fins. 24 The yield of azoxyalkane is thus limited, but variation of reaction conditions may permit augmented N-alkylation and better yields. Note that alkylation of the diazotates' other nitrogen (yielding N-alkyl-N-nitrosoamines) is a minor process. Synthesis of the authentic N-nitrosoamines, followed by gc analysis of the crude reaction mixtures accompanying 1 and 6, limit N-nitrosoalkane formation to less than 5%.

By uv^{9a,b} and nmr, ^{9,12} our azoxyalkanes are trans (see eq 1 and 2). ²⁵ Because the diazotates from which they come are probably of syn configuration, ²⁶ reactions 1 and 2 could lead directly to *trans*-azoxyalkanes by nucleophilic attack of the diazotate on RX, with retention of the N=N configuration.

The new axoxyalkane synthesis meets generality requirements 1-3. Our synthesis of (S)-4 from (S)-butane-2-diazotate (method 1) shows that it can partly meet the chirality requirement, 4. The CD spectrum of (S)-4 closely resembled those of (S)-ONN-1-cyclohexylazoxyethane²¹ and elaiomycin. We are studying stereospecific synthetic routes to azoxyalkanes in thich the chiral center is bonded at the =N(O) position.

Our synthesis generates primary and secondary trans-azoxyalkanes of varied structure. Superior syntheses of tert-azoxyalkanes 15 complement our work. Coupled with photoisomerization, 8.9 we can gain access to new O-position isomers, cis-azoxyalkanes, and oxadiaziridines as well. The potential for the synthesis of naturally occurring azoxyalkanes is patent, and we are exploring such possibilities.

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 - (28) American Cyanamid Co. Educational Awardee.

Robert A. Moss,* 27 Mildred J. Landon 28 Karen M. Luchter, Andrew Mamantov

Wright Laboratory, School of Chemistry Rutgers, The State University of New Jersey New Brunswick, New Jersey 08903 Received April 7, 1972

Geometry of Nickel(II) Complexes

Sir:

Nickel(II) forms many complexes with octahedral, square-planar, and tetrahedral geometries and a smaller number of five-coordinate compounds¹ with other stereochemical arrangements. It is generally considered that a combination of steric and electronic factors determines which of the three common geometries is assumed by a given compound. Steric factors clearly operate in the sense that bulky ligands are most favorable to tetrahedral geometry and least favorable to octahedral geometry. The mode of operation of the electronic effects is much less clear in spite of ex-

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tensive discussion of the subject. 2-4 We wish to present some new data on the structure of thiourea (tu) complexes of nickel(II) in solution and to suggest a simple rationale for their geometries.

Measurements of visible spectra, magnetic moments, conductivity, and molecular weights of nickel(II) complexes of thiourea and substituted thiourea at room temperature have been reported2,5 and have provided evidence for all three geometries. We have undertaken nmr and other studies of a number of these complexes over a wide range of temperature primarily to elucidate ligand exchange mechanisms. We report here data on four complexes chosen to illustrate the geometric possibilities. Ni(tu)₆(ClO₄)₂ gives conducting solutions in acetone and has a magnetic moment ranging from 2.3 $(+27^{\circ})$ to 3.2 BM (-90°) , and the nmr spectrum indicates fast ligand exchange involving a paramagnetic complex at room temperature. In the presence of excess ligand the exchange is barely frozen out at -90° . (The dimethylthiourea complex is similar but the ligand exchange is slow at -90° giving complexed resonances at -101.4, -19.9, and -12.1 ppm from TMS.) All data are consistent with octahedral Ni(tu)₆²⁺ being the only species present at -90° with some dissociation to square-planar Ni(tu)₄²⁺ at higher temperatures. Solutions of Ni(tu)₄Cl₂ in acetone are nonconducting at all temperatures and the magnetic moment varies from 3.5 $(+27^{\circ})$ to 3.8 BM (-90°) . The nmr of this complex shows fast exchange with dissociated ligand at $+27^{\circ}$, but at -90° one of the two complexed tu protons (chemical shift -104.8 ppm) which result from restricted rotation about the C-N bond is no longer exchanging with free ligand. Free ligand and the second complexed ligand proton give an averaged resonance at -11.3ppm. The species present is tetrahedral Ni(tu)2Cl2 at all temperatures. Ni(tu)6Br2 in acetone has a moment varying from 3.6 BM at $+27^{\circ}$ to 1.2 BM at -94° . It has a small conductivity at room temperature which increases at low temperature. The nmr spectrum at -90° has four resonances. Two show contact shifts (-110.3 and -20.2 ppm) and are attributed to tetrahedral Ni(tu)₂Br₂. One arises from free ligand (-8.9 ppm) and the fourth at -9.3 ppm is assigned to a diamagnetic complex. This latter compound must be ionic since its formation is accompanied by an increase in conductivity. The concentration of the analogous iodide complex is decreased by addition of (CH₃)₄NI (experiment carried out at -50° in the fast exchange region). On the other hand it cannot be Ni(tu)42+ since at -90° in the presence of excess ligand this species is completely converted to Ni(tu)62+. It must therefore be square-planar Ni(tu)₃Br⁺. Ni(tu)₆I₂ has a

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(6) A referee has suggested that the species formulated as Ni(tu)₂²+ or Ni(tu)₃X+ may be diamagnetic, five-coordinated Ni(tu)₂²+ or Ni(tu)₊X+. We consider these assignments less likely for several reasons. At room temperature optical spectra consistent with square-planar Ni(tu)₂²+ have been reported. The susceptibility and nmr data show that diamagnetic Ni(tu)₃²+ is not formed at low temperatures in the perchlorate solutions. At −90° the relative intensities of the "free ligand" and "diamagnetic complex" nmr peaks agree better with the ratios expected for Ni(tu)₃X+ than they do for Ni(tu)₃X+. We also find that this complex exchanges ligands by an associative process. A dissociative mechanism might have been expected for a five-coordinate compound. Although not conclusive these arguments incline us against postulating five-coordinate complexes.

moment of 3.15 BM at 27° which falls to 0.8 BM at -75° and rises again to 1.36 BM at -94° . Its conductivity is greater than that of the bromide. Nmr measurements confirm that the main species present at -90° is square-planar Ni(tu)₃I+ together with a small amount of octahedral Ni(tu)₆²⁺. At room temperature it exists mostly as tetrahedral Ni(tu)₂I₂. In all of these complexes there is some displacement of tu by solvent acetone (particularly at high temperatures) which can be conveniently monitored by nmr, but this is not pertinent to the present arguments. A variety of N-substituted thiourea complexes with both coordinating and noncoordinating anions give results which conform to the above pattern.

We believe that the significant generalization from these results is that under identical conditions (solvent acetone, -90°, excess ligand present) the neutral complexes are tetrahedral (Ni(tu)₂X₂), the monopositive ions are square planar (Ni(tu)₃X⁺), and the dipositive ions are octahedral (Ni(tu)62+). We suggest that the geometry is determined by a competition involving energy gained by forming more or stronger bonds vs. energy lost through interelectron repulsion between bonding electrons. Bond energy is maximized in the series octahedral > square planar > tetrahedral. Interelectron repulsion is minimized in the series tetrahedral < square planar < octahedral. Increasing the positive charge on the metal increases bonding energy for either ionic or covalent bonding and this gradually becomes the dominant factor. Competition between d electron repulsion and ligand field stabilization energy is of course the dominant theme in crystal field theory. The role of interelectron repulsion between bonding (and lone pair) electrons in determining molecular geometry has long been advocated.7 It seems reasonable that similar factors should play a part in the stereochemistry of nickel. It is noteworthy that in cases where there is an equilibrium between square-planar and tetrahedral complexes (e.g., aminotroponeiminates) electron-withdrawing substituents, which will increase the positive charge on the metal, always favor the square-planar form.8

Finally we note a pertinent observation concerning the rates of thiourea ligand exchange in these complexes. For the tetrahedral compounds ligand exchange rates decrease in the series $Ni(tu)_2Cl_2 > Ni(tu)_2Br_2 > Ni$ (tu)₂I₂. (There is a similar trend in the analogous triphenylphosphine complexes.9) For the square-planar complexes $Ni(tu)_3I^+ > Ni(tu)_3Br^+$. All reactions proceed by an associative mechanism and apparently the rates as well as the geometries depend on the metal charge. A plausible supposition is that for the tetrahedral complexes formation of the five-coordinate intermediate is the rate-determining step and this takes place more readily as the positive charge on the metal is increased. For the square-planar complexes the positive charge is sufficient to ensure that formation of the intermediate is rapid and loss of the fifth ligand becomes rate determining, leading to an inversion of the order.

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D. R. Eaton,* K. Zaw

Department of Chemistry, McMaster University Hamilton, Ontario, Canada Received March 18, 1972

A Method for Stereospecific Synthesis of 1,3and 1,4-Dienes via Organocopper Reagents

Sir:

In connection with the study of a new stereocontrolled approach to the synthesis of prostaglandins, we required a synthesis of a Diels-Alder component of structure 3. We outline here the solution to this specific problem by a new method and provide evidence of generality by examples of synthesis for a range of 1,3- and 1,4-dienes.

The highly stereospecific cis addition of alkylcopper reagents to α,β -acetylenic carbonyl compounds has previously been described, as has the application of this reaction to the stereospecific synthesis of olefins with di-, tri-, and tetrasubstitution patterns. The extraordinary effectiveness of vinylcopper reagents in conjugate addition processes has also been demonstrated.^{2,3} Taken together, these studies form the basis for the method of synthesis of 3 which is summarized in Chart I. Methyl 4-trimethylsiloxy-2-nony-

Chart I

noate (1) was prepared in a single step by sequential treatment of methyl propynoate in tetrahydrofuran (THF) (12 ml/g of ester) at -78° with *n*-butyllithium (1 equiv, -78° , 1 hr, N_2 atmosphere), hexanal (1 equiv, dissolved in 2 vol of THF, added dropwise at -78° followed by stirring at -78° for 1 hr), and trimethylchlorosilane (1.5 equiv, added at -78° : gradual warming to 25° and 1 hr at 25°). Analytically pure 1 was obtained as a colorless liquid from the reaction mixture (71% yield) by concentration under reduced pressure, addition of water, extraction, and distillation: 4 bp 63.5-64.5° (0.07 mm); ir max (neat) 2222, 1720 cm⁻¹. Slow addition (with rapid stirring) of a cold solution of $1 (-50^{\circ})$ in THF (1 ml/g of 1) to a solution of divinylcopperlithium² (1.25 equiv, ca. 0.4 M in THF, -90°) followed by stirring at

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