Reduction of Bis(dichloroboryl)methane (3). Using the same procedure described for the reduction of tris(dichloroboryl)methane (**2**), 0.80 g (6.0 mmol) of aluminum trichloride and 1.40 g (64.4 mmol) of lithium borohydride in 10 ml of paraffin oil were allowed to react with 0.834 g (4.71 mmol) of bis(dichloroboryl)methane (**3**). The material collected in the −196° trap was refractionated separately under high vacuum through traps at −97 and −196°. The material from the reaction flask was fractionated through traps at −78 and −196°, and the material from the −196° trap were refractionated through traps at −95 and −196°. The diborane in the −196° traps was destroyed by passing through acetone in a stream of nitrogen. The product in the warmer traps was combined. From the nmr spectrum, the yield of diborylmethane dimer 4 was estimated to be about 1%: infrared[9] (gas phase) 2975 (w), 2895 (m, CH), 2590 (m), 2520 (vs, BH), 1570–1630 (vs, BHB), 1375 (m), 1215 (ms), 1160 (s), 1120 (ms), 862 (m), 770 (w), 717 (w), and below 600 cm^{-1} (m or s); nmr (CCl_4) δ 0.37 (s, broad, CH_2); mass spectrum[9] *m/e* 78 ($C_2{}^{11}B_4H_{10}{}^+$), weaker peak (15–20%) at *m/e* 79 ($C_2{}^{11}B_4H_{11}{}^+$).

Pyrolysis of Reduction Products from Tris(dichloroboryl)methane (2). Tris(dichloroboryl)methane (**2**) was reduced with lithium borohydride and aluminum chloride under the conditions already described, and the volatile products were collected under high vacuum in traps at −78 and −196°. The material in the −78° trap was held at −42° for 2 hr and allowed to vaporize under high vacuum through a 3 cm diameter 15 cm long Vycor tube packed with stainless steel sponge and heated to about 350°, with collection of the pyrolysate in a −196° trap. The source trap was then held at −23° for 1 hr and room temperature for 0.5 hr while pyrolysis was continued. The pyrolysate was fractionated under high vacuum through traps at 0, −78, and −196°. Nothing condensed in the 0° trap. The material in the −78° trap was a mixture and showed carborane-like mass patterns at *m/e* 90, 98, 111, and 120. The infrared spectrum which lacked any BHB band near 1600 cm^{-1} showed prominent bands at 2995 (m), 2615 (s), 1275 (vs), 1105 (s), 1080 (vs), 845 (vs), 820 (vs), and 685 cm^{-1} (w). The peaks at 1275, 1080, 845, and 820 cm^{-1} are believed to be due to chloroalkane or ether contaminants, being found also in the spectrum of the unpyrolyzed reduction product. The material in the −196° trap was refractionated through traps at −112 and −196°. The material collected at −112° showed a sharp cutoff in the mass spectrum[9] at *m/e* 98 ($C_2{}^{11}B_6H_8{}^+$). The infrared spectrum (gas phase) showed no BHB peak near 1600 cm^{-1} and showed prominent bands at 2980 (w), 2615 (vs), 1285 (s), 1215 (s), 1175 (vs), 1100 (s), and 900 cm^{-1} (m).

Registry No. $HC(BCl_2)_3$, 40710-69-8; $HC[B(OCH_3)_2]_3$, 18067-51-1; $H_2C(BCl_2)_2$, 40710-68-7; $H_2C[B(OCH_3)_2]_2$, 17936-82-2; 4, 40802-62-8; BCl_3, 10294-34-5.

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Study of the Ligand Exchange Reaction of a Five-Coordinate Nickel(II) Complex

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In recent years a great deal of interest has been directed toward the preparation and characterization of five-coordinate complexes of the first row transition metal ions. However, relatively little work has been done to characterize the solution behavior of five-coordinate complexes. Thus, we have undertaken a program to explore the properties of some five-coordinate complexes of Ni(II) and Co(II) in nonaqueous solvents. In the present paper we report our results concerning the ligand exchange reaction of $Ni(LUNO)_5{}^{2+}$ with excess LUNO, where LUNO represents 2,6-lutidine 1-oxide, in the solvent acetone-d_6.

The complex $[Ni(LUNO)_4](ClO_4)_2$ was prepared and characterized according to previously reported methods.[1-3] This compound when dissolved in nonaqueous solvents containing large amounts of excess LUNO gives a yellow solution having an electronic spectrum characteristic of a five-coordinate trigonal-bipyramidal Ni(II) complex[2,4-6] presumably due to formation of the $Ni(LUNO)_5{}^{2+}$ species. To establish the conditions under which the complex $Ni(LUNO)_5{}^{2+}$ is the only important species in solution, the electronic spectrum was observed as a function of the ratio of the concentrations of excess LUNO and $[Ni(LUNO)_4](ClO_4)_2$ in the solvents acetone and propylene carbonate. In propylene carbonate Beer's law behavior was observed at ligand to complex ratios above 250:1 (where the complex concentration was in the range 0.01–0.05 *M*) and under these conditions $Ni(LUNO)_5{}^{2+}$ appears to be the only complex present in detectable amounts. At lower ligand to complex ratios significant deviations from Beer's law are observed. The band found at ~1250 mμ at high ligand to complex ratios shifts toward higher energy and the intensities of the other four bands increase as the ligand to complex ratio decreases. These results seem to suggest that another five-coordinate species becomes significant in solutions with low ligand to complex ratios. The spectral results obtained in acetone as solvent are similar except that the $Ni(LUNO)_5{}^{2+}$ species appears to be more stable in acetone. Beer's law behavior and the absence of any changes in the spectrum are observed in solutions containing a ligand to complex ratio of approximately 100:1 or greater (where the complex concentration was in the range of 0.02–0.05 *M*).

To study the exchange reaction between the $Ni(LUNO)_5{}^{2+}$ complex and LUNO acetone solutions were prepared containing large excesses of ligand, and the chemical shift and line width of the nmr signal due to the 2,6-methyl protons were studied as a function of temperature. Typical results of the line width measurements are shown in Figure 1. Note that these data are characteristic of a system undergoing chemical exchange at rates in the range which affect the line width of the exchanging ligand. The system appears to be in the near-fast-exchange region at high temperatures and the signal exhibits characteristic behavior as the temperature is lowered and the exchange rate slows down.[7] In Figure 2 the observed chemical shift of the methyl signal from that of the free ligand is shown as a function of temperature. The behavior of the chemical shift is consistent with the line width data discussed above. However, note that at temperatures which should correspond to the slow-exchange-limiting region ($10^3/T >$ 4.1), the observed chemical shift is more than 10 Hz from the free ligand position and increases as the temperature is lowered. This strongly indicates that another exchanging species is present in solution. This conclusion is supported by the fact that at low temperatures ($10^3/T > 4.4$) the slope of the line width plot is about twice that expected for a relaxation process controlled by the electron spin relaxation rate.[8] It is possible that the behavior of the chemical shift at low temperatures is due to pseudocontact shifts of ligand mole-

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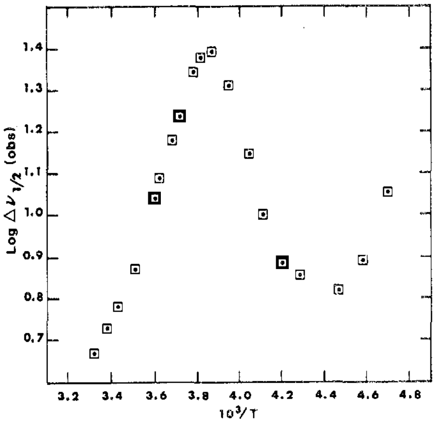

Figure 1. Plot of the log of the observed line width (Hz) at half-height as a function of temperature of the signal due to the 2,6-methyl protons in an acetone solution containing 0.0252 *M* [Ni(LUNO)$_4$](ClO$_4$)$_2$ and 6.40 *M* LUNO.

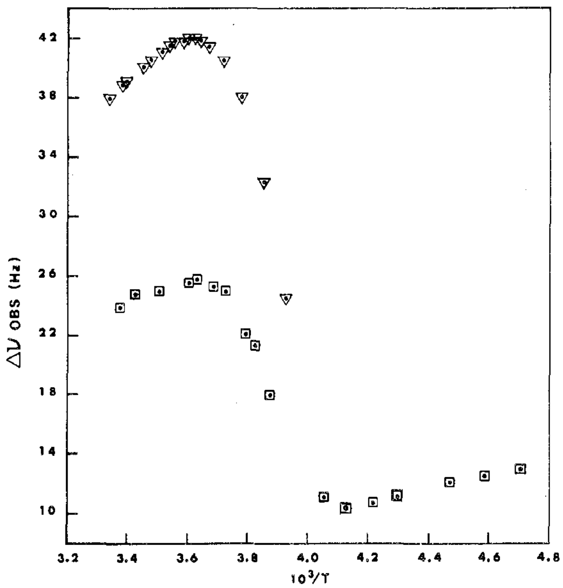

Figure 2. Plot of the observed chemical shift (Hz) from the free ligand position as a function of temperature of the 2,6-methyl protons for acetone solutions containing: □, 0.0252 *M* [Ni(LUNO)$_4$](ClO$_4$)$_2$ and 6.40 *M* LUNO; ∇, 0.0431 *M* [Ni(LUNO)$_4$](ClO$_4$)$_2$ and 6.20 *M* LUNO.

cules in the outer sphere of the complex which do not average to zero as the ligand fast exchanges between the various outer sphere positions. This phenomenon has recently been observed by Forster[9] in pseudooctahedral complexes of Co(II) and Fe(II). However, the large amount of line broadening observed in the low-temperature region makes us prefer the former explanation. The situation could be clarified by going to lower temperatures but this was prevented by the freezing of the solutions.

If a second type of exchanging ligand is present, it could result from the presence in solution of a complex other than Ni(LUNO)$_5{}^{2+}$. However, we believe that the spectral results preclude a second complex being present in the amounts necessary to produce the magnitudes of chemical shifts and line widths observed at low temperatures. Thus, we are led to conclude that the complex Ni(LUNO)$_5{}^{2+}$ contains two types of ligands which exchange at significantly different rates. This is not entirely unexpected if Ni(LUNO)$_5{}^{2+}$ is similar in structure to Co(pic-NO)$_5{}^{2+}$, where pic-NO represent 2-picoline 1-oxide. An X-ray crystallographic study by Coyle and Ibers[10] of [Co(pic-NO)$_5$](ClO$_4$)$_2$ has shown that the coordination sphere is trigonal bipyramidal with the axial Co–O bonds approximately 0.1 Å longer than the equatorial Co–O bonds. If this situation, which may result from ligand–ligand repulsions, is also present in the Ni(LUNO)$_5{}^{2+}$ species where ligand–ligand repulsions may be expected to be greater than in the 2-picoline 1-oxide complex, it is not unreasonable to expect the axial Ni–O bonds to be weaker than the equatorial Ni–O bonds. If the exchange process is controlled by dissociation of a coordinated LUNO (*vide infra*), then one might expect the axial ligands to exchange at a faster rate than the equatorial ligands.

Thus, we believe that the best interpretation of the data involves the axial ligands existing in the fast-exchange-limiting region down to temperatures of a least −25° and that the behavior of the line width and chemical shift at temperatures higher than this can be attributed to the equatorial ligands going from the near-fast-exchange region at higher temperatures to the slow-exchange-limiting region at low temperatures.

To obtain the rates of exchange for the equatorial ligands, eq 1 has been employed, where all of the symbols have their

$$\Delta\omega_f = \frac{P_M \Delta\omega_M}{((\tau_M/T_{2M}) + 1)^2 + (\tau_M \Delta\omega_M)^2} \qquad (1)$$

usual meaning.[7] (In this case $\Delta\omega_M$ is the paramagnetic shift of the equatorial ligands and $\Delta\omega_f$ is the difference between the observed signal position and the calculated position of the free ligand fast exchanging with the axial ligands.) This equation was used because it is relatively insensitive to errors in T_{2M}. Values of the paramagnetic shift for the two types of ligands were obtained by extrapolating the observed shifts at low temperatures ($10^3/T > 4.1$), which are attributed to the axial ligands fast exchanging with bulk ligand, to temperatures where the equatorial ligand shifts also exhibit fast-exchange behavior. Since the mole fractions of axial and equatorial ligands are known, the paramagnetic shifts of both types of ligands can be calculated. This analysis resulted in calculated paramagnetic shifts for the 2,6-methyl groups at 25° of 900 ± 75 Hz for the axial ligands and 1400 ± 100 Hz for the equatorial ligands. Values of T_{2M} were estimated from the observed line width at high temperatures assuming the equatorial and axial ligands have the same natural line widths. This produced a value of 200 Hz for $1/\pi T_{2M}$ at 25°. An apparent activation energy of 2 kcal was assumed to calculate values of T_{2M} at lower temperatures.[8] Fortunately, the calculations were found to be relatively insensitive to the particular value of $1/T_{2M}$ chosen in the range of the values obtained from the above procedure.

The values of τ_M obtained from eq 1 were interpreted in terms of the absolute rate theory and are summarized in Figure 3. The kinetic parameters obtained in this way are $1/\tau_M$ $(0°) = 4.5 \times 10^4$ sec^{-1}, $\Delta H^\ddagger = 14 \pm 2$ kcal/mol, and $\Delta S^\ddagger \simeq$ 14 eu. The error limits assigned to $\Delta H^\ddagger$ were estimated by including consideration of the errors in the extrapolated axial chemical shifts and in the estimation of values of T_{2M}.

Although, because of the instability of the Ni(LUNO)$_5{}^{2+}$ at lower excess ligand concentrations, the concentration of LUNO could not be varied effectively, the data suggest that the exchange process of this five-coordinate Ni(II) complex is dissociatively controlled. Note that the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ parameters obtained in the present study agree quite well with those obtained for the exchange reactions of octahedral

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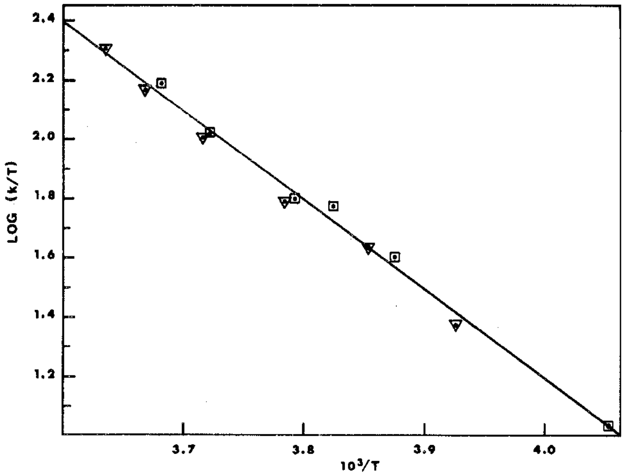

Figure 3. Plot of log (k/T), where $k = 1/\tau_M$, *vs.* $10^3/T$ for acetone solutions containing: □, 0.0252 *M* $[Ni(LUNO)_4](ClO_4)_2$ and 6.40 *M* LUNO; ∇, 0.0431 *M* $Ni[LUNO]_4(ClO_4)_2$ and 6.20 *M* LUNO.

Ni(II) complexes[8,11-14] where a dissociatively controlled mechanism is undoubtedly operating. Also the values of $1/\tau_M$ calculated in the present study do not show any detectable dependence on the ligand/complex ratio which is also consistent with a dissociative rate-controlling step.[8,11-14]

In view of the remote but finite possibility that the behavior of the chemical shift and line width data can be interpreted in terms of five exchanging ligands, calculations were carried out under this assumption using eq 1. This analysis produces a paramagnetic shift of 825 ± 75 Hz for the methyl protons at 25° and the following kinetic parameters: $1/\tau_M$ $(0°) = 4.9 \times 10^4$ sec^{-1}, $\Delta H^\ddagger \simeq 18$ kcal/mol, and $\Delta S^\ddagger \simeq 29$ eu.

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Registry No. $[Ni(LUNO)_4](ClO_4)_2$, 22455-33-0; $Ni(LUNO)_5(ClO_4)_2$, 40959-52-2; LUNO, 1073-23-0.

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Complexes Containing Multidentate Ligands. IV.[1] Unique Bis(S-dealkylation) Reactions of Bis(*o*-diphenylarsinophenylthio)alkanes Catalyzed by Nickel(II) Salts

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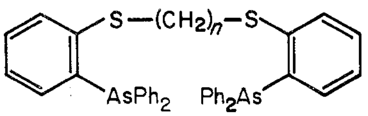
As part of a program initiated to study the effects of altering chelate chain length in multidentate ligand systems we have studied the reaction of nickel(II) salts with 1,2-bis(*o*-diphenylarsinophenylthio)ethane (C_2) (first prepared by Venanzi and coworkers[2]) and the 1,3-propane (C_3) and 1,4-butane (C_4) analogs. We wish to report here the spontaneous bis(S-dealkylation) of these ligands upon reaction with nickel(II) salts in an acetone–ethanol mixture at 30°.



C_2, $n = 2$
C_3, $n = 3$
C_4, $n = 4$

Experimental Section

The Ligands. 1,2-Bis(*o*-diphenylarsinophenylthio)ethane (C_2) was prepared according to the method of Cannon, Chiswell, and Venanzi.[2] The C_3 and C_4 ligands were prepared by analogous methods.

The Complexes. The ligand (0.001 mol) in acetone (10 ml) was mixed with the nickel(II) salt (0.001 mol) in ethanol with stirring. At room temperature no reaction was apparent even with continued stirring, but on warming gently to 30° a deep blue-purple color developed, followed almost at once by the deposition of green crystals. These were filtered, washed with ethanol, and dried *in vacuo* over P_4O_{10}. From the hydrated and anhydrous NiX_2 ($X = ClO_4$, NO_3, Cl, Br) salts used all products had identical carbon and hydrogen analyses. *Anal.* Calcd for $NiC_{36}H_{28}As_2S_2$: C, 58.9; H, 3.8. Found: C, 59.1; H, 4.0. Yields were ~80%.

$Ni[o\text{-}C_6H_4(AsPh_2)S]_2$. Nickel(II) perchlorate hexahydrate (0.001 mol) in ethanol (10 ml) was added to a solution of *o*-mercaptophenyldiphenylarsine (0.002 mol) in hot ethanol (20 ml) with stirring. No deep blue-purple color was seen, but the green solution yielded green crystals on cooling. *Anal.* Calcd for $NiC_{36}H_{28}As_2S_2$: C, 58.9; H, 3.8. Found: C, 59.0; H, 4.0.

Physical Measurements. Magnetic measurements, infrared and visible–ultraviolet spectra, and conductivity measurements were obtained as previously described.[3]

Results and Discussion

Although Cannon, *et al.*,[2] have reported some palladium(II) complexes of C_2, no first transition series complexes have been isolated of C_2, C_3, or C_4. When these ligands are mixed with $Ni(H_2O)_6(ClO_4)_2$ in an ethanol–acetone mixture at room temperature, there is no apparent reaction until the solution is warmed to 30°, after which an intense blue-purple color is formed. This is followed almost immediately by the precipitation of a green microcrystalline material. An infrared spectrum of this material indicated that there were no ClO_4^- groups present in this complex by the complete absence of the characteristic ClO_4^- absorptions at ~1100 and ~630 cm^{-1}.[4] An early suspicion that reduction of ClO_4^- to Cl^- ion was taking place (perchlorate reduction by phosphines is now well established[5]) was shown not to be true when it was discovered that all nickel(II) salts used (the chloride, bromide, and nitrate) yielded the same green complex with identical analyses and infrared and electronic spectra.

The absence of any anions in the resulting complexes pointed to the fact that the nickel(II) ion was complexed

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