Table IV. Experimental Values of the Ratio k_l/k_s for the Reactions of NiS_6^{2+} and $NiClS_5^+$ with Various Incoming Ligands Y in S = Methanol at 25°C

Y	log (k_l/k_s)	
	NiS_6^{2+}	$NiClS_5^+$
4-Phenylpyridine	−0.9	−1.4
Phenanthroline	−0.2	−2.2
Bipyridine	−1.0	−2.1
Terpyridine	−1.4	−2.5
All Y[a]	−0.4	−0.4

[a] Value predicted by eq 3 of ref 2 for the following conditions: solvent exchange is rate limiting and no interaction occurs between the inner and outer coordination spheres.

The conclusions reached here have implications for the general theory of ligand substitution kinetics proposed by Bennetto and Caldin[11,19] to account for correlations observed between the kinetic parameters (k_l/k_s) and ($\Delta H^{\ddagger}_l - \Delta H^{\ddagger}_s$) on the one hand and quantities related to solvent structure, such as its enthalpy of vaporization and its fluidity, on the other. The correlations involved eight solvents, including water, methanol, dimethyl sulfoxide, and acetonitrile, but were restricted to bipyridine (mainly) and terpyridine, and, subsequently,[20] to the bidentate ligand pyridine-2-azo-*p*-dimethylaniline. In order to account for the proposed influence of solvent structure, an elegant theory was developed in which passage of a solvent molecule from the disordered region surrounding the solvation sphere into the bulk solvent is thought to contribute to the kinetics to the extent that the ligand modifies local solvent structure. We have given a preliminary critique of the theory elsewhere.[4] As a probe into the solvent dependence of ligand substitution kinetics, a ligand such as bipyridine presents serious complications, such as its severe steric requirements, both in first-bond formation[13] and in ring closure,[4,12] and its polarity and aromatic character. It has been found subsequently that simple inorganic ligands, and even unidentate ligands such as pyridine or 4-phenylpyridine, show little correlation with solvent structure,[3,4,21,22] but the unidentate (not the multidentate) ligands do show a correlation with the ligand strength of the solvent.[22] Furthermore, it was recently shown by Langford that solvent exchange is insensitive to bulk solvent structure when the entering group, leaving group, and nonlabile ligands all are kept invariant.[23] This led Langford to suggest that Bennetto and Caldin's correlations apply to the outer-sphere complexation step. However, the evidence presented in this paper has shown that other factors also must be considered. The observed correlations reflect the complex interplay of such factors as the size and ligand strength of solvent molecules present in the inner sphere, the structure of the solvent in the outer sphere and in the bulk medium, and the steric requirements, polarity, and aromaticity of the ligand, various combinations of which affect outer-sphere complexation, first-bond formation, and ring closure.

Acknowledgment. We thank the National Science Foundation for financial support under Grant GP-38762X and Dr. H. P. Bennetto for providing us with his results before publication.

Registry No. $Ni(MeOH)_6^{2+}$, 18443-63-5; $NiCl(MeOH)_5^+$, 24445-82-7; $NiBr(MeOH)_5^+$, 25999-77-3; $NiI(MeOH)_5^+$, 25999-78-4; $Ni(SCN)(MeOH)_5^+$, 41119-86-2; 4-phenylpyridine, 939-23-1; 2,2'-bipyridine, 366-18-7; 1,10-phenanthroline, 66-71-7; 2,2',2''-terpyridine, 1148-79-4.

References and Notes

(1) Taken in part from the M.S. thesis of D.M.G., University of Pittsburgh, 1974.
(2) P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, preceding paper in this issue.
(3) P. K. Chattopadhyay and J. F. Coetzee, *Anal. Chem.*, **46**, 2014 (1974).
(4) P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, **12**, 113 (1973).
(5) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).
(6) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).
(7) F. Dickert, H. Hoffmann, and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.*, **74**, 500 (1970).
(8) P. Fischer, H. Hoffmann, and G. Platz, *Ber. Bunsenges. Phys. Chem.*, **76**, 1060 (1972).
(9) J. Williams, S. Petrucci, B. Sesta, and M. Battistini, *Inorg. Chem.*, **13**, 1968 (1974).
(10) M. L. Sanduja and W. MacF. Smith, *Can. J. Chem.*, **50**, 3861 (1972).
(11) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A* 2191, 2198, 2207 (1971); H. P. Bennetto, *ibid.*, 2211 (1971).
(12) D. J. Benton and P. Moore, *J. Chem. Soc., Dalton Trans.*, 399 (1973).
(13) D. M. W. Buck and P. Moore, *J. Chem. Soc., Dalton Trans.*, 2082 (1974).
(14) G. Macri and S. Petrucci, *Inorg. Chem.*, **9**, 1009 (1970).
(15) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).
(16) R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965); **5**, 622 (1966).
(17) E. Hsu, Ph.D. Thesis, University of Pittsburgh, 1975.
(18) Z. Luz, *J. Chem. Phys.*, **51**, 1206 (1969).
(19) E. F. Caldin and H. P. Bennetto, *J. Solution Chem.*, **2**, 217 (1973).
(20) H. P. Bennetto and Z. S. Imani, *J. Chem. Soc.*, in press.
(21) J. F. Coetzee and E. Hsu, *J. Solution Chem.*, **4**, 45 (1975).
(22) F. Dickert, H. Hoffmann, and T. Janjic, *Ber. Bunsenges. Phys. Chem.*, **78**, 712 (1974).
(23) C. H. Langford and J. P. K. Tong, *Can. J. Chem.*, **53**, 702 (1975).

Contribution from the W. A. Noyes Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

N-Alkylation of Macrocyclic Secondary Amine Complexes of Nickel(II)

F. WAGNER and E. KENT BAREFIELD*

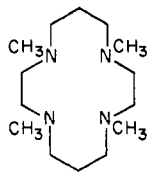
Received August 25, 1975 AIC50664B

The utility of deprotonation–alkylation reaction sequences in macrocyclic amine–nickel complexes for the synthesis of new *N*-alkyl complexes is outlined. Extensive use is made of DMSO as solvent with KOH and $CH_3S(O)CH_2Na$ as bases in these reactions. Special consideration is given to stereochemical aspects of the synthetic method. Fast proton transfer between acid and conjugate base strongly affects the stereoselectivity of the alkylation reactions in certain cases. Because of the strongly basic nature of the amide species produced in the deprotonation reaction only alkylating agents without β hydrogens have been studied. Chemical reactions of the new complexes are described; these include both metal and ligand oxidation and ligand protonation. The kinetic stability of the N-alkylated complexes increases with increased N-substitution. Spectral studies suggest that the ligand field strength steadily decreases for a given ligand system as the number of *N*-alkyl groups is increased.

Introduction

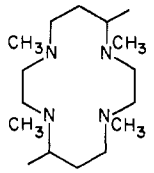
Although macrocyclic amine ligands and their metal complexes have been the subject of extensive investigation over the past 14 years, only recently have these ligands incorporated *tertiary* amine donors. As a part of our study of the redox chemistry of Ni(III) complexes of macrocyclic amine ligands we required a complex of a saturated ligand without amine protons.[1] Only a few examples of macrocyclic ligands with tertiary donors were known when we began our investigation.[2] None of these met our needs, either because the chelate ring

size was improper or because all nitrogens were not tertiary. Our initial approach was to synthesize N-methylated cyclam,



1

1 (TMC).[3] As outlined in a previous report, Ni(II), Cu(II), and Zn(II) complexes of this ligand were prepared and studied.[3] Two striking properties of these complexes were their very high labilities and propensities for pentacoordination. Kaden and co-workers have recently investigated complexes of ligand 1 and the related ligands 2 and 3.[4] Complexes of



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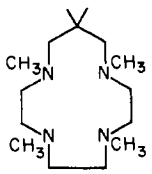

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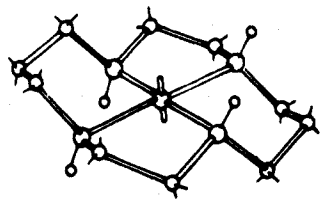
the latter two ligands are also pentacoordinate when coordinating solvents or anions are available. On the basis of NMR data obtained on the nickel(II) and zinc(II) complexes of 1 we suggested a planar array of nitrogen donors existed in these complexes and that all *N*-methyl substituents in both four- and five-coordinate forms were on the same side of the coordination plane.[3] Kaden and co-workers did not prepare any four-coordinate complexes and considered the pentacoordinate forms to be trigonal bipyramidal with the tertiary amine ligands in folded conformations.[4] Their conclusion was reached on the basis of electronic spectra obtained on nickel(II) complexes. A recent crystal structure determination on $[Ni(TMC)N_3]ClO_4$ confirms our earlier conclusion based on the NMR measurements; that is, the nitrogen donors are coplanar and all methyl substituents are on the same side of the coordination plane.[5]

It has been established that the thermodynamically most stable form of complexes of macrocyclic 14-membered secondary amine ligands in the absence of *C*-methyl group influences, is that shown by[6-9]



This structure, often referred to as the cyclam or *trans*-III[6] form, minimizes proton–proton interactions in the chelate rings and it is virtually free of torsional bond strain. It is known, however, that an isolable intermediate is formed during the formation of the Cu(II) analogue of 4 (Figure 1).[9] This intermediate and the more thermodynamically stable form are related by inversions of nitrogen donors. In mildly basic solution proton dissociation is rapid and amine inversions may take place in the conjugate base (amide) form. In the case of ligand 1, nitrogen inversion is blocked upon binding to the metal ion. Thus, only forms allowed by the kinetic processes leading to complex formation are possible.

Since the metal complexes prepared with 1 as the macrocyclic ligand were so labile, stable complexes in high oxidation states could not be prepared. Methods for preparation of complexes of 1 with other sets of nitrogen configuration were sought. One reasonable approach to the synthesis of a new isomer appeared to us to be N-alkylation of a preformed complex of a macrocyclic secondary amine ligand. Alkylation of coordinated mercaptides is a well-known synthetic method for generating coordinated thioethers.[10] However, a coordinated mercaptide has nonbonding electron pairs available for nucleophilic attack on an alkylating agent. Coordinated amines are nonnucleophilic but there is ample evidence available that indicates that coordinated primary and secondary amines may be deprotonated and that the deprotonated forms are nucleophilic.[11] Coordinated amines may have acidities which are 10^{16}–10^{25} times greater than the free amine depending upon the metal ion to which they are bound. pK_a's of amines coordinated to divalent metal ions are estimated to be on the order of 14–18. Second and third protons will have much larger pK_a's. Thus a strong base in an aprotic solvent is required for even a single quantitative deprotonation. A systematic study of coordinated amine acidities was done earlier by Watt and co-workers.[11] These workers used potassium amide as base in liquid ammonia. Many deprotonated species were isolated by these workers and some alkylation reactions were accomplished. The heterogeneous conditions that were utilized in these alkylation reactions often made reaction times excessively long for practical synthetic use. When we first considered N-alkylation of coordinated macrocyclic ligands as a route to tertiary amine ligands, our goal was a completely N-alkylated system. It was soon obvious that complete alkylation, using Watt's method, would require a multistep reaction sequence and an excessively long time to complete the sequence. We directed our efforts to investigating methods that would reduce the number of steps and time required for complete N-alkylation. This report describes a general method for alkylation of macrocyclic amine complexes of nickel(II),[12] which utilizes DMSO as solvent and strong bases such as KOH and $NaCH_2S(O)CH_3$ for deprotonation of the coordinated secondary amine donors. Using the synthetic procedures we have developed, we have prepared a number of complexes with macrocyclic ligands containing tertiary donors. The properties of these new complexes are presented along with detailed considerations of the stereochemical aspects of the alkylation reactions.

Results and Discussion

Deprotonations of Secondary Amine Complexes. Preliminary experiments that were conducted with $[Ni(cyclam)](ClO_4)_2$, **16**, and KNH_2 in liquid ammonia indicated that stepwise removal of two protons could be accomplished. Removal of the first proton generated a deep purple solution and the second a brick red precipitate. Additional equivalents of potassium amide produced no further changes. It was clear that alkylation of all four secondary amine nitrogens would require at least a four-step sequence with purification of intermediates. Furthermore, alkylation reaction times utilized by Watt and co-workers were so long as to make this method unattractive, if not impossible.

Consideration of aprotic solvents that were suitable for dissolution of the ionic macrocyclic amine complexes and that were compatible with strong bases suggested that DMSO or HMPA might be useful. Both of these are stable to a variety of strong bases and they are good solvents for practically all of the complexes that we planned to study. Cost, availability, and rapid success caused us to settle on DMSO as the solvent for most of our studies.

Stepwise removal of two protons from complexes that contained two or more secondary amine donors was accomplished with both pulverized KOH and $NaCH_2S(O)CH_3$. All

ionic complexes were quite soluble in DMSO whereas neutral species tended to be somewhat less soluble. Thus, monodeprotonation of **16** yielded an intense purple color and removal of a second proton produced a brick red precipitate. Complexes **12** and **14** yielded orange precipitates on monodeprotonation but each gave a dark orange solution when a second proton was removed. Proton removal tended to be faster with $CH_3S(O)CH_2^-$ than with KOH. The most extreme difference in behavior occurred with **16**. Both deprotonation steps were essentially instantaneous with $CH_3S(O)CH_2^-$ but the second deprotonation step was not complete in 1 hr with KOH.

Complex **4** exhibited a behavior unlike any of the several other systems that we studied. In many trials over several months, using either KOH or $CH_3S(O)CH_2^-$ as base, we observed a blue monodeprotonated species upon addition of 1 equiv of base and a red doubly deprotonated species upon addition of a second equivalent. However, more recent efforts to produce the red doubly deprotonated species by use of either KOH or $CH_3S(O)CH_2^-$ resulted instead in the formation of a green crystalline species which began to appear as the second equivalent of base was added (in the case of $CH_3S(O)CH_2^-$). Addition of about 2.5 equiv of $CH_3S(O)CH_2^-$ generated the red color that was observed earlier. Characterization of the green material was hampered by its extreme sensitivity to the atmosphere; it smoked and charred (but did not inflame) when it was exposed. Hydrolysis of the green product followed by titration indicated that there were 2 equiv of base per mole of complex and an NMR spectrum obtained on the hydrolysis products (38% DCl) indicated that there were two DMSO fragments per complex (by integration). Nickel analyses on both the green product and its hydrolysis solution products, plus the above data, suggested that the green product should be formulated as an adduct of the monodeprotonated complex with $CH_3S(O)CH_2^-$ and DMSO. A completely adequate explanation for the above behavior is not available. As many variables as we could reasonably check have not allowed us to obtain again the red doubly deprotonated material with only 2 equiv of base. Presumably the energetics of the two situations are quite similar, and once crystallization of the green material was seeded, the other form could not be obtained under conditions of exact stoichiometry.

The deprotonated species are stable in DMSO for long periods in the absence of moisture. The doubly deprotonated form of **16** was isolated in good yield as a result of its high insolubility in DMSO, and when dry, it was not rapidly affected by exposure to the air. It is not clear whether the amide species are sensitive to oxygen in solution. In any event all manipulations were conducted under a nitrogen atmosphere.

Very little is known about the structure of the deprotonated complexes. The infrared spectrum of the doubly deprotonated form of $[Ni(cyclam)]^{2+}$ shows no evidence of the 3220-cm^{-1} N–H stretching absorption that is present in the starting material. Instead there is a broad structured absorption in the region 2400–2800 cm^{-1} that is indicative of a strongly hydrogen-bonded system. This evidence suggests only that the deprotonated complex must be involved in strong intermolecular hydrogen bonding in the solid form. One might speculate that the two amido functions in [Ni(cyclam-2H)] are either in 1,4 or 1,5 positions and not in 1,8 positions. This speculation is based on two pieces of information. *cis*-$[Pt(NH_3)_2(OH_2)_2]$ has pK_a values of 5.6 and 7.3 ($\Delta pK = 1.7$) whereas the trans isomer has pK_a values of 4.3 and 7.4 ($\Delta pK = 3.1$).[13] If similar differences exist for amine complexes such as **16**, then cis deprotonation should be favored over trans; however, a prediction of a *cis*-diamido structure for the solid-state form assumes that there are no lattice energy effects. Second, Watt has reported that methylation of $[Pt(en)_2\text{-}2H]$ yields $[Pt(sdmen)(en)]^{2+}$.[14] This methylation reaction apparently was conducted under essentially heterogeneous conditions where proton transfer should be negligible. If this is true, then the doubly deprotonated species must have contained cis amido functions, i.e., [Pt(en-2H)(en)]. Although a specific form of deprotonated complex might exist in the solid state and even predominate in solution, a static structure in solution can be eliminated on the basis of NMR results that were obtained on **4** in DMSO-d_6 as a function of added base ($CH_3S(O)CH_2^-$). Only slight changes in the overall appearance of the spectrum were observed although there were changes in the chemical shifts of the methyl resonances. Thus, proton transfer is rapid on the NMR time scale. This is not an unexpected result since proton transfers between acid and base are expected to be rapid in DMSO.[15] It is not possible to determine whether all protons are equally involved in the acid–base equilibria. The facility of proton transfer has consequences for reactions that involve alkylation of only part of the nitrogen donors. These reactions will be discussed in a later section.

Because of the strongly basic nature of the metal–amide species only alkyl halides without β hydrogens or acidic protons have been successfully used for alkylation. Alkyl halides with β hydrogens undergo extensive elimination of HX rather than S_N2 displacement of the halide function. Thus most of our work has been restricted to nucleophilic displacement in methyl and benzylic halides although preliminary results with allyl halides and haloacetates are encouraging.

N-Alkylation Reactions and Product Stereochemistry. Methylation of all the secondary amine functions in a complex (see Figures 1 and 2) was generally achieved in a single operation using KOH–DMSO as the base–solvent system. Addition of methyl iodide to these mixtures at any point after the combination of complex and KOH resulted in a vigorous, exothermic reaction. Since a maximum of two protons can be removed at once in DMSO, addition of four methyl groups to a complex such as **4**, **7**, or **16** obviously involves several successive steps of deprotonation and nucleophilic displacement. S-Methylation of DMSO occurs to some extent so that a moderate excess of methyl iodide was utilized. Further methylation of any partially methylated complex was readily accomplished to yield permethylated species.

Only a single stereoisomer was isolated for each permethylated complex which was prepared by the deprotonation–alkylation route. In the case of the tetramine complexes the products have the cyclam or *trans*-III structure. This has been unambiguously established for **17** by an x-ray structure determination.[12] Complexes **5** and **8** also have the *trans*-III structure based on their ^1H NMR spectra. Five methyl resonances are observed for each complex. Three of these are accounted for by *C*-methyl groups and the other two by *N*-methyl groups. Arguments made by Warner and Busch for the structures of **4** and **7** based on the number and positions of the *C*-methyl resonances[7,8] apply to **5** and **8** exactly. Two *N*-methyl resonances are required for a molecule with a center of symmetry, **5**, or a twofold rotation axis as in **8**. Two sets of pairwise equivalent methyl groups can only be positioned as shown in **5** and **8**. All of the evidence that is available indicates that the stereochemistry of any alkylated product is determined by the most favorable set of chelate ring conformations that can be achieved by the starting complex. In the absence of substituent effects this means that six-membered chelate rings will have the chair conformation and five-membered chelate rings will be gauche. Such is clearly the case for **5**, **8**, and **17**. Based on the results that have been obtained for secondary amine systems, we believe that the formation of these products is thermodynamically controlled. (Unfortunately it is not possible to equilibrate **28** and **17** in

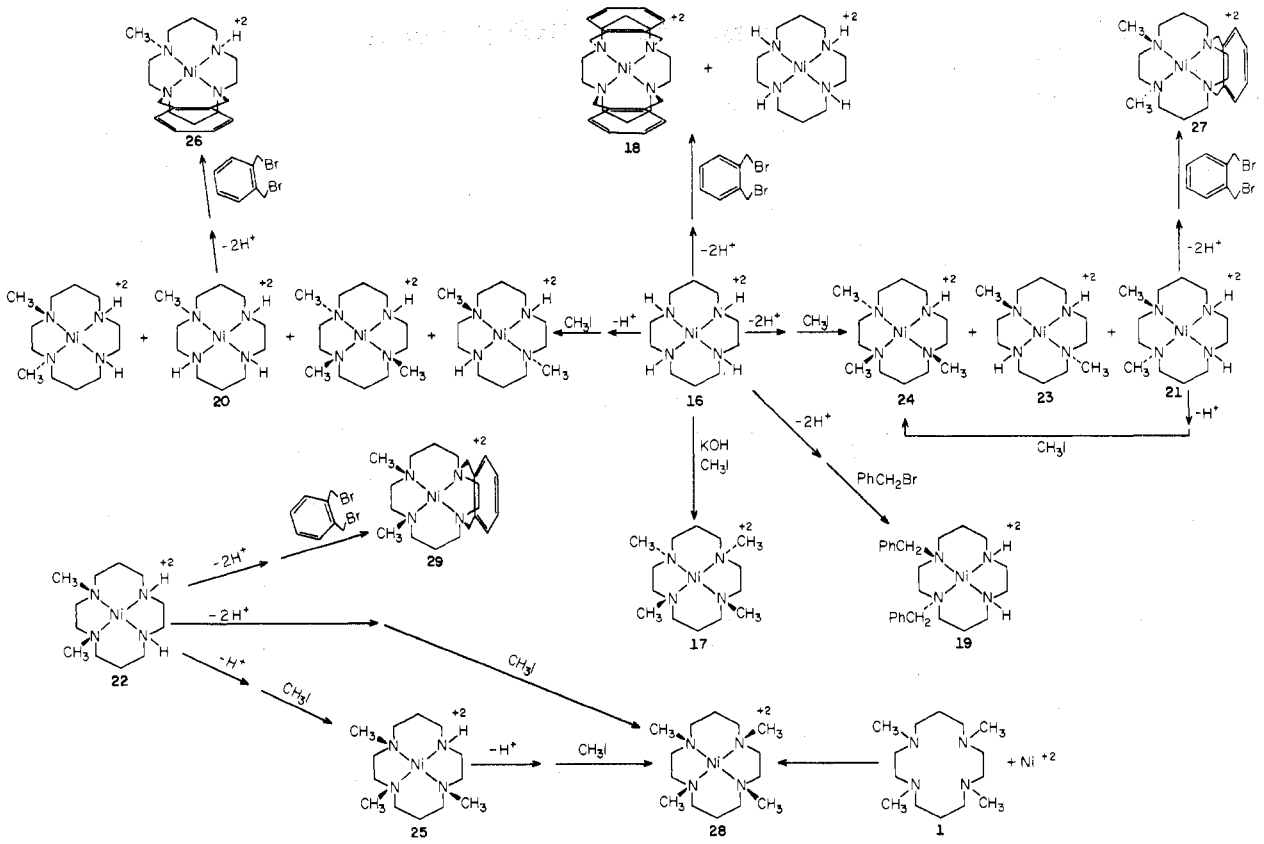
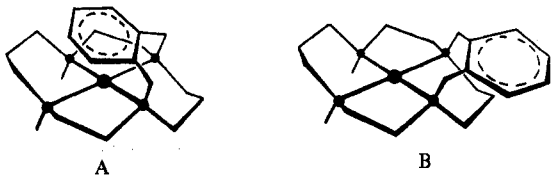


Figure 1. N-Alkylation reactions of $[Ni(cyclam)]^{2+}$ and derivatives.

order to obtain some measure of the difference in energy between these two forms.) On this same basis we assume that complex **13** is the racemic form and that **15** is the meso form since these stereochemistries would have gauche and chair conformations, respectively, for the saturated five- and six-membered chelate rings.

The cyclam complex **16** can be tetraalkylated with 2 mol of the dihalide α,α'-dibromo-*o*-xylene to yield **18**. The maximum yield of this material that was obtained was 40% and no completely satisfactory method was established for its production. The first synthesis of this material was quite accidental and involved the combination of 2 equiv of monodeprotonated $[Ni(cyclam)]^{2+}$ with 1 equiv of dihalide, a reaction originally designed as a means of coupling two macrocyclic complexes together. The only material that contained the *o*-xylene function was **18** and the yield obtained was adequate to account for most of the base originally used. This clearly indicates that proton transfers, which are known to be rapid in DMSO, are very important in determining the nature of the products. In retrospect it is not surprising that cyclization occurs since ring closure by a second nucleophilic displacement should be a kinetically favored process (compared to the intermolecular reaction) where proton exchange is rapid.[16] However, it is very surprising that introduction of one *o*-xylene substituent would activate that complex molecule toward subsequent deprotonation and alkylation. Complexes **20–22** have been further alkylated with the *o*-xylene reagent to yield **26**, **27**, and **29**.

Direct evidence for the stereochemistry of **18** is not available. Although there are four possible isomers for this complex, the stereochemistry shown is the *trans*-III form which should be the thermodynamically most stable as it contains the six-membered chelate rings in the chair form and the five-membered rings in the gauche form. A study of models of **18** suggests that the *o*-xylene residue could adopt either of two low-energy conformations. These two forms are shown by A and B (only one of the *o*-xylene rings has been shown for



A B

clarity). In A the aromatic ring lies over the metal and in B it is over the six-membered chelate ring; when this ring is in the chair form as shown, the axial C–H of the center carbon is pointed directly toward the C–C bond of the aromatic ring. This particular interaction could be eliminated by formation of the higher energy boat conformation for the six-membered chelate ring but other C–H ring interactions would result. Thus, neglecting chair and boat conformations of the six-membered chelate rings, there could in principle be three conformational isomers for **18**: species having both rings of type A or both of type B and one having one conformation of each type. The fact that **18** does not bind cyanide ion to form either a five- or six-coordinate complex, as do all the other alkylated complexes, vide infra, is strong evidence that both rings adopt conformation A and thus block the axial coordination sites of the metal ion. Furthermore, no anomalous chemical shifts are observed for any protons of the macrocyclic chelate ring. Substantial shifts might have been expected if the aromatic ring currents were in close proximity to C–H groups as in conformation B.

The stereochemistry of **27** is determined by that of the starting material. It should be noted that this complex was only obtained in low yield. This could be a reflection of the unfavorable stereochemistry that this complex must adopt. In the case of **29** there are two possibilities; however, the alternative form would have the least favorable set of chelate ring configurations and can be discounted.

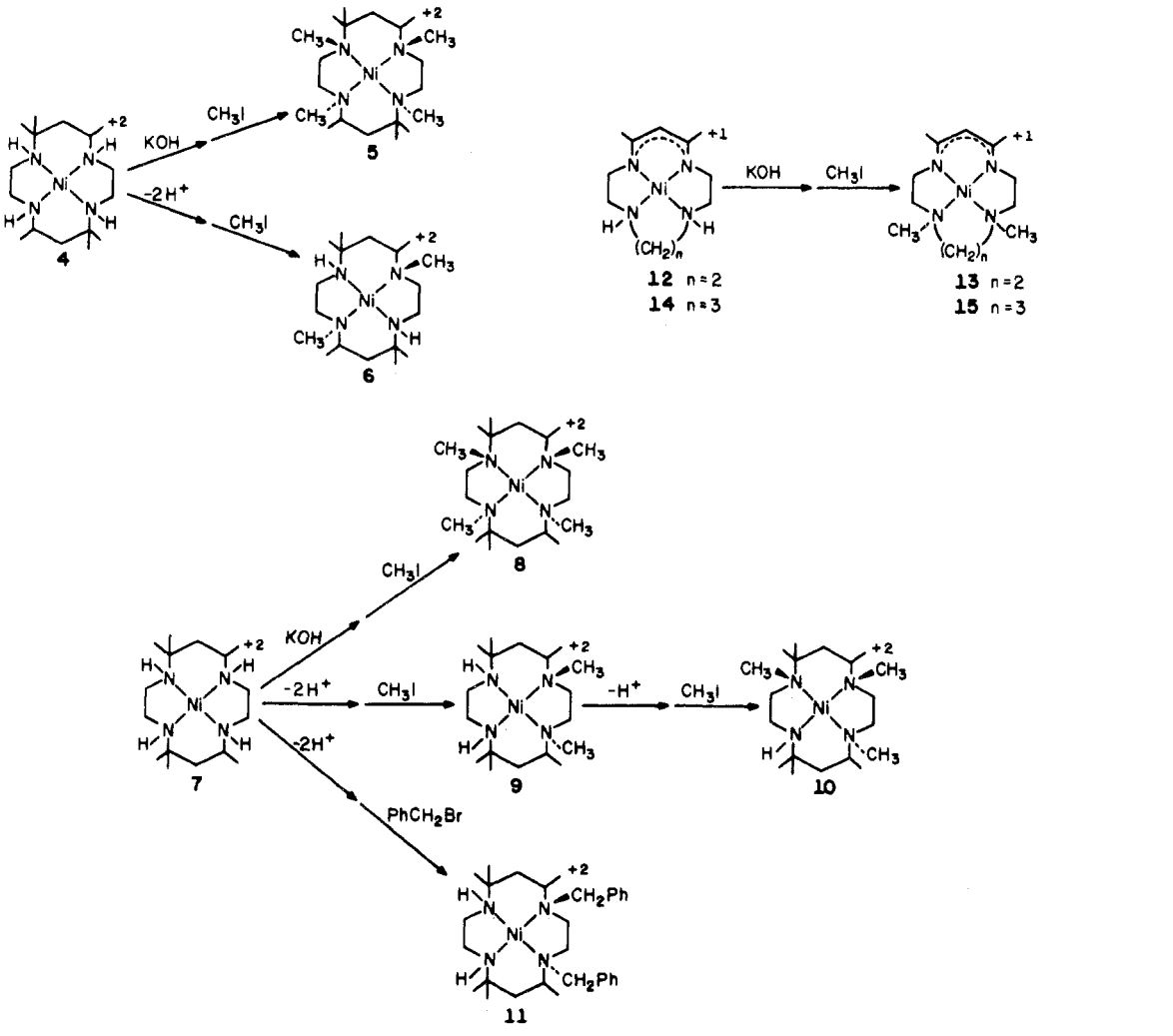
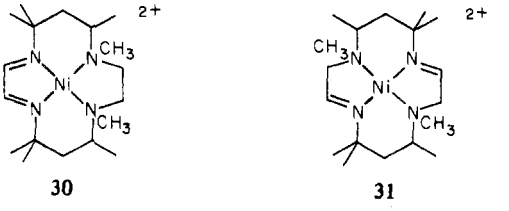


Figure 2. N-Alkylation reactions of macrocyclic ligand complexes of Ni(II).

Partial Alkylation Reactions and Product Stereochemistry. Utilizing $NaCH_2S(O)CH_3$, one or two protons can be easily and selectively removed from a complex that has two or more secondary amine donors. These deprotonated species undergo alkylation reactions when treated with alkyl halide to yield partially alkylated products. Several products may be formed in such reactions as several of the examples discussed below demonstrate. There are two important considerations which bear on this point. The total number of alkyl groups introduced in the complex cannot exceed the number of basic sites. However, since proton transfers between protonated and deprotonated species are more rapid than the nucleophilic reaction, the distribution of the alkyl groups among complex ions may not be uniform. Structural isomers may also be formed in a dialkylation reaction. Dialkylation of a tetramine complex (with monofunctional alkylating agents) could result in the formation of three different isomers. Although two stereoisomers could exist for each structural isomer, only one should be formed by this route.

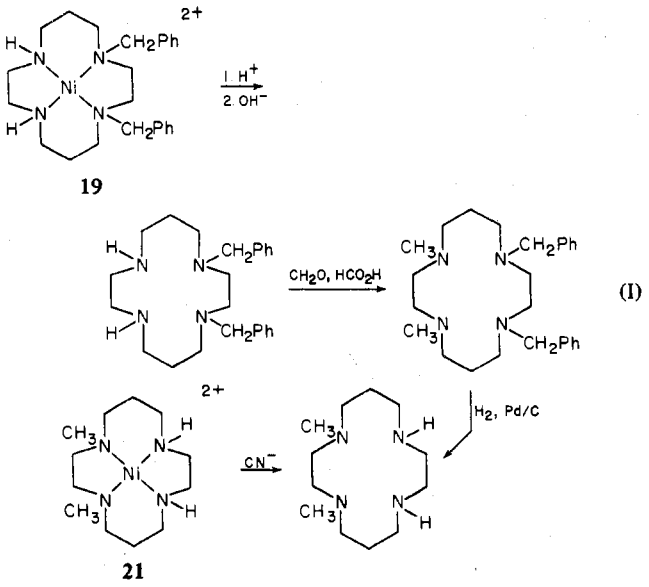
Dialkylation reactions of the doubly deprotonated form of **7** with methyl iodide and benzyl bromide gave high yields of a single isomer in each case. The NMR spectra of these derivatives indicated that they have the same symmetry as the starting complex. Oxidation of **9** at 60° with concentrated HNO_3 yielded a complex whose NMR spectrum is only consistent with **30**; this unambiguously proves the stereochemistry of **9**. The dibenzylated complex **11** is assumed to have the same 1,4 structure. Monodeprotonation and alkylation of **9** yielded the trimethyl derivative **10** but further



30 31

benzylation of **11** was not possible. Prior to the onset of our difficulties with the red, doubly deprotonated complex derived from **4**, which were described earlier, addition of methyl iodide resulted in the formation of a high yield of **6**. Addition of the methyl iodide to the green adduct of $CH_3S(O)CH_2^-$ and the monodeprotonated species yielded several products. About 50% of the mixture was **6**. The structure of **6** was determined by conversion to **31** with concentrated HNO_3 (at room temperature). The structure of **31** was unambiguously established by its NMR spectrum. From these results it is obvious that there is high selectivity in alkylation reactions of **4** and **7**. Such a selectivity is most likely due to a difference in acidity of the N–H groups adjacent to the methine carbon. It seems unlikely that if the acidities of the two types of N–H functions were nearly the same that the nucleophilicities of the amide functions could be so different. The reason(s) for such a difference in acidity is not clear.

The reaction of doubly deprotonated $[Ni(cyclam)]^{2+}$ with benzyl bromide also proceeded smoothly to yield a single isomer. This material was shown to be the 1,4 isomer by reaction sequence I.



Reactions of monodeprotonated and doubly deprotonated forms of **16** with methyl iodide gave mixtures of products. A complete separation of the product mixtures from these reactions was not achieved. However, by a combination of chromatography and fractional crystallization the mixtures were separated to a point where their composition could be established by NMR spectroscopy. This was accomplished by comparison of chemical shifts of methyl resonances in NMR spectra of the partially separated fractions with those of independently prepared, pure samples of possible components.[17] All possible products except the 1,8-dimethyl derivative were available for comparison. On this basis we have established that methylation of [Ni(cyclam-2H)] produced a mixture of 1,8-dimethylated, trimethylated, and 1,4-dimethylated derivatives in the ratio 1:1.3:2. There was also a small amount of a fourth methylated product which was either 1,5-dimethyl or the monomethyl complex **20**. The chemical shift differences in the methyl resonances of these two complexes is too small to distinguish between them in a mixture. This particular component amounted to less than 10% of the products (isolated yield ~90%). The assignment of the structure of the 1,8-dimethyl complex was primarily by elimination of other possibilities. This component was obtained in pure form and its chemical analysis indicated that it was a dimethyl product. Since its NMR spectrum was not that of the 1,4- or 1,5-dimethyl complex it must be the 1,8 isomer; however, we are presently attempting to prepare this complex by an unambiguous route. The products from the methylation of $[Ni(cyclam\text{-}H)]^+$ were the same as those from the doubly deprotonated complex except that there was only a small amount of the trimethylated complex and there was a substantial amount of the compound of uncertain structure. It seems reasonable that this material must be the monomethylated complex in this case. The ratio of 1,4-dimethyl to 1,8-dimethyl was again about 2. Some $[Ni(cyclam)]^{2+}$ was recovered from these reactions.

Any of the partially methylated complexes shown in Figure 2 may be further methylated. For example complex **21** may be converted to **24** or **17** by reaction of the monodeprotonated or doubly deprotonated forms with methyl iodide. These reactions proceed smoothly and give the product in high yield. On the other hand, attempts to monomethylate **20** yielded, as expected, a mixture of products that was essentially identical with that described above from the reaction of methyl iodide with [Ni(cyclam-2H)]. The bis(benzyl) complex **19** could not be further benzylated and attempts to methylate it were not straightforward.

Reactions of N-Alkylated Complexes. The surprising lability of the metal complexes prepared from tetramethylcyclam caused us to seek an alternative method of preparation. One property of the new complexes of considerable interest to us was their kinetic stability in acid solution and in cyanide medium. We earlier reported that permethylated complexes **5**, **8**, and **17** are quite inert.[12] In fact their stability in strongly acidic media is considerably greater than that of the secondary amine analogs. In 6 *M* HCl at 50° complex **17** has a half-life of about 3 hr which is about 6 times that of $[Ni(cyclam)]^{2+}$ under the same conditions. Tetramethyl derivatives **5** and **8** were unaffected at the end of 2 days under the same conditions although the secondary amine complexes show some decomposition after several hours. Complex **18** was very resistant to protonation and showed less than 10% decomposition after 5 days in 6 *M* HCl at 60°. Unfortunately this precludes isolation of the free amine with a known stereochemistry but preparation of this amine for study is being attempted using cyclam and the *o*-xylene reagent.

All of the methylated cyclam complexes show a greater resistance to protonation of the ligand than the cyclam complex itself. Although no quantitative data are yet available on the effect of geometrical isomerism on kinetic stability, it is clear that stereoisomerism effects are important as demonstrated in the case of the 1,4-dimethyl isomers **21** and **22**. Thus, the isomer expected to be thermodynamically less stable (**22**) decomposes measurably faster than the more stable form **21**. However **22** is much more resistant to protonation than the TMC complex which decomposes immediately in 6 *M* HCl at room temperature.

The nickel complexes of cyclam and its N-methylated derivatives were very much more resistant to protonation in 6 *M* $HClO_4$ than in HCl at the same concentration. For example, neither $[Ni(cyclam)]^{2+}$ nor its tetramethylated derivative, **17**, show any decomposition after 2 days in 6 *M* $HClO_4$ at 60°. Clearly chloride ion assists in ligand dissociation. Similar effects were observed by Cabbiness for dissociation of $[Cu(2.3.2\text{-}tet)]^{2+}$ and the copper(II) analogue of **4**.[18] In the range 0.05–1 *M* HCl the rate of dissociation was independent of HCl concentration but there was nearly a second-order dependence in the 6–12 *M* range. Further investigations of the Ni(II) macrocyclic ligand complexes described in this paper showed that in 0.7 *M* HCl the rate of dissociation was similar to that in 6 *M* $HClO_4$.

When the amines obtained by decomposition of complexes **21** and **24** were used to regenerate nickel(II) complexes, mixtures of products were obtained in both cases. A 3:2 mixture of **21** and **22** was obtained for the dimethyl ligand and a 1:1 mixture of **24** and **25** was obtained with the trimethyl ligand. It should be noted that there are four isomers that could form in the latter reaction but we can rule out the presence of more than a few percent of any other form. The trend is clearly toward an increasing amount of a less stable form as the degree of N-substitution increases and when the degree of substitution is four, as in TMC, the reaction is specific for the less stable form. Complex **22** does not convert to measurable amounts of **21** (by NMR) upon refluxing in water for 14 hr. We suppose that **22** has the same set of nitrogen donor configurations as the complex prepared from **1**, i.e., all four N substituents up, although this is based only on the fact that complete alkylation of **22** yields **28**. If this is true, it is obvious that it is substantially more stable than the tetramethyl derivative **28** but the reasons for this additional stability are not entirely obvious.

Complex **17** is considerably more resistant to displacement of the ligand by cyanide than is $[Ni(cyclam)]^{2+}$. Refluxing **17** in an 8–10-fold excess of cyanide for 12–15 hr was required to decompose the complex completely which is in considerable

contrast to the 1-hr period required for the cyclam analog. The behavior of **17** in the cyanide solution was quite different from that of $[Ni(cyclam)]^{2+}$. The tetramethyl complex apparently coordinates a single cyanide anion to form a bright blue complex which is quite soluble. It is well known that at high cyanide concentrations $[Ni(cyclam)]^{2+}$ forms a mauve, highly insoluble biscyanide complex.[19] In fact it has been shown that the rate of decomposition of **16** by cyanide shows an inverse dependence on the cyanide concentration because of the formation of this trans complex.[19] A similar mauve biscyanide of **17** can be crystallized from concentrated cyanide solution but its stability is low in solution.

Coordination of axial ligands other than cyanide is observed for **17** under a variety of conditions. The absorption spectrum of **17** as the perchlorate salt in water contains bands for a species other than the planar form. When hydroxide is added to the solution, the color is green and new bands appear in the absorption spectrum. As described in the Experimental Section a number of six-coordinate species were prepared. These are soluble in chloroform and alcohol where they have absorption spectra that are typical of tetragonal nickel(II). A blue aquo–azide complex of a blue **17** was also isolated. This complex formed bright green nitromethane solutions where it behaved and as a 1:1 electrolyte. Six-coordinate complexes can also be prepared with the complexes having 1–3 *N*-methyl substituents.

Oxidation of all of the methylated species derived from alkylation reactions of $[Ni(cyclam)]^{2+}$ to their trivalent forms was accomplished using NO^+ salts. The trivalent complex obtained from the tetramethylated form is much less stable than the trivalent cyclam complex. A study of the base-induced redox reactions of this complex has been initiated and the results will be published in a separate paper.[20] Nitrosonium reagents did not appear to react with permethylated complexes **5** and **8**. Although no effort was made to prepare Ni(III) complexes of dimethylated complexes **6** and **9**, the fact that these complexes can be oxidized to the diimine form strongly suggests that the trivalent form could be prepared.[1] Tetraalkylated complexes **5** and **8** did not react with nitrosonium salts in acetonitrile or with nitric acid (except with degradation). A better understanding of the redox properties of the methylated complexes must await the results of electrochemical studies.

Spectral Properties and Ligand Field Strength. The effect of introducing *N*-alkyl substituents into the ligand on the electronic structure of the nickel ion is a point of considerable interest. Spectra obtained on four series of four-coordinate complexes suggest that the introduction of *N*-methyl substituents produced a regular change in the ligand field strength of the macrocyclic tetramine. The steady decrease in absorption maximum of the planar diamagnetic complexes as the number of *N*-methyl substituents is increased is illustrated in Figure 3. Since this absorption should be due primarily to the promotion of an electron from the d_{xy} to $d_{x^2-y^2}$ orbital ($^1A_{2g} \leftarrow {}^1A_{1g}$ in D_{4h} symmetry), the variation in absorption maximum must represent the effect of changes in the donor properties on the separation between these orbitals. There is of course the possibility that nitromethane may interact in one or both of the axial positions and thus influence the separation between these orbitals although the singlet ground state is certainly maintained.

In order to investigate further the change in ligand field properties of the alkylated ligands, the *trans*-dichloro complexes of **17**, **20**, and **21** were prepared and their absorption spectra obtained. Reproductions of these spectra, along with that of *trans*-$[Ni(cyclam)Cl_2]$, are given in Figure 4. Here too, there are steady shifts to lower energy for the absorption maxima that suggest a decrease in ligand field strength with

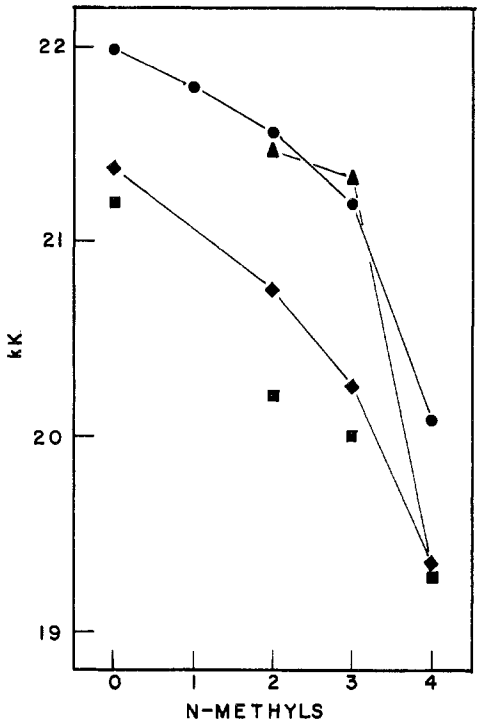


Figure 3. Change in absorption maximum of alkylated forms of **4** (◆), **7** (■), **16** (●), and **22** (▲) as a function of the number of N-methyl groups. Data were obtained on the bisperchlorate salts in nitromethane.

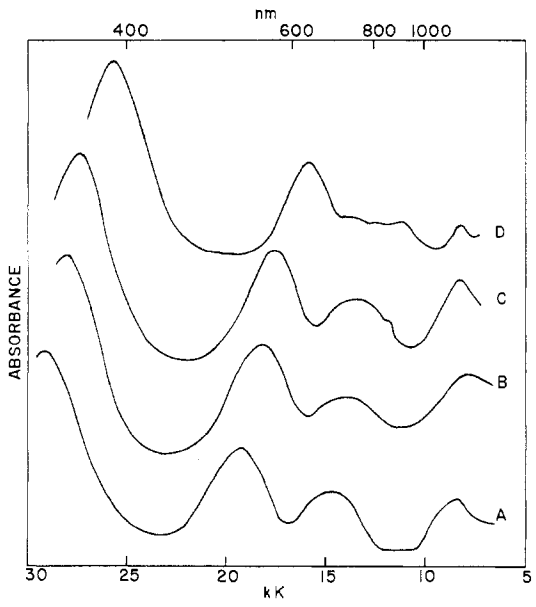


Figure 4. Solid-state absorption spectra of *trans*-dichloro derivatives of **16** and three of its N-methylated derivatives: A, **16**; B, **20**; C, **21**; D, **17**.

increasing N-methylation. If the bands at 7770 and 11300 cm^{-1} for the dichloro derivative of **17** (spectrum D in Figure 4) are assigned to the $^3E_g \leftarrow {}^3B_{1g}$ and $^3B_{2g} \leftarrow {}^3B_{1g}$ transitions, respectively, then Dq_{xy} for the tetramethylated ligand is 1130 cm^{-1}. The corresponding value for cyclam is about 1450 cm^{-1} (determined for the *trans*-dichloro complex).[21] Since completely resolved spectra for the methylated derivatives are not available, it is impossible to do a complete, unambiguous analysis. It seems reasonable to conclude, however, that the tetramethylated ligand is a considerably weaker ligand than cyclam and that the partially N-methylated analogs are intermediate in their ligand field strengths.

Clearly more work is needed to prove the above analysis. However, assuming that it is basically correct, we then assume that there should be a predictable decrease in the average ligand field strength for the four in-plane donors as the number of tertiary donors is increased. The reason for this decrease in ligand field strength of a tertiary nitrogen donor compared to a secondary nitrogen is not obvious. The intrinsic basicity of tertiary amines, as determined by gas-phase studies, is greater than that of secondary amines, contrary to what is often assumed on the basis of aqueous pK values.[22] Thus on the basis of inductive effects a tertiary nitrogen donor should place more charge in the σ-bonding orbital which is directed toward nickel. Steric and solvation effects that might be important in determining the strength of the metal–donor interaction in octahedral complexes of amines should not be nearly as important in the case of the macrocyclic ligands. In fact structural data obtained on a six-coordinate diazido complex of **17** show no significant interaction between the methyl groups and other groups in the complex.[12] The nickel–nitrogen bond lengths are about 0.1 Å longer than those in [Ni(cyclam)Cl_2],[6] but since the azide ion is an appreciably stronger ligand toward nickel than chloride ion, these bond length differences cannot be directly related to the differences in Dq for the two ligands.

Summary

Deprotonation–alkylation reactions have been shown to be a versatile means of preparing new nickel complexes of macrocyclic amine ligands that contain tertiary donors. Some of these new ligands may have considerable utility for future studies. For example, we anticipate that a study of the rates of formation and dissociation of the three di-N-methylated complexes will provide a greater insight into the stepwise mechanisms of these processes. N-Alkylation obviously provides a method of varying the in-plane ligand field strength without appreciably changing the steric interactions with axial groups.

The N-alkylation provides a direct route to a number of new ligand systems not discussed here. For example use of $BrCH_2CO_2C_2H_5$ as an alkylating agent with the doubly deprotonated form of **21** allows the formation of a hexadentate ligand. Similarly reaction of deprotonated **24** or **26** with the bromoacetate produces pentadentate systems. Some preliminary experiments indicate that chloromethylated polystyrene reacts with $[Ni(cyclam\text{-}H)]^+$ to incorporate the macrocyclic ligand complex into the polymer.

Most of the ligands discussed can be removed from nickel and utilized for complexing other metal ions. However, the stereochemistry is not completely transferrable in most cases. Only by alkylation of coordinated ligands can the thermodynamically most stable set of nitrogen configurations be obtained. We have shown that certain copper and zinc complexes can be alkylated in the same fashion as their nickel analogs. Our future synthetic efforts will be directed toward several extensions of the alkylation reaction to other metal ion systems, especially those of iron.

Experimental Section

All chemicals in the following preparations not specifically mentioned here were reagent grade and were used without further purification. Dimethyl sulfoxide, methyl iodide, and benzyl bromide were dried over Linde 4A molecular sieves for at least 24 hr prior to use. α,α'-Dibromo-o-xylene was prepared according to a literature preparation.[23] Silica gel was Brinkman 60, 70–230 mesh. When obtained, this material was used directly; however, if regenerated, addition of 20–25% water (by weight) was necessary in order to match the resolution obtained with new material. Secondary amine complexes **4**,[24] **7**,[24] **12**,[25a] **14**,[25b] and **16**[17] were prepared by published methods. Complexes **20**, **21**, and **22** were prepared by the procedure described earlier for $[Ni(cyclam)]^{2+}$ using the appropriate tetramine.[17] Carefully dried samples were utilized in all deprotonation studies. Where appropriate, the isomeric purity of starting materials was carefully determined by NMR.

All deprotonation and alkylation reactions were conducted in a dry nitrogen atmosphere.

Characterization of the metal complexes whose preparations are described below was by chemical analysis and NMR, infrared, and absorption spectroscopy as appropriate unless otherwise stated. Analytical data for all complexes reported were within acceptable limits. A table containing these results is included as an appendix to the microfilm edition. Figures of NMR spectra are also available as supplementary material to this paper.

Sodium Methylsulfinylmethide. This reagent was prepared as a DMSO solution according to Corey's procedure to give a solution of approximately 1 M.[26] These solutions were generally quite dark and often contained some insoluble material. Accordingly they were allowed to set for 4–5 hr before use to allow this material to settle. These solutions were standardized by pipetting a 1-ml aliquot of the clear solution into water and titrating the basic solution with 0.1 N HCl. Such a procedure actually gives the total base concentration but solutions standardized in this manner were suitable for our purposes. Such solutions could be kept for 3–4 days at room temperature before decomposition commenced or for several weeks if refrigerated (0°).

Permethylation of 4 and 7—Preparation of 5 and 8. Five grams of the secondary amine complexes (perchlorate salts) was dissolved in 40 ml of DMSO. About 10 g of finely pulverized KOH[27] was added and the mixture was stirred vigorously for 15 min. The flask was fitted with an efficient reflux condenser and 10 ml of methyl iodide was added slowly over 5–10 min. A vigorous reaction took place and the temperature of the reaction mixture rose abruptly. After 10–15 min a brick red precipitate began to form. The mixture was allowed to cool and an equal volume of ethanol was added. The red powder and the excess KOH were removed by filtration and the potassium hydroxide was removed by washing with absolute ethanol. The iodide salt was converted to the perchlorate by dissolving the red precipitate in 200 ml of hot water, filtering, and adding an excess of sodium perchlorate. Crystallization of a red product was immediate. This product was collected, washed with ethanol and ether, and dried in vacuo. Recrystallization, when necessary, was from hot water. Yields of both isomers were 85%.

Permethylation of 12 and 14—Preparation of 13 and 15. These complexes were prepared by a procedure similar to that described above using hexafluorophosphate salts as starting materials. After completion of the reaction, excess KOH was removed by filtration and an equal volume of ethanol was added to the DMSO solution, followed by a few milliliters of 4 M NH_4PF_6. Ether was then added to precipitate the product as the hexafluorophosphate salt. **15** was obtained as brown needles in 40% yield. It was recrystallized from water–acetone mixtures by evaporation of the acetone. **13** was obtained as red-orange plates in 55% yield. It was recrystallized from nitromethane by addition of ether. These derivatives could also be prepared using stoichiometric quantities of $NaCH_2S(O)CH_3$ for the deprotonation step.

Permethylation of 16—Preparation of 17. A single-step procedure similar to those described above gave low yields of this complex. A two-step reaction sequence was developed which gives a higher yield of product although it is not clear why the procedure works so much better. Two grams of **16** was dissolved in 50 ml of DMSO and about 8 g of pulverized KOH was added. The reaction mixture was stirred vigorously for 3–5 min and the KOH was removed by filtration through a coarse frit. The deep purple filtrate was treated with 2 ml of methyl iodide. The solution rapidly turned orange. A second charge of pulverized KOH was added and the mixture was stirred until a light green color persisted. The mixture was again filtered with a coarse frit and 3 ml of methyl iodide was added to the green filtrate. After stirring for 30 min a brick red precipitate formed. An equal volume of ethanol was added and the product was collected by filtration. The red iodide salt was dissolved in 50 ml of hot water and treated with 2 equiv of silver perchlorate. The silver iodide that formed was removed by filtration and the filtrate was treated with a small amount of concentrated perchloric acid. Upon cooling, large red needles formed. The yield was 1.98 g or 88%. Note that yields were not always reproducible and attempts to scale up this procedure were not successful.

Six-coordinate complexes of the type $NiLX_2$ ($X^- = N_3^-$, OCN^-, CN^-, SCN^-) volunteered from solution by addition of a twofold excess

of the appropriate sodium salt to an aqueous solution of the perchlorate salt. The precipitated complexes were extracted into $CHCl_3$. The aqueous layer was discarded and the $CHCl_3$ layer was dried over anhydrous Na_2SO_4. Filtration and slow evaporation of the $CHCl_3$ yielded the crystalline six-coordinate complexes. Yields are nearly quantitative. The biscyanide complex crystallized from water as a mauve hexahydrate which could be dehydrated by heating the complex in vacuo at 80°C. The preparation and structure of a complex of stoichiometry $Ni_2L_2(N_3)_3I$ has been described.[12] If an excess of NaN_3 was added to a hot solution of $NiL(ClO_4)_2$, fine blue needles of $[NiL(N_3)H_2O]ClO_4$ separated on cooling.

Reaction of [Ni(cyclam-2H)] with α,α'-Dibromo-*o*-xylene—Preparation of 18. One gram of $[Ni(cyclam)](ClO_4)_2$ dissolved in 20 ml of DMSO was treated with 2 equiv of a DMSO solution of sodium methylsulfinylmethide. The resulting red mixture was treated with 1 g of the dibromo reagent. After reaction was complete, the deep orange solution was poured into an aqueous sodium perchlorate solution (about 100 ml of a 1 *M* solution) and the product was extracted into nitromethane. After drying of the nitromethane extracts, the solvent was evaporated to yield a pinkish solid, 0.6 g, 40%. About 0.4 g of the starting material could be extracted as the thiocyanate complex by extraction of the DMSO–water mixture after addition of sodium thiocyanate.

Partial Alkylation Reactions. All partial alkylation reactions were performed in the same fashion except for isolation of the product. A typical reaction involved the addition of 1 or 2 equiv of a DMSO solution of $NaCH_2S(O)CH_3$ to a solution of complex in DMSO (1–2 g of perchlorate salt in 20–30 ml) followed by a modest excess of the alkylating agent. After reaction was complete, the DMSO solutions of products were treated in one of the following ways.

Method 1. The DMSO solution was poured into an aqueous solution of sodium thiocyanate and the product was extracted as the thiocyanate complex using $CHCl_3$. After drying, the chloroform was evaporated to yield the product(s). Perchlorate salts were prepared when required by treating the thiocyanate complexes with silver perchlorate in water. Complexes **24** (75%) (when prepared from **21**) and **25** (75%) were isolated in this fashion. These materials were generally isolated as pure complexes when the base:complex stoichiometry was carefully controlled. On occasions where material of a higher and/or lower degree of substitution was also obtained, purification was achieved by chromatographing the thiocyanate complex on a silica gel column with nitromethane. The rate of travel of N-methylated compounds on the column was such that the more highly substituted compound traveled fastest. Complex **6** was originally isolated in 85% yield by the simple procedure described. However, after we could no longer obtain the soluble form of the doubly deprotonated form of **4**, addition of methyl iodide to the green $CH_2S(O)CH_3$ adduct of the monodeprotonated form (see text) gave a mixture of several products. The dimethylated product was obtained in ~50% yield by chromatography of the mixture of products (as perchlorate salts) on silica gel.

Method 2. The DMSO solution was poured into an aqueous solution of sodium perchlorate and the product was extracted with nitromethane. Evaporation of the nitromethane yielded the products which were purified by recrystallization from water and by chromatography on silica gel with nitromethane. This method was utilized for isolation and purification of **9** (85%), **10** (70%), **11** (50%), **19** (50%), **26** (60%), **27** (20%), and **29** (20%). The latter two were obtained as leading red bands by chromatography of the mixture of products on silica gel. Other products were not studied.

The structures of most of the above complexes are determined by that of the starting material; however, there are some cases such as **6**, **9**, **11**, and **19** where ambiguity exists. Experiments performed to prove their structure are described in later sections.

Partial alkylation reactions of **16**, $Ni(cyclam)^{2+}$, were much more complicated than those described above. Treatment of monodeprotonated or doubly deprotonated $Ni(cyclam)^{2+}$ with methyl iodide always resulted in a complex mixture of products. These mixtures were partially separated by chromatography and fractional crystallization until a fairly certain identification of the components could be made. The outline given below for the separation of the products from the reaction of [Ni(cyclam-2H)] was also utilized for the separation of the products from the corresponding reaction of $[Ni(cyclam\text{-}H)]^+$. Method 1 described above was utilized to obtain the thiocyanate derivative of the mixture (80% as $[Ni(cyclam)Me_2(NCS)_2]$ from 1 g of starting material). This product was dissolved in 10 ml of nitromethane and placed on a 2.5 × 750 cm silica gel column. Elution with nitromethane resulted in separation of a rapidly moving light purple band followed by a broad orange band. The purple band was removed and shown to be pure **24** (trimethyl) by NMR. The orange band was rapidly removed with a solution of methanolic sodium thiocyanate (10 g/300 ml). Evaporation of methanol followed by extraction of the solid with chloroform yielded a violet solution free of excess thiocyanate. After evaporation of chloroform, the mixture was converted to perchlorate salts with $AgClO_4$ in water. An NMR spectrum (trifluoroacetic acid, TMS) of the mixture revealed peaks at τ 7, 7.12, and 7.2. The resonance at τ 7 corresponds to that of **21**. That at τ 7.12 corresponds to either **20** or the 1,5-dimethyl derivative. However we were unable to achieve a sufficient separation to distinguish between these. The third resonance would most likely be the 1,8-dimethyl derivative. Careful fractional crystallization of the mixture from water gave a few dark orange crystals of a material whose NMR spectrum contained only the methyl resonance at τ 7.2 and whose analysis corresponds to a dimethyl derivative. Thus we assign the structure of this species as **23**.

Proof of Structure of 19. The structure of this complex was determined as follows. Three grams of the complex (4.7 mmol) was decomposed by refluxing for 12 hr in 30 ml of 9 *M* HCl. After this time the light green solution was evaporated to dryness, the solid was washed with ethanol, and the remaining white solid was reserved for further reaction. (NMR, D_2O, TSP;[28] τ 7.6, multiplet, I = 2; τ 6.3, multiplet, I = 8; τ 5.5, singlet, I = 2; τ 2.4, singlet, I = 5. These data are consistent with an *N*,*N*'-dibenzyl structure.) The above product was dissolved in 40 ml of water which contained 5 g of NaOH, and this solution was extracted with three 20-ml portions of chloroform. The chloroform extracts were combined, dried over anhydrous sodium sulfate, and evaporated to yield an oil. This oil was dissolved in a mixture of 20 ml of formic acid and 18 ml of formaldehyde and the solution was refluxed for 8 hr. The reaction mixture was evaporated to dryness. A small amount of the residue was dissolved in acidic D_2O and an NMR spectrum was obtained on the solution: TSP, τ 7.63, multiplet, I = 2; τ 6.8, singlet, I = 3; τ 6.3, multiplet, I = 8; τ 5.46, singlet, I = 2; τ 2.4, singlet, I = 5. This spectrum is consistent with a *N*,*N*'-dibenzyl-*N*'',*N*'''-dimethyl structure. The remainder of the residue was taken up in 50 ml of water that contained 5 g of sodium hydroxide and this solution was extracted with three 20-ml portions of chloroform. After the extracts were dried over sodium sulfate, they were evaporated to yield an oil. This oil was dissolved in 100 ml of a 1:1 mixture of acetic acid and water and hydrogenated at 50 psig of hydrogen over 30% Pd on charcoal. When hydrogen uptake ceased the mixture was filtered and the filtrate evaporated to a solid. This solid was dissolved in a small amount of strong base and the solution was extracted with three 20-ml portions of chloroform. The chloroform extracts were dried with sodium sulfate and evaporated to yield an oil. A small amount of this material was dissolved in acidic D_2O for an NMR spectrum: TSP, τ 7.73, multiplet, I = 2; τ 6.83, singlet, I = 3; τ 6.33, multiplet, I = 8. This spectrum was identical with that of an authentic sample of 1,4-dimethylcyclam. The 1,4-dimethylcyclam was dissolved in 50 ml of water and 2 g (5.4 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ was added. An orange color soon developed; the solution was stirred at 60° for 15 min, after which it was evaporated to dryness and the solid that remained was washed thoroughly with ethanol. After drying, 1.1 g of an orange product remained. The NMR spectrum of this product indicated that it was a 3:2 mixture of **21** and **22**. Yield 48% based on starting complex.

Proof of Structure of 6 and 9 by Nitric Acid Oxidation—Preparation of Diimine Complexes 30 and 31. About 200 mg of **6** or **9** was dissolved in 1 ml of concentrated nitric acid. In the case of **6** oxidation occurred readily at room temperature and after 24 hr only the diimine complex was detectable by NMR. Complex **9** required heating for about 45 min at 70° for complete conversion to the diimine form. These products were not analyzed since their NMR spectra provided the required information regarding the structures of the dimethylated starting materials. Structural evidence in both cases was derived from the fact that the NMR spectrum contained a doublet for the methyl groups that are coupled to the methine proton and a low-field resonance for the vinylic protons as required for both **30** and **31**. Thus the structures of **6** and **9** must be those shown in Figure 2.

Preparation of *trans*-Dichloro Complexes of 17, 20, and 21. In a typical preparation about 500 mg of the perchlorate salt of the N-methylated complex was dissolved in 25 ml of water and treated with an excess of potassium chloride. The solution was then evaporated

to dryness and the residue was extracted with 10–20 ml of ethanol. After evaporation of the ethanol, the solid that remained was checked by infrared spectroscopy for the presence of perchlorate. If any absorption for the anion was present in the spectrum, the solid was dissolved in 5–10 ml of water and passed over an anion-exchange column (Dowex 1-X8, 100–200 mesh, Cl^- form). The eluent was evaporated to dryness and the solid collected. All products, regardless of origin, were dried in vacuo over P_4O_{10}.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **4**, 57456-81-2; **5**$(ClO_4)_2$, 57427-09-5; **5**$(Cl)_2$, 57379-16-5; **5**$(CN)ClO_4$, 57379-18-7; **6**, 57379-20-1; **7**, 57427-11-9; **8**, 57427-13-1; **9**, 57379-22-3; **10**, 57379-24-5; **11**, 57379-26-7; **12**, 55701-26-3; **13**, 57379-28-9; **14**, 39042-83-6; **15**, 57379-30-3; **16**, 57456-82-3; **17**$(ClO_4)_2$, 57427-14-2; **17**$(Cl)_2$, 57379-31-4; **17**$(CN)_2$, 57427-15-3; **17**$(N_3)_2$, 57379-32-5; **17**$(SCN)_2$, 57427-01-7; **17**$(OCN)_2$, 57378-95-7; **17**$(N_3)(H_2O)(ClO_4)$, 57427-74-4; **(17)**$_2(N_3)_3(I)$, 52588-40-6; **18**, 57378-97-9; **19**, 57378-99-1; **20**, 57379-01-8; **21**, 57379-03-0; **22**, 57427-03-9; **23**, 57379-05-2; **24**, 57379-07-4; **25**, 57427-05-1; **26**, 57379-09-6; **27**, 57379-11-0; **28**, 48175-68-4; **29**, 57427-07-3; **30**, 57379-12-1; **31**, 57379-13-2; **20**$(Cl)_2$, 57379-14-3; **21**$(Cl)_2$, 57379-15-4; α,α'-dibromo-*o*-xylene, 91-13-4; *N,N'*-dibenzylcyclam, 57325-55-0; *N,N'*-dibenzyl-*N'',N'''*-dimethylcyclam, 57325-56-1; sodium methylsulfinylmethide, 32249-19-7; potassium hydroxide, 1310-58-3.

Supplementary Material Available: Table of analytical data and NMR spectra of N-alkylated complexes (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) E. K. Barefield and M. T. Mocella, Abstracts, 165th National Meeting of American Chemical Society, Dallas, Tex., April 1973, No. INOR 139; *J. Am. Chem. Soc.* **97**, 4238 (1975).
(2) G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, **11**, 1145 (1972); L. L. Rusnak and R. B. Jordan, *ibid.*, **10**, 2686 (1971).
(3) E. K. Barefield and F. Wagner, *Inorg. Chem.*, **2**, 2435 (1973).
(4) (a) R. Buxtorf, W. Steinmann, and T. A. Kaden, *Chimia*, **28**, 19 (1974); (b) R. Buxtorf and T. A. Kaden, *Helv. Chim. Acta*, **57**, 1035 (1974); (c) L. Hertli and T. A. Kaden, *ibid.*, **57**, 1328 (1974).
(5) M. J. D'Aniello, Jr., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, **97**, 192 (1975).
(6) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4** 1102 (1965); B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).
(7) L. G. Warner and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4092 (1969).
(8) L. G. Warner and D. H. Busch, "Coordination Chemistry: Papers Presented in Honor of J. C. Bailar, Jr.", Plenum Press, New York, N.Y., 1969, p 1.
(9) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 2151 (1970).
(10) L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969).
(11) G. W. Watt and P. W. Alexander, *Inorg. Chem.*, **7**, 537 (1968).
(12) A preliminary account of part of this work has appeared: F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr., A. H.-J. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).
(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 32.
(14) G. W. Watt and D. H. Carter, *Inorg. Chem.*, **7**, 2451 (1968).
(15) C. P. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 1730 (1967).
(16) E. L. Blinn and D. H. Busch, *Inorg. Chem.*, **7**, 820 (1968).
(17) Complexes **20**, **21**, and **22** were prepared by the same procedure utilized for $[Ni(cyclam)]^{2+}$ using the appropriate tetramine. See E. K. Barefield, *Inorg. Chem.*, **11**, 2273 (1972), and E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Synth.*, in press, for the cyclam procedure. A publication describing the preparations and properties of these complexes and others prepared by glyoxal condensation methods has been submitted.
(18) D. K. Cabbiness, Ph.D. Thesis, Purdue University, 1970. 2.3.2-tet is 1,4,8,11-tetraazaundecane.
(19) F. Hinz, Ph.D. Thesis, Purdue University, 1973.
(20) M. T. Mocella, Ph.D. Thesis, University of Illinois, 1974.
(21) C. R. Sperati, Ph.D. Thesis, The Ohio State University, 1971.
(22) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973).
(23) W. H. Perkin, *J. Chem. Soc.*, 5 (1888).
(24) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).
(25) (a) W. H. Elfring, Jr., Ph.D. Thesis, University of Washington, 1972; S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, **9** 1131 (1970); (b) J. G. Martin and S. C. Cummings, *ibid.*, **12**, 1477 (1973).
(26) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); **87**, 1345 (1965).
(27) Potassium hydroxide pellets were pulverized in a Waring blender. Caution should be exercised when handling this material as the dust is very irritating to the eyes and nose. Material thus prepared could be kept in a tightly sealed bottle for long periods of time.
(28) TSP is sodium 3-trimethylsilylpropionate-2,2,3,3-d_4.

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

The Ylide–Metal Complex. Preparations and Structures of Palladium(II) and Platinum(II) Halide Complexes with Some Phenacylides

HIROSHI KOEZUKA, GEN-ETSU MATSUBAYASHI, and TOSHIO TANAKA*

Received July 28, 1975 AIC505500

Platinum(II) halide complexes of some phenacylides, *p*-$CH_3C_5H_4N^+$–$CHC(O)C_6H_5$ (=Ny), $CH_3(C_6H_5)_2P^+$–$CHC(O)C_6H_5$ (=Py), $(C_6H_5)_3As^+$–$CHC(O)C_6H_5$ (=Ay), and $(CH_3)_2S^+$–$CHC(O)C_6H_5$ (=Sy), were synthesized and their configurations elucidated on the basis of infrared and ^1H NMR spectra. The coupling constant between the ^{195}Pt nucleus and the ylide methine proton, ^2J(Pt–CH), in *trans*-$PtCl_2LY$ (L = $PPhMe_2$, PMe_3; Y = Ny, Py, Ay, Sy) increases with increasing basicity of the ylide: Ny > Ay > Sy > Py. In *trans*-$PtX_2(PPhMe_2)Y$ (X = Cl, Br, I; Y = Ny, Py, Sy), the ^2J(Pt–CH) value also increases in the order of Cl < Br < I and at the same time the ν(Pt–C) band moves to high frequencies. This result is interpreted in terms of the interaction of the positively charged ylide heteroatom with halogen. Palladium(II) ylide complexes $PdCl_2LY$ (L = $PPhMe_2$, PMe_3; Y = Py, Ay, Sy) were also prepared and their structures are discussed.

Introduction

Ylide molecules differ from other organic ligands in that ylides coordinate to metal ions as a *neutral* ligand to form a σ bond between the ylide carbon and the metal atom. This was shown by means of x-ray analyses of some ylide–metal complexes, in which the configuration of the ylide carbon is tetrahedral rather than planar.[1-3] The copper,[4] silver,[4] gold,[5] nickel,[6,7] and thallium[8] compounds of ylides are known to be thermally stable and the stability has been ascribed to the role of the onium center of the ylide.[7-9] Previously we reported several stable palladium(II) and platinum(II) ylide complexes.[10] We attempted to perform more systematic studies on the configurations of metal–ylide complexes and the interactions between metal ions and some phenacylides.

This paper reports the preparative, infrared, and ^1H NMR studies of palladium(II) and platinum(II) halide complexes with some stable phenacylides as in

$$Z\text{–}\overset{+}{C}H\text{–}\overset{\overset{O}{\|}}{C}C_6H_5$$

Z = *p*-$CH_3C_5H_4N$ (Ny), $CH_3(C_6H_5)_2P$ (Py), $(C_6H_5)_3As$ (Ay), $(CH_3)_2S$ (Sy)