rate enhancement for *p*-nitrotrifluoroacetanilide over other ring-substituted trifluoroacetanilides. The hydroxide ion catalyzed rate constant is about 10 times faster for *p*-nitrotrifluoroacetanilide and the Tris catalyzed rate constant is virtually identical with that for trifluoroacetanilide itself.[5,12] The small variation of these rate constants with substituent shows that little or no negative charge is formed on the amide nitrogen at the transition state, even for *p*-nitrotrifluoroacetanilide, and is consistent with the leaving group being the free nitroaniline molecule rather than a negative anilide ion. In addition, the observation of general catalysis for this pathway demands that the base be present in the activated complex, although several functions can be envisioned for the base molecule.[11]

We find the difference in mode of breakdown of these two intermediates surprising, especially in view of the fact that for other anilides the monoanion and the dianion have been found to decompose by the same mechanism.[9] Even when a change in mechanism with substituent is postulated, it appears that the change occurs at the same place for both the monoanion and the dianion.[9]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Helpful discussions with Professor R. L. Schowen are also greatly appreciated.

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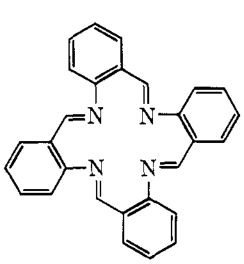
Alkoxyethylidene Functions as Reactive Sites for the Attachment of Pendent Groups to Complexes of Macrocyclic Ligands. Crystal Structure and Reactivity Patterns

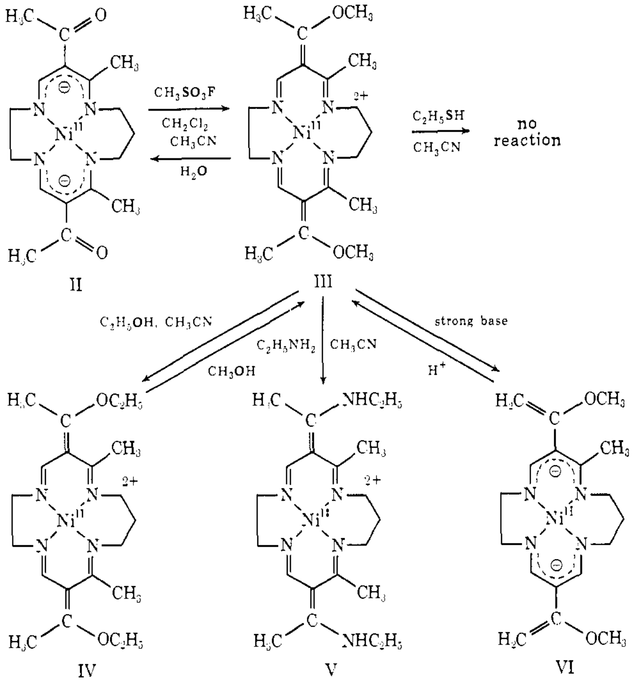
Sir:

Among the major synthetic goals related to the use of macrocyclic transition metal complexes as models for biological systems is activation of the planar chelate rings toward attachment of other functional groups properly oriented to allow interaction with the central metal ion *via* its axial coordination sites. Synthetic macrocyclic complexes having such pendent functional groups could then be used to examine the chemistry associated with these features in naturally occurring systems. One possible route to this type of system has been reported involving the reversible addition of a variety of nucleophiles to the azomethine carbon atoms in Ni(II) and Cu(II) complexes of the macrocycle I.[1-3]



I

Scheme I



We wish to report the results of our studies on the alkylation of the carbonyl groups of II[4-6] (Scheme I) leading to the formation of III. Treatment of II with methyl fluorosulfonate in dichloromethane produced III, originally formulated as the product of N-alkylation.[6] The X-ray crystal structure, however, establishes the site of alkylation to be as shown in III, and the methoxyethylidene groups display an interesting selectivity in their reactions with nucleophiles, providing a convenient route for the attachment of side chains to the ligand framework.

6,14-Bis(1-methoxyethylidene)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraenenickel(II) perchlorate, $C_{12}H_{30}N_4O_{10}NiCl_2$ (III):[7] yellow rods from acetone; orthorhombic; *Pbcm*; $a = 8.257$ (4), $b = 13.94$ (1), $c = 22.11$ (1) Å; $M = 604.09$; $D_{\text{measd}} = 1.574$ g/cm³, $Z = 4$, $D_{\text{calcd}} = 1.577$ g/cm³; μ (Mo Kα) 10.3 cm^{-1}. $R = 0.046$ for 2228 independent reflections above background for a structure with molecular parameters shown in Figure 1. The molecule lies astride a crystallographic mirror plane. The bond lengths and angles are consistent with a bonding scheme involving localized double bonds. Remarkably, the central six-membered ring exists in the *boat* form, the Ni and C segments being tilted up 35 and 56°, respectively, from the central four atom plane defined

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(1) L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 1072 (1969).

(2) V. Katović, L. T. Taylor, and D. H. Busch, *ibid.*, **91**, 2172 (1969).

(3) V. Katović, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, **10**, 4581 (1971).

(4) 6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenatonickel(II) (II) was prepared by the method of Jäger.[5] Satisfactory elemental analyses were obtained for all complexes reported.

(5) E. Jäger, *Z. Chem.*, **8**, 392 (1968).

(6) C. J. Hipp and D. H. Busch, *J. Chem. Soc., Chem. Commun.*, 737 (1972).

(7) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4465. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

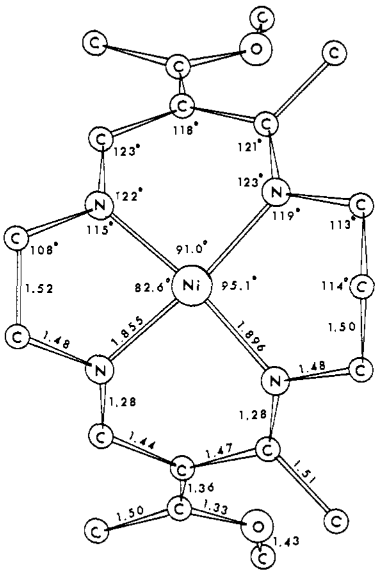

Figure 1. Bond lengths and angles in III. The angles and distances involving light atoms have been rounded off for clarity (av esd C–C 0.004 Å, C–C–C 0.3°).

by the C–N bonds. The conjugated system is not planar, the unsaturated chelate rings also adopting the boat form, with the C=N bonds approximately parallel, and the Ni and C segments tilted up 33 and 25°, respectively. The nickel atom lies 0.05 Å out of the plane of the nitrogen atoms.

The methoxyethylidene groups of III were found to undergo two types of reactions with nucleophiles. First, in addition to the previously reported hydrolysis leading to II (Scheme I), reactions with alcohols, ethylamine, and sodium ethoxide have been characterized. In acetonitrile solution III reacts with excess ethanol to form IV, indistinguishable from IV prepared by alkylation of II with triethyloxonium fluoborate. Yellow crystalline IV was isolated as a perchlorate salt, a 2:1 electrolyte in acetonitrile, whose pmr spectrum (CD_3NO_2) shows $-OC_2H_5$(triplet, 6 H, $J \sim 7$ Hz at τ 8.54 and a quartet, 4 H, $J \sim 7$ Hz at τ 4.51 and no OCH_3. This reaction is reversible (IV → III in the presence of excess methanol). Excess ethylamine also reacts with III in acetonitrile giving V, a brown crystalline solid. This material (ν(N–H) at 3280 cm^{-1} in Nujol mull, a 2:1 electrolyte in acetonitrile) is readily characterized by its pmr spectrum (CD_3NO_2) (CH_3 triplet, 6 H, $J \sim 7$ Hz at τ 8.67 and a broad N–H singlet, 2 H at τ 2.54). No reaction was observed, however, upon exposure of III to excess ethyl mercaptan in CH_3CN solution after several days.

Another type of product was observed in the presence of strong bases, or bases which are either sterically hindered, or poor nucleophiles toward the carbon atom in question. Thus, upon addition of excess triethylamine, alkoxide, mercaptide anion, or sodium carbonate to III in acetonitrile, the amber solution turned dark red. This reaction, which is readily reversible on addition of excess acid was shown to involve deprotonation of III at the ethylidene methyl groups leading to VI. Treatment of III in acetonitrile solution with excess sodium ethoxide, followed by reduction of the solution volume, produced a dark green material, formulated as VI. The salient features of its pmr spectrum ($CHCl_3$) include the absence of a methyl singlet in the region expected for CH_3COCH_3 and the presence at τ 6.12 of a multiplet, 4 H, assigned to $CH_2{=}COCH_3$. Reaction of VI with deuteriotrifluoroacetic acid gave a product whose pmr spectrum was indistinguishable from that of III in the same solvent, except for reduction of the intensity of the methyl singlet at τ 7.47 to two-thirds of its initial value. The competition between these two kinds of processes, nucleophilic attack and deprotonation, is responsible for the selectivity toward nucleophiles exhibited by the compound. The increased electron density of the deprotonation product prevents its reaction with nucleophiles.

The selectivity toward nucleophiles displayed by III and its analogs affords a possible route to the attachment of additional chelate rings to the macrocyclic structure. It is especially significant that deprotonation can be effected on these derivatives for this both produces an anionic ligand and enhances the freedom of rotation about the bond connecting the newly constructed pendent group to the macrocycle proper. Synthetic applications of these new reactions are the subject of on-going studies.

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Hydrogenation of Highly Hindered Compounds in the Study of Structure Sensitivity

Sir:

Of the many parameters which would be needed completely to characterize the surface of a metallic particle, there is one, the fraction of surface atoms which project in some degree from the surface at edges, vertices, or steps, which is of particular interest with respect to an important current problem in heterogeneous catalysis, structure sensitive (demanding) *vs.* structure insensitive (facile).[1] At present, it appears likely that the rates of some heterogeneous catalytic reactions depend primarily upon metallic surface area and are nearly independent of details of catalyst preparation (structure insensitive) whereas the rates of other reactions vary markedly with catalyst preparation (structure sensitive). A number of correlations of structure sensitive features with metallic particle size (presumably inversely related to the fraction of projecting atoms) in metallic catalysts have been proposed.[2,3] However, no such correlations have been attempted with two types of reactions of im-

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(2) R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, 60, 1043 (1956).

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