reactions. Since it is now recognized that solutions of the nickel(I) macrocycles can readily be prepared[12] directly by electrochemical or photochemical[4] procedures and that some of them are reasonably stable in alkaline, aqueous solutions, it becomes possible to investigate directly the nature of the homogeneous Ni(I)–RX reactions. Moreover, the characterization[13] of Factor F430 found in methane-forming bacteria as a nickel complex of an unsaturated tetraaza macrocycle provides additional motivation for this work. To our knowledge no claim has been made for a methylnickel complex as a precursor to methane formation. The connection is indeed tenuous at this point, albeit not unlike the established relation between Vitamin $B_{12}$ and model cobalt complexes of saturated macrocycles. The reactions of organic halides with organonickel complexes, both the alkylnickel macrocycles[14] and $\pi$-allyl halides,[15] provide further motivation for continued effort in the area.

Reduced metal complexes are known[16] to react with alkyl halides by a variety of mechanisms, including halogen atom abstraction, electron transfer, and nucleophilic substitution. The first two are not easily distinguished from one another unless the oxidized metal product undergoes slow ligand substitution, which $\mathrm{Ni(tmc)^{2+}}$ does not. Both involve free radical intermediates. We have earlier presented[4] several lines of evidence supporting the involvement of free alkyl radicals in the reactions of *R,R,S,S*-$\mathrm{[Ni(tmc)]^{+}}$ with RX. This scheme, shown in eq 1 and 2, leads to an overall 2:1 reaction stoichiometry (eq 3).

$$\mathrm{Ni(tmc)^{+} + RX \rightarrow XNi(tmc)^{+}\ (or\ X^{-} + Ni(tmc)^{2+}) + R\bullet} \tag{1}$$

$$\mathrm{Ni(tmc)^{+} + R\bullet \rightarrow RNi(tmc)^{+}} \tag{2}$$

$$\mathrm{net:\ 2Ni(tmc)^{+} + RX = RNi(tmc)^{+} + X^{-} + Ni(tmc)^{2+}} \tag{3}$$

Although many similarities are evident between the isomeric nickel complexes of the tmc ligand, some striking differences between the two have been reported. For example, in the 2+ state, the $\mathrm{Ni(tmc)^{2+}}$ isomers differ as regards the proportions of four-, five-, and six-coordinate forms and their ligand-exchange rates.[6] It is not known, however, whether any of these differences carries over to the chemistry and reactivity of the univalent complexes or to the subsequent reactivity of the alkylnickel derivatives.

Studies were thus initiated with the other available isomeric nickel macrocycle, *R,S,R,S*-$\mathrm{[Ni(tmc)]^{2+}}$, to identify both similarities and differences. Among the questions addressed are whether the nickel(I) complex *R,S,R,S*-$\mathrm{[Ni(tmc)]^{+}}$ can be prepared, whether reduction of alkyl halides by nickel(I) also occurs, whether the same stoichiometry and mechanism apply, whether organonickel complexes are obtained, and whether their chemical reactions, such as the hydrolysis of the nickel–carbon bond (eq 4) and alkyl transfer to cobalt macrocycles (eq 5, with L = bis(dimethylglyoximato)) parallel those of the *R,R,S,S* isomer.

$$\mathrm{RNi(tmc)^{+} + H_2O \rightarrow RH + Ni(tmc)^{2+} + OH^{-}} \tag{4}$$

$$\mathrm{RNi(tmc)^{+} + 2Co^{II}L \rightarrow Ni(tmc)^{2+} + RCoL + Co^{I}L^{-}} \tag{5}$$

## Experimental Section

**Reagents.** The complex *R,S,R,S*-$\mathrm{[Ni(tmc)](ClO_4)_2}$, prepared by the literature procedure,[5] was redissolved in water and allowed to stand for 2 days. This solution was concentrated to 2 mL at 35 °C, treated with 0.5 mL of saturated sodium perchlorate, and refrigerated. The crystalline product so obtained was washed with ether and vacuum-dried. *Provided the indicated standing and reprecipitation steps were performed* (the purpose of which we presume is to allow complete conversion to the preferred isomer), the spectral data for the complex agreed with the literature values. The complex shows a pH-dependent absorption spectrum. In water at ca. 20 °C, maxima are seen at 392 and 511 nm, with $\epsilon$ 108 and 75 $\mathrm{M^{-1}\ cm^{-1}}$, respectively (see Figure 1A). The literature reports the same maxima and consistent molar absorptivities of 104[5] and 112[17] for the former and 71[5] and 70[17] for the latter. The spectrum changes in 0.01 M sodium hydroxide to one with a maximum at 419 nm ($\epsilon$ 127 $\mathrm{M^{-1}\ cm^{-1}}$) (Figure 1A), accompanying the conversion of $\mathrm{H_2ONi(tmc)^{2+}}$ to $\mathrm{HONi(tmc)^{+}}$, $\mathrm{p}K_a$ = 10.82.[17,18] The NMR spectra compared well with literature values:[17] the $^1$H spectrum in $\mathrm{D_2O}$ shows resonances at ~100, 61, 47 (2 H), 27, 7.5, and −6.5 ppm (referenced to dioxane at 3.6 ppm), and the $^{13}$C spectrum in $\mathrm{CD_3NO_2}$ gave four (only) resonances at 60.8, 59.0, 45.3, and 22.1 ppm (referenced to dioxane carbon at 67.3 ppm). In particular, the NMR spectra confirmed the absence of any of the *R,S,R,R* isomer.[17] The cyclic voltammetry of the $\mathrm{Ni(tmc)^{2+}}$ complex ($2 \times 10^{-3}$ M) in 0.02 M NaOH/0.08 M $\mathrm{LiClO_4}$ showed one reversible peak ($E_a - E_c$ = 74 mV) on a glassy-carbon electrode. The value of $E_{1/2}$ is −1.09 V referred to Ag/AgCl.

The complex *R,S,R,S*-$\mathrm{[Ni(tmc)](CF_3SO_3)_2}$ was prepared[19] by stirring the Ni(II) salt (2.7 g in 10 mL of water) with the ligand (0.75 g in 20 mL of ethanol) for 3 h at 60 °C. The filtered solution was evaporated to complete dryness at 80 °C to obtain the crystalline solid. The triflate and perchlorate salts have identical visible spectra in water. Other reagents were prepared by standard methods or were available commercially.

**Reaction Conditions.** In the work reported here, the "standard conditions" consisted of 0.020 M sodium hydroxide, 0.080 M lithium perchlorate at 25.0 °C, and a constant ionic strength of 0.10 M. The rigorously air-free conditions required by the highly oxygen-sensitive materials (Ni(I), alkylnickel complexes, and free radicals) required the use of $\mathrm{Cr^{2+}}$-scrubbed argon and extremely careful syringe–septa methods.

**Nickel(I).** The nickel(I) complex *R,S,R,S*-$\mathrm{[Ni(tmc)]^{+}}$, apparently previously unreported, was prepared in alkaline solution by photochemical and electrochemical techniques. The photochemical preparation utilizes reduction of $\mathrm{Ni(tmc)^{2+}}$ by the radical $\mathrm{C(CH_3)_2O\bullet^{-}}$, generated by photolyzing acetone (typically 0.4 M) in solutions containing 2-propanol (1.8 M). The electrochemical preparation, which was used in most of the experiments, consists of controlled-potential reduction at a mercury-pool cathode. These are the same methods that proved successful for *R,R,S,S*-$\mathrm{[Ni(tmc)]^{+}}$.[4] The solutions of *R,S,R,S*-$\mathrm{[Ni(tmc)]^{+}}$ are quite air-sensitive, although a little less so than those of the exceptionally reactive *R,R,S,S* isomer. Also, even if some of the *R,S,R,S*-$\mathrm{[Ni(tmc)]^{+}}$ isomer should be destroyed by oxygen, it (unlike the *R,R,S,S* system[4]) can be rereduced electrochemically and photochemically. Solutions of *R,S,R,S*-$\mathrm{[Ni(tmc)]^{+}}$ are characterized by a single, intense UV peak at 352 nm, $\epsilon$ $(4.0 \pm 0.2) \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$ (see Figure 1A). The molar absorptivity was evaluated by spectrophotometric titrations with $\mathrm{Co(NH_3)_5F^{2+}}$ and $\mathrm{Co(en)_3^{3+}}$. The spectrum compares to that of *R,R,S,S*-$\mathrm{[Ni(tmc)]^{+}}$ with $\lambda_{max}$ 360 nm and $\epsilon$ $4.0 \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$.

**Products.** The organonickel complexes were detected by their UV-visible absorption spectra and identified by the products of their reactions, including hydrolysis. Hydrolysis[20] produces *R,S,R,S*-$\mathrm{[Ni(tmc)]^{2+}}$ in each case. The organic products were hydrocarbons whose identities were determined on the solution or the gas phase above it by VPC using appropriate commercially available columns in a Hewlett-Packard Model 5790 gas chromatograph. The retention times and amounts were calibrated with known materials.

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[15] Hegedus, L. S.; Thompson, D. H. P. *J. Am. Chem. Soc.* **1985**, *107*, 5663.

[16] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapter 7. (b) See, for example, ref 1–13 in ref 4.

[17] Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89.

[18] Generally speaking, we write $\mathrm{Ni(tmc)^{2+}}$ to represent the equilibrium mixture of four-coordinate and five-coordinate species (monoaquo and monohydroxo).

[19] Lincoln, S. F.; Coates, J. H.; Hadi, D. A. *Inorg. Chim. Acta* **1984**, *81*, L9.

[20] The full account of hydrolysis reactions will be reported separately. When R is a halo- or tosyl-substituted alkyl group, other decomposition modes are observed (Ram, M. S.; Espenson, J. H.; Bakac, A., unpublished observations).

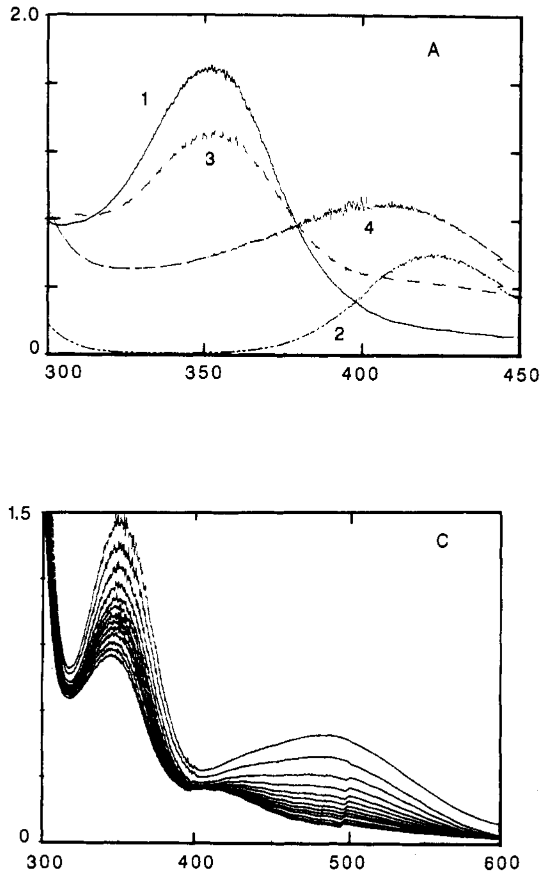

**Figure 1.** Various absorption spectra of Ni(tmc)$^{n+}$ complexes and reactions: (A) spectra of (1) *R,S,R,S*-[Ni(tmc)]$^+$ (0.9 mM in a cell of 0.5-cm optical path) and (in 1-cm cells) of (2) *R,S,R,S*-[Ni(tmc)]$^{2+}$ at pH 12.0 (4.7 mM) and of (3) methyl (0.47 mM) and (4) 1-propyl (0.45 mM) nickel complexes; (B) rapid-scan stopped-flow spectra during the reaction of Ni(tmc)$^+$ (0.2 mM) with ethyl iodide (2.0 mM), the 16 spectra taken in a total elapsed time of 400 ms taken in the 2-cm cell of the Durrum instrument using the OLIS rapid-scan instrumentation; (C) spectra recorded during the hydrolysis of $PhCH_2Ni(tmc)^+$ at intervals of 36 s by using a diode-array spectrophotometer, showing the gradual decay of the absorption spectrum; (D) progress of the hydrolysis of the (3-hydroxy-1-propyl)nickel complex, from 2.7 s after mixing 0.7 mM Ni(tmc)$^+$ and 0.35 mM $Br(CH_2)_3OH$, showing successive spectra in 2-cm cells recorded at intervals of 0.625 s.

The reactions between RNi(tmc)$^+$ and cobalt(II) complexes were carried out by adding a solution of the Co(II) complex (0.25 mM) to the freshly prepared organonickel complex (typically, by reaction of 0.7 mM Ni(I) with 0.35 mM RX, although other experiments were done with one reagent or the other in excess). The blue color of the cobalt(I) anion was immediately evident; $Co(dmgH)_2^-$ decomposed when acidified, whereas $Co(dmgBF_2)_2^-$ was usually oxidized to the Co(III) state by $H_2O_2$ or $Fe^{3+}$, since acidification alone produces a stable, highly colored Co(II) complex. The same reaction occurred when the organonickel reactant was prepared with excess alkyl halide. This proves that the Co(I) was not the product of a direct reaction between excess Ni(tmc)$^+$ and Co(II) (which is known to occur). The organocobalt products from the alkyl-transfer reactions were identified by their UV-visible and NMR spectra. Spectrophotometric titrations were used to establish the reaction stoichiometry. Typical reaction conditions were [Ni(tmc)$^+$] = 0.5-1 mM and [RX] = 0.2-0.5 mM.

**Kinetics.** The rates of reaction between the nickel(I) complex and alkyl halide were generally monitored by the stopped-flow technique. These determinations used a Canterbury SF-3A instrument interfaced with the OLIS 3820 data acquisition and numerical-analysis system. A similarly interfaced Durrum stopped-flow instrument, a Perkin-Elmer diode-array spectrophotometer, or conventional spectrophotometers were also used in the rate measurements. The 352-nm absorption of Ni(tmc)$^+$ proved most generally useful, although in special cases the absorption bands of the organonickel or of free I$^-$ ions ($\epsilon_{228}$ 1.46 × $10^4$ M$^{-1}$ cm$^{-1}$) were also monitored. The kinetic data were collected under conditions where a first-order or pseudo-first-order kinetic equation is applicable. Rate constants were calculated from the absorbance-time data by least-squares fitting to the equation ($D$ = absorbance) $D_t = D_\infty + (D_0 - D_\infty)\exp(-kt)$. In most instances these calculations were performed as a part of the data acquisition-analysis procedure and utilized >100 data points per determination; otherwise, numerical analysis of separately acquired data was conducted independently. Rate constants determined from stopped-flow runs were generally the average of 2-6 determinations using the same set of solutions. When the value of $k$ depends on other concentration variables (e.g., [RX]), a series of determinations were carried out at different values of the concentration.

**Table I.** Absorption Spectra and Products of Hydrolysis of Organonickel Macrocycles *R,S,R,S*-[RNi(tmc)]$^+$

| R | $\lambda_{max}$/nm ($10^{-3}\epsilon$/(M$^{-1}$ cm$^{-1}$)) | organic product[a] |
|---|---|---|
| methyl | 356 (1.7) | methane |
| ethyl | 406 (1.9) | ethane |
| 1-propyl | 410 (1.9) | propane |
| 2-propyl | 400 (1.8) | propane |
| benzyl | 350 (4.1)<br>494 (1.7) | b,c |
| cyclopropyl | 372 | cyclopropane |
| cyclobutyl | 410 | cyclobutane |
| methoxymethyl[d] | | b |
| 3-hydroxy-1-propyl | 405 | 1-propanol |
| 4-hydroxy-1-butyl | 405 | 1-butanol |
| 1-hex-6-enyl | 405 | 1-hexene and methylcyclopentane[e] |

[a] Determined by GC on VZ-10, FFAP, and OV-101 columns. [b] Not determined. [c] Presumably toluene. [d] Prepared by UV photolysis of 1 M acetone in pH 12 solutions of Ni(tmc)$^{2+}$ saturated with dimethyl ether. [e] The relative yield depends on the initial ratio of reactants (see text).

## Results

**Organonickel Complexes.** The formation of an organonickel complex was generally indicated by the immediate appearance of a bright yellow color on injection of the alkyl halide into the pale green solution of the electrochemically prepared nickel(I) complex, which inevitably also contains unreduced nickel(II). (The benzylnickel complex, with an additional absorption maximum

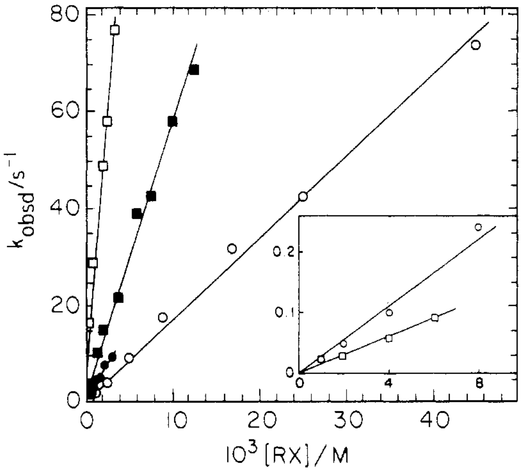

**Figure 2.** Reactions of *R,S,R,S*-[Ni(tmc)]$^+$ with alkyl halides characterized by linear dependences of the pseudo-first-order rate constants on the concentrations of the iodide RI for R = 2-propyl (□), ethyl (■), 1-propyl (●), and methyl (○). The inset shows data for cyclopropyl bromide (○) and 2-propyl chloride (□).

at 494 nm, as in Figure 1C, is a deep red). As the organonickel complex hydrolyzes (eq 4), the solution fades to the lighter yellow color characteristic of the hydroxynickel(II) complex in alkaline solution. Table I lists the absorption spectrum of each complex. The identical methyl complex, *R,S,R,S*-[$CH_3$Ni(tmc)]$^+$, was formed by four different methods: (a) Ni(tmc)$^+$ with $CH_3I$, (b) Ni(tmc)$^+$ with *t*-BuOOH, (c) Ni(tmc)$^+$ (0.7 mM) with $H_2O_2$ (0.4 mM) in the presence of 1 M $(CH_3)_2SO$, and (d) $CH_3MgCl$ with [Ni(tmc)]$(CF_3SO_3)_2$. The Grignard synthesis was done with an excess of the nickel(II) complex in dry THF, and the first three were done in alkaline aqueous solutions. Confirmation that the same product was formed in each case, including the last, was provided by the match in the absorption spectrum of the species formed ($\lambda_{max}$ 356 nm, $\epsilon$ $1.7 \times 10^3$ $M^{-1}$ $cm^{-1}$) and by the observation of the same rate and same product ($CH_4$ only) from its hydrolysis.

**Stoichiometry and Kinetics.** The reaction of Ni(tmc)$^+$ with $CH_3I$ occurs with a 2:1 stoichiometry, with 1.9:1 for $CH_3CH_2I$ and with 1.6:1 for *t*-BuOOH. In the latter case, the $\beta$-scission[21] of the alkyloxy radical (eq 6) is responsible for $\bullet CH_3$ formation.

$$(CH_3)_3CO\bullet \rightarrow (CH_3)_2CO + \bullet CH_3 \qquad (6)$$

The reaction between OH• and $(CH_3)_2SO$ is well-known to yield $\bullet CH_3$.[22,23] The side reactions in this system[23,24] are presumably responsible for the formation of less than the stoichiometric amount of $CH_3$Ni(tmc)$^+$. Since blank experiments with either $(CH_3)_2SO$ or $H_2O_2$ omitted did not give the organonickel product, the observations are consistent with the following sequence:

$$H_2O_2 + Ni(tmc)^+ \rightarrow HONi(tmc)^+ + HO\bullet \qquad (7)$$

$$HO\bullet + (CH_3)_2SO \rightarrow HOS(O)CH_3 + \bullet CH_3 \qquad (8)$$

$$\bullet CH_3 + Ni(tmc)^+ \rightarrow CH_3Ni(tmc)^+ \qquad (9)$$

**Table II.** Rate Constants[a] for the Reactions of Alkyl Halides with *R,S,R,S*-[Ni(tmc)]$^+$

| R | $k/(M^{-1}\ s^{-1})$ RI[b] | RBr[b] | RCl |
|---|---|---|---|
| (A) Primary Alkyl | | | |
| methyl | $1.7 \times 10^3$ (0.65)[c] | | |
| ethyl | $6.2 \times 10^3$ (0.77) | $9.5 \times 10^2$ (0.82) | |
| 1-propyl | $3.3 \times 10^3$ (1.2) | $6.9 \times 10^2$ | 2.2 |
| 1-butyl | | $1.5 \times 10^3$ | |
| 1-amyl | | $1 \times 10^3$ | |
| 1-hexyl | | $5 \times 10^2$ | |
| (B) Substituted Primary Alkyl | | | |
| 2-hydroxy-1-ethyl | | $3.0 \times 10^3$ | |
| 3-hydroxy-1-propyl | | $3.4 \times 10^3$ | |
| 2-hydroxy-1-propyl | | $3.1 \times 10^3$ | |
| (C) Secondary Alkyl; Cycloalkyl | | | |
| 2-propyl | $2.4 \times 10^4$ (0.75) | $2.8 \times 10^3$ | $1.6 \times 10$ |
| cyclopropyl | | $2.57 \times 10$ | |
| cyclobutyl | | $8.9 \times 10^2$ | |
| cyclopentyl | $1.0 \times 10^4$ | | $3.6 \times 10$ |
| (D) Other | | | |
| allyl | | $2 \times 10^5$ | $6 \times 10^4$ |
| 1-hex-6-enyl | | $2.0 \times 10^3$ (1.5) | |
| benzyl | | | $2 \times 10^6$ |

[a] Conditions: 25.0 °C, 0.020 M NaOH, 0.080 M $LiClO_4$ ($\mu = 0.10$ M); the rate constant cited is $k$, the slope of $k_{obsd}$ vs. [RX] (eq 10); generally, $k_1 = k/2$, (see text). [b] The number in parentheses is the ratio of rate constants for this complex to that[4] for *R,R,S,S*-[Ni(tmc)]$^+$. [c] The rate constant with *tert*-butyl hydroperoxide is $3.8 \times 10^5$ $M^{-1}$ $s^{-1}$ and is the same for both Ni(tmc)$^+$ isomers.

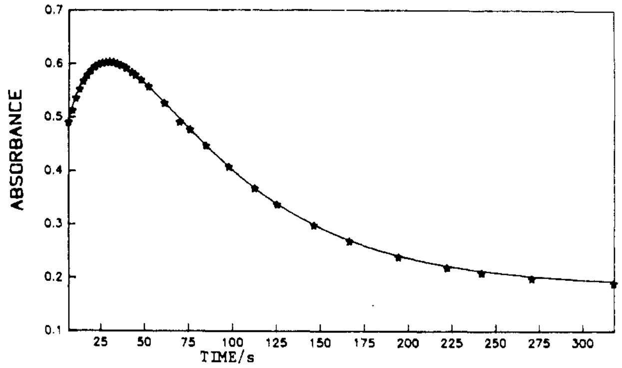

**Figure 3.** Absorbance–time profile during the reaction of *R,S,R,S*-[Ni(tmc)]$^+$ (0.75 mM) with relatively low concentrations of 2-propyl chloride (1.6 mM) such that the rates of formation and hydrolysis of $(CH_3)_2CHNi(tmc)^+$ are comparable. The solid line shows the theoretical profile simulated from the known values of the rate constants, initial concentrations, and molar absorptivities by use of the program KINSIM.[25]

The pseudo-first-order rate constants obtained with $[RX]_0 \gg [Ni(tmc)^+]_0$ vary linearly with [RX], as illustrated in Figure 2. This pattern establishes the second-order rate law of eq 10 and provides the values summarized in Table II.

$$-d[Ni(tmc)^+]/dt = k[Ni(tmc)^+][RX] \qquad (10)$$

Tosylates do not react with Ni(tmc)$^+$. The upper limit for 1-propyl tosylate, for example, is $k < 0.05$ $M^{-1}$ $s^{-1}$.

**Special Cases.** Some of the most interesting cases are those where the isomeric complexes give substantially different results. Several such instances were encountered, as follows.

**(a) R = 2-Propyl.** An organonickel complex derived from a 2-propyl halide was not detected in the earlier work[4] on the *R,R,S,S* isomer of the nickel complex. Either it did not form or it is simply too short lived to accumulate in the solution. We favored the former alternative, although the 2-propyl radical was surely formed in the initial step. The reaction of *R,S,R,S*-[Ni(tmc)]$^+$ with 2-propyl chloride does form an organonickel complex in nearly quantitative yield, and 2-propyl iodide yields the same

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(21) Early work on the well-known $\beta$-scission reaction is reviewed by: (a) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 470–473. (b) Gray, P.; Williams, A. *Chem. Rev.* **1959**, *59*, 239. See also: (c) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593. (d) Walling, C.; Wagner, P. *J. Am. Chem. Soc.* **1964**, *86*, 3368. (e) Howard, J. A. *Adv. Free-Radical Chem.* **1972**, *4*, 49.

(22) (a) Gilbert, B. C.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1975**, *308*. (b) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463. (c) Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2462.

(23) Meissner, G.; Henglein, A.; Baeck, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1967**, *22*, 13.

(24) These include direct oxidation of Ni(I) by the radical $(CH_3)_2S(O\bullet)OH$, the intermediate addition product in eq 8. Complications such as this have been discussed elsewhere.[23]

species in about 25% yield. The yields were judged from the absorption spectra and from the GC-determined hydrolysis products. The reaction of 2-propyl chloride is sufficiently slow that the formation and hydrolysis of the complex occur on comparable time scales, particularly in experiments without a large excess of the halide.

The difference between the two halides suggests that there exists a competition between two reactions, formation of the organonickel from the free radical (eq 2) vs. bimolecular self-reactions (dimerization and disproportionation) of the radical. When the rate of reaction with Ni(I) is higher (e.g., 2-propyl iodide), the resulting higher steady-state concentration favors the latter, and vice-versa. Figure 3 compares the experimental absorbance–time profile with that calculated from the two rate constants independently determined under other conditions by using KINSIM,[25] a program for the numerical integration of kinetic equations. Evidently, the rate constant for capture of the 2-propyl radical by *R,R,S,S*-[Ni(tmc)]$^+$ is just a little smaller, such that little organonickel accumulates with either halide. Indeed, this result and others of a similar character allow rough estimation of the radical capture rate constant ($k_2$), as developed later.

**(b) R = Benzyl.** The reaction of benzyl chloride with *R,S,-R,S*-[Ni(tmc)]$^+$ yields a reasonably stable, red organometallic complex. The spectrum and the progress of the hydrolysis reaction are shown in Figure 1C. In contrast, the *R,R,S,S* isomer on reaction with benzyl halides gave but a "flash of red color", attributed to a transient benzylnickel complex that hydrolyzes with $t_{1/2}$ = 0.8 s. The reaction of benzyl chloride with Ni(tmc)$^+$ is the fastest one measured (see Table I); the reaction of benzyl bromide was too fast for the stopped-flow technique. With excess benzyl chloride, bibenzyl precipitated from aqueous solution; to avoid that, the reactions were run in 1–2 M acetone. Bibenzyl formation is consistent with the general reaction noted[14] between (most) organonickel complexes and organic halides:

$$\mathrm{RNi(tmc)^+ + R'X \rightarrow Ni(tmc)^{2+} + R'R + X^-} \qquad (11)$$

**(c) R = Cycloalkyl and Allyl.** Cyclopropyl bromide forms an organonickel complex which, upon hydrolysis, yields cyclopropane. This shows that the cyclopropyl radical does not rearrange before reacting with the Ni(I) complex. Similarly, cyclobutyl bromide yielded an organonickel complex, but it hydrolyzed to cyclobutane very rapidly. The higher cycloalkyls (c-$C_5H_9Br$ and c-$C_6H_{11}I$) do react with the Ni(I) complex but with a 1:1 stoichiometry. No organonickel complexes were detected spectrophotometrically, and the organic products determined in a reaction of ca. 1 mM RBr or RI with 1 mM Ni(I) consists of a mixture of cycloalkane and cycloalkene in a 1:1 ratio. Similar reactions of RCl gave largely the cycloalkane. These results are consistent with formation of a free radical that may either disproportionate or be captured by Ni(I) to form a hydrolytically unstable organometallic complex. The situation, aside from the reactivity toward hydrolysis, is thus analogous to that for the 2-propyl and 2-butyl halides. Allyl chloride and bromide react very rapidly. They do not form a detectable allylnickel complex.

**(d) RX = 6-Bromo-1-hexene.** This reaction forms a mixture of hexenyl and cyclopentylmethyl complexes, as indicated by the organic products obtained upon hydrolysis with acid.[26] As discussed earlier,[4] this suggests the intermediacy of the 1-hexenyl radical, a species known to undergo rapid, unimolecular cyclization.[27,28] This can be taken as further indication of a free-radical intermediate although it is not fully definitive in this system, not so much because cyclization can be promoted by other mechanisms[29,30] but because there is now good evidence in the *R,R,-S,S*-[Ni(tmc)] complex for cyclization of the 1-hexenyl group *while coordinated to nickel.*[31] Without this possible complication, the ratio of products, 1-hexene and methylcyclopentane, then permits an estimate of $k_2$ for the case R• = 1-hexenyl relative to the (known) rate constant for unimolecular cyclization of this radical.[28] The $k_2$ value so estimated (see below) compares with values arrived at for other radicals. This provides some evidence that no cyclization occurs during the lifetime of *R,S,R,S*-[1-hex-6-enyl-Ni(tmc)]$^+$ or during its hydrolysis.

**Reactions of Organonickel Complexes.** Several observations were made on the chemical reactions of these new complexes, with the objective of using the results to identify them and to characterize their reactivity.

**(a) Hydrolysis.** The organonickel complexes described in this work decomposed in alkaline solution exclusively by the hydrolysis[20] reaction shown in eq 4. Table I lists the chromatographically identified decomposition products.

**(b) Alkyl Transfer to Cobalt.** The reaction of certain cobalt(II) macrocycles with organonickel complexes provides a useful method of confirming their precise identity. The most useful complexes are the cobaloxime, $Co(dmgH)_2$, and a closely related derivative, $Co(dmgBF_2)_2$. The reaction between RNi(tmc)$^+$ and Co$^{II}$L was successful whenever tried and was used to confirm the identity of the organonickel complexes for R = $C_2H_5$, $CH_3OCH_2$, and $PhCH_2$. The most immediate indication of its success was the appearance of the intense blue coloration characteristic of the cobalt(I) product. The organocobalt complex was identified unambiguously in each case listed by its $^1$H NMR spectrum.[32] In addition, the characteristic UV–visible spectrum of the organocobalt was clearly evident in the original reaction solutions, after subtraction of the Ni(tmc)$^{2+}$ spectrum and decomposition or oxidation of Co$^I$L$^-$ and Co$^{II}$L.

Quantitative kinetic measurements were attempted, but (with one exception) the reactions proved too fast even for the stopped-flow technique. The reactions of RNi(tmc)$^+$ (R = alkyl) with the Co(II) complexes have $k > 2 \times 10^6$ M$^{-1}$ s$^{-1}$. The $CH_2OCH_3$ complex reacts with $Co(dmgBF_2)_2$ at a measurable rate, with $k \sim 1.4 \times 10^5$ M$^{-1}$ s$^{-1}$ at 25 °C, $\mu$ = 0.1 M.

The reactions (eq 5) probably take place by one of the two distinctly different schemes, an $S_H2$ displacement process (eq 12, 13) or electron transfer (eq 14, 15).

$$\mathrm{RNi(tmc)^+ + Co^{II}L \rightarrow Ni(tmc)^+ + RCo^{III}L} \qquad (12)$$

$$\mathrm{Ni(tmc)^+ + Co^{II}L \rightarrow Ni(tmc)^{2+} + Co^{I}L^-} \qquad (13)$$

$$\mathrm{RNi(tmc)^+ + Co^{II}L \rightarrow Ni(tmc)^{2+} + R\bullet + Co^{I}L^-} \qquad (14)$$

$$\mathrm{R\bullet + Co^{II}L \rightarrow RCoL} \qquad (15)$$

Our preference for the latter is based on the demonstrated reducing strength of the organonickel complexes.[14] The reactivity order within a series of alkylnickel complexes, which is expected to be very different for the two mechanisms, has not yet been established owing to the extremely high rates of alkyl transfer in the cases examined.

**(c) Other Co(II) Complexes.** Alkyl transfer to other complexes was attempted but proved unsuccessful. The complex Co$^{II}$([14]aneN$_4$)$^{2+}$, for example, did not yield organocobalt products, even at high [Co(II)], and the rates of disappearance of the absorption spectrum of the RNi(tmc)$^+$ cations were the same as the hydrolysis rates in the absence of the cobalt complex. It is

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(25) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. We are grateful to the authors for providing a copy of this program.

(26) The reaction of excess 6-bromo-1-hexene (1.0 mM) with Ni(tmc)$^+$ (0.25–1.0 mM), carried out in 0.1 M DMF, yielded methylcyclopentane (90–96%) and 1-hexene (4–10%) upon acidification.

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(31) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.*, in press.

(32) A typical experiment is the following. About 50 mg of [Ni(tmc)]-$(ClO_4)_2$ in 25 mL of solution was electrolyzed to obtain 1.5–1.6 mM Ni(tmc)$^+$. Alkyl halide (ca. 0.7 mM) was added, followed by Co(II) (10 mL of 5 mM) and pyridine (0.05 M). The organocobalt complex was extracted with dichloromethane and dried on a rotary evaporator; its NMR spectrum was recorded in $CDCl_3$.

interesting to note that this Co(II) complex was also not reduced by Ni(tmc)$^+$. This further shows that electron transfer, a property influenced by the ligands bound to cobalt, may be important in alkyl transfer. Attempted transfers of alkyl groups to $Co(NH_3)_5^{2+}$ were not successful.

**(d) Alkyl Halides.** The reaction of RNi(tmc)$^+$ with R′X (eq 11) occurs readily in the *R,R,S,S* series.[14] The same reaction occurs here; as before, the methyl complex does not react with alkyl iodides. The reactions in this series occur somewhat more slowly, but quantitative kinetic data were not determined. The cyclopropylnickel cation does not react with cyclopropyl bromide.

**(e) Cobalt(III) Oxidants.** The complex *R,S,R,S*-[$C_2H_5$Ni(tmc)]$^+$ reacts with $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, and $(NH_3)_5CoF^{2+}$ These reactions were examined because the Co(III) complexes, which react quite rapidly with Ni(tmc)$^+$, seemed likely to be useful reagents to use in a search for homolysis. The reactions with the organonickel complex occur relatively slowly; since they were not much faster than the hydrolysis, high concentrations of the Co(III) reagent were required. Assuming a second-order rate law (which was not fully verified), the approximate second-order rate constants are 6, 1, and 9 $M^{-1}$ $s^{-1}$, respectively.

**(f) Attempted Nickel–Carbon Homolysis Reactions.** Many metal alkyls, including organocobalt and $(H_2O)_5Cr{-}R^{2+}$ complexes,[33] undergo a reversible, unimolecular homolysis process. This is the reverse of the bond formation reaction by radical capture (eq 2). Among other characteristics, homolytic cleavage of the nickel–carbon bond, an uphill process, would need to be drawn to completion by addition of a reagent capable of reacting rapidly with the products of homolysis, Ni(I) and the radical, but not able to react rapidly with the organonickel complex. No homolysis reaction was observed in any of the *R,R,S,S*-[RNi(tmc)]$^+$ complexes.[4] *In no instances was evidence obtained that suggested the occurrence of nickel–carbon bond homolysis in any of the complexes under any conditions.* Even the benzyl complex, which might be expected to be among the most reactive toward homolysis, gave no indication of such reactions.

## Discussion

In one sense the lack of nickel–carbon bond homolysis is not surprising. The thermodynamic tendency of the metal–carbon bond in a given $L_nM{-}R$ complex to homolyze is related to the one-electron-reduction potential of the inorganic constituent (i.e., to $E°$ for Ni(tmc)$^{2+/+}$ or $Cr^{3+/2+}$, etc.). The reduction potential for Ni(tmc)$^{2+}$ is so negative ($E° = -0.87$ V vs. NHE) that bond homolysis is expected to be quite unfavorable. Since the radical capture rate constants ($k_2$) are quite substantial ($\gtrsim 10^7$ $M^{-1}$ $s^{-1}$, comparable to the values for R• + $Cr_{aq}^{2+}$), this thermodynamic barrier $K_{hom} = k_{-2}/k_2$) translates into a kinetic barrier and an immeasurably small value for $k_{-2}$.

**Mechanism.** The kinetic data for this isomer are more extensive than those reported earlier for the *R,R,S,S* isomer.[4] The principal trends remain the same, however, and support the assignment of a scheme (eq 1, 2) in which carbon-centered free radicals are generated and then captured by a second Ni(I). These trends consist of the following reactivity orders: (a) benzyl > allyl > secondary > primary > methyl > cyclopropyl, and (b) RI > RBr > RCl. In addition, the observation that a mixture of cyclized and uncyclized hydrocarbons results from the reaction of 6-bromo-1-hexene with Ni(tmc)$^+$ also suggests the formation of alkyl radical intermediates.[27]

Similarly, the 2:1 stoichiometry supports a two-step radical mechanism, and even the cases that deviate from it (e.g., 2-propyl and allyl halides) do so in a way that also supports the indicated scheme, as described subsequently. The rate constant $k_1$ is accordingly given by $k/2$ *in those cases where the 2:1 stoichiometry holds.*

We suggest that the radical-forming reaction (eq 1) occurs by an atom abstraction mechanism (i.e., inner-sphere electron transfer). The trends in the kinetic data are, as noted previously,[4] consistent with that assignment. Nonetheless, we cannot rule out an outer-sphere electron-transfer process, because the proper basis for this distinction, the observation (or not) of a halonickel(II) complex, is not permitted by the lability of this complex toward axial ligand substitution. Furthermore, the kinetic trends, while supportive of the atom abstraction pathway, do not uniquely define the mechanism, in the absence of a bona fide example of outer-sphere electron transfer, which might show different trends in its kinetic profile. The failure of tosylates to react with Ni(tmc)$^+$ clearly establishes the basic process to be electron transfer, not nucleophilic substitution.

**Radical Capture Rate Constants.** Several of these systems provided data that allow us to estimate $k_2$, the rate constant for the reaction (eq 2) between the alkyl radical and Ni(tmc)$^+$. As alluded to, 1-hexene and methylcyclopentane are both formed in the reaction of the 1-hexenyl radical. Their ratio, when analyzed as described previously,[4] gives $k_2 \sim 3 \times 10^7$ $M^{-1}$ $s^{-1}$ for R• = 1-hexenyl.

The other systems permitting such an analysis are the cases where only a partial yield of the organonickel complex forms. One makes the assumption that the process competing with eq 2 is the self-reaction of a pair of radicals (dimerization/disproportionation). Either on the basis of a steady-state treatment or by the use of a more rigorous solution (aided by KINSIM), the following estimates were obtained: 2-propyl, $10^6$ $M^{-1}$ $s^{-1}$; cyclopentyl and cyclohexyl, $10^5$ $M^{-1}$ $s^{-1}$; benzyl, $\sim 10^8$ $M^{-1}$ $s^{-1}$; allyl $<10^6$ $M^{-1}$ $s^{-1}$.

The fact that primary radicals are the most reactive is consistent with the high and presumably quantitative yields in every case. The low reactivity of the highly delocalized allyl radical is not surprising. The 2-propyl and cycloalkyl radicals, which are the most sterically hindered, are also less reactive. In fact, only a relatively small change in the relative decrease in the value of $k_2$ as compared to the rate constant for the reaction R• + R• would be sufficient to prevent the formation of an appreciable quantity of an organonickel complex. That, evidently, is the situation with the *R,R,S,S*-[Ni(tmc)] isomer. The molecular conformation (arising from different orientations of the trimethylene rings and the four methyl groups) is crucial in determining a good deal of the coordination chemistry of the isomeric nickel(II) complexes of this ligand; its influence evidently extends to the radical capture rates as well.

**Summary.** Electron transfer to alkyl halides from *R,S,R,S*-[Ni(tmc)]$^+$, a very strong reductant, results in the formation of free alkyl radicals. The latter, captured by a second Ni(I) in a more rapid reaction, form organonickel complexes. This process occurs for a wide range of alkyl groups. These organometallic complexes show considerable stability toward hydrolysis and permit a study of other reactions, including the transfer of the alkyl group to cobalt and the formation of new carbon–carbon bonds by reaction with alkyl halides. Both of the latter are best accounted for as electron-transfer reactions, further evidence that the organonickel complexes are themselves good electron donors. Bond homolysis is not an observable reaction of the organonickel complexes under any of the conditions examined.

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