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Associative and Dissociative Reactions for $Rh(CNR)_4^+$

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The $Rh[CNC(CH_3)_3]_4^+$ cation[1] exhibits a doublet isonitrile ^{13}C resonance due to ^{103}Rh-^{13}C coupling, which "disappears" at temperatures above −110°. These nmr line shape changes might be ascribed to a facile, dissociative Rh-C bond-breaking process, but other data establish an alternative explanation based on an intrinsically long relaxation time for the bound isonitrile carbon nucleus.

A solution of $Rh[CNC(CH_3)_3]_4^+PF_6^-$ in dichloromethane-chlorodifluoromethane shows a four-line ^{13}C nmr spectrum at low temperatures. Two of the lines represent the CH_3 and the C carbon atoms of the tertiary butyl group. The remaining two arise from the isocyanide carbon atom which is spin coupled with ^{107}Rh ($I = 1/2$), $J = {\sim}54$ Hz. Around −110°, the doublet begins to broaden somewhat and then disappears. Attempts to discern this isocyanide resonance at higher temperatures were unsuccessful even at 25° and with extended multihour FT nmr experiments and different pulse sequences, although the signals for the other carbon atoms were evident. It is unlikely that this doublet disappearance is due to a rapid dissociation of ligand in $Rh[CNC(CH_3)_3]_4^+$ since 16-electron transition metal complexes do not normally undergo facile ligand dissociation processes.[2] An obvious rationale is the presence of adventitious traces of free ligand which would (*vide infra*) cause the disappearance of the doublet through rapid associative-dissociative reaction with the cation. To circumvent this potential complication, the complex was subjected to extensive vacuum drying and also a solution of the complex was pretreated with palladium(II) chloride, which reacts with isocyanide. These procedures did not significantly alter the character of the ^{13}C spectra as a function of temperature. The possibility of an oxygen-based exchange mechanism, $RhL_4O_2^+ \rightleftharpoons RhL_3O_2^+ + L$, was also eliminated by scrupulously maintaining a nitrogen atmosphere. One alternative to a 14-electron exchange intermediate is an $[RhL_3PF_6]$ complex, but the electronic spectrum of $RhL_4^+PF_6^-$ was unaltered at 25° in the presence of a tenfold excess of $R_4N^+PF_6^-$. Another alternative is a bimolecular exchange leading to an isocyanide-bridged dimer which type of structure has precedence;[3] however, the ^{13}C spectral changes seemed insensitive to concentration changes. Electronic spectral studies showed that $Rh[CNC(CH_3)_3]_4^+PF_6^-$ obeys Beer's law at 25°

The disappearance of the ^{13}C signal for the isocyanide carbon atom might be due simply to the long relaxation time for this particular carbon nucleus. A ^{13}C nmr experiment with $Cr(acac)_3$ added to the CH_2Cl_2 solution of $Rh[CNC(CH_3)_3]_4^+PF_6^-$ resolved the question. This solution at 25° yielded a ^{13}C spectrum that consisted of a single CH_3 resonance, a triplet ($J_{CN} = 5$ Hz) tertiary butyl C resonance, and a sextet ($J_{CRh} = 54$ Hz and $J_{CN} = 19$ Hz) isonitrile carbon resonance. Clearly, ligand dissociation in the rhodium complex is slow with respect to the nmr time scale.

$Rh[CNC(CH_3)_3]_4^+$ does react with $CNC(CH_3)_3$ as evidenced by the nmr data for (A) the cation, (B) the free ligand, and (C) mixtures of the cation plus free ligand. The proton nmr resonance of the cation shifts to lower fields with temperature decrease, whereas the free ligand resonance shifts modestly in the opposite direction. For the 1:1 mixture of $(CH_3)_3CNC$ and $Rh[CNC(CH_3)_3]_4^+$, the proton resonance is in a position that is consistent with a mixture in which fast ligand exchange occurs through an intermediate of low concentration. The position of the resonance begins to fall sharply to lower fields at temperatures below −30° and beyond this point the chemical shift plot departs significantly from that for a hypothetical freely exchanging 1:1 mixture. Here a pentacoordinate complex, $Rh[CNC(CH_3)_3]_5^+$, must be present in substantial concentrations (the analogous cobalt complex is well characterized).[4] Ligand lability in the pentacoordinate complex is evident even at −160° where only a single ^1H nmr resonance[5] was detected for mixtures of the cation and more than 1 equiv of of free ligand. Extrapolation of shift data provides a maximal estimate for the heat of dissociation of ~6 kcal/mol.

Tetracoordinate rhodium(I) cation complexes based on phosphine ligands react with oxygen to form stable $RhL_4O_2^+$ complexes.[6] The isocyanide complex showed no spectroscopic evidence of oxygen complex formation; for example, the electronic spectrum of $Rh[CNC(CH_3)_3]_4^+$ was invariant to changes in atmospheres ranging from N_2 to O_2. However, the electronic spectrum was altered on prolonged exposure to oxygen (gross decrease in extinction coefficients) which might be taken as an implication of a transitory oxygen complex.[7]

Experimental Section

Preparation of $Rh[CNC(CH_3)_3]_4^+PF_6^-$. The following operations were effected in a nitrogen atmosphere. *tert*-Butyl isocyanide (17.06 g, 0.206 mol) was added to a solution of $[(C_2H_4)_2RhCl]_2$ (10.0 g, 0.0257 mol) in 450 ml of tetrahydrofuran. The reaction mixture was stirred for 1 hr. A solution of NH_4PF_6 in tetrahydrofuran was added to precipitate the hexafluorophosphate salt. All solvent was removed *in vacuo*. Residue was extracted with dichloromethane. Then petroleum ether was added to the dichloromethane extract to the point of incipient precipitation, and the mixture on cooling gave yellow crystals which were collected. This procedure was repeated twice, and the final crop of crystals was vacuum dried. *Anal.* Calcd for $C_{20}H_{36}N_4RhPF_6$: C, 41.39; H, 6.25; N, 9.66; P, 5.34. Found: C, 41.42; H, 6.27; N, 9.98; P, 5.66. Electronic spectra (CH_2Cl_2), λ_{max} (ϵ): 3090 (28,100), 3350 (350), 3840 (1100), 4400 (330). The ^{13}C spectrum (CH_2Cl_2-$CHClF_2$) consists at −130° of a doublet (54 Hz) at −58.8 ppm, a singlet at −132.7 ppm, and a singlet at −160.8 ppm (to lower frequency from CS_2 zero reference) for the a, b, and c carbon atoms in $C^aNC^bC^cH_3)_3$. The proton nmr resonance at 30° (CD_2Cl_2) is a triplet at +1.41 ppm (TMS reference) with $J_{NH} = 2.1$ Hz.

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(1) The general class of $Rh[CNR]_4^+$ salts and the specific $Rh[CNC(CH_3)_3]_4^+PF_6^-$ salt have been described by J. W. Dart, M. K. Lloyd, J. A. McCleverty, and R. Mason, *Chem. Commun.*, 1197 (1971).

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(5) These solutions also show only one isocyanide carbon, one C tertiary butyl carbon, and one CH_3 carbon atom ^{13}C resonance down to −160°.

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(7) Circumstantially identified[4] for $Co(CNR)_4^+$.

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Pressure-Induced Reversible Conversion of $Ni(CN)_5{}^{3-}$ from Trigonal-Bipyramidal to Square-Pyramidal Geometry[1]

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In an X-ray diffraction study of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$,[3] it was found that the unit cell contained both trigonal-bipyramidal (TBP) and square-pyramidal (SQP) $[Ni(CN)_5]^{3-}$ ions. The water of crystallization participates in hydrogen bonding with these $[Ni(CN)_5]^{3-}$ ions, and dehydration of crystal water converts the TBP to SQP ions.[4] Vibrational spectroscopy has played an important role in characterizing the hydrated and anhydrous solids. The infrared and Raman spectra of these solids in the cyanide stretching region have been used to distinguish these two $[Ni(CN)_5]^{3-}$ ions.[4]

The energy difference between the TBP and SQP ions is known to be small.[3] This suggests a possibility that the TBP ion may be converted into the SQP ion under high pressure. Previous studies with five-coordinate complexes have demonstrated some changes in configuration with pressure.[5,6] It is, therefore, of particular interest to study the effect of pressure on $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. This note reports the spectral change observed in the cyanide stretching region as a function of external pressure, which indicates the reversible pressure-induced conversion of the TBP to SQP $[Ni(CN)_5]^{3-}$ ion.

Experimental Section

Preparation of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. This compound was prepared using the method of Raymond and Basolo.[7] *Anal.* Calcd for $NiCrN_{11}C_{11}H_{24}\cdot 1.5H_2O$: C, 29.45; H, 6.02; N, 34.40. Found: C, 29.26; H, 5.96; N, 34.44.

Spectroscopic Studies. The infrared spectra under pressure were obtained using sapphire windows on an opposed anvil cell (normally used with diamond windows) in a Beckman IR-12 interfaced with a 6X beam condenser. It was necessary to use sapphire windows because of the diamond absorption in the cyanide stretching region. The details of the technique and method of calibration of pressure have been previously reported.[8-10] Low-temperature studies were made using a cell with an inlet and outlet for circulating cold helium or liquid nitrogen.

Results and Discussion

It has been established[4] that for the $Ni(CN)_5{}^{3-}$ ion, in C_{4v} symmetry, four cyanide stretching vibrations are to be expected

$$\Gamma_{CN_{SQP}} = 2A_1(R, ir) + B_2(R) + E(R, ir)$$

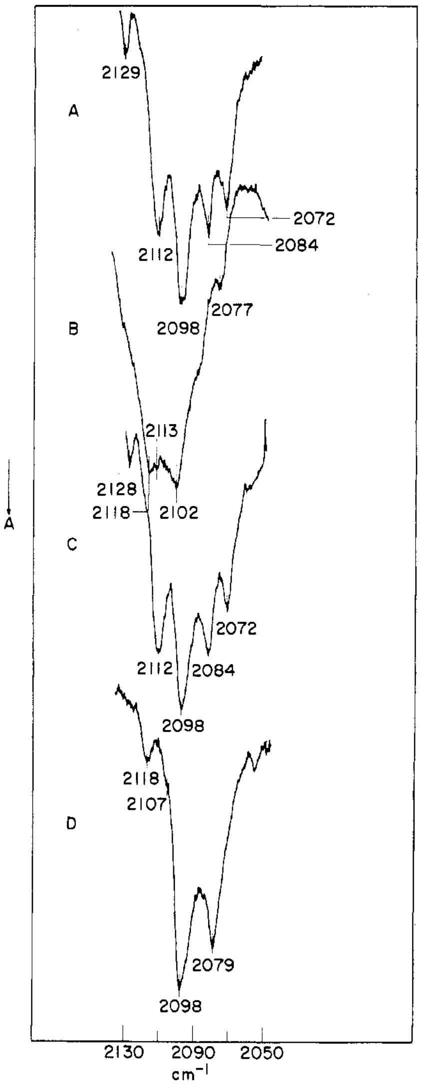

Figure 1. (A) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ at liquid nitrogen temperature and ambient pressure. (B) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ at liquid nitrogen temperature and ∿7 kbars pressure. (C) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ at liquid nitrogen temperature and ambient pressure, after release of pressure. (D) Spectrum of anhydrous $[Cr(en)_3][Ni(CN)_5]$ at ambient pressure and temperature.

In a distorted trigonal-bipyramidal (C_{2v}) environment, five cyanide stretching vibrations are expected

$$\Gamma_{CN_{TBP}} = 3A_1(R, ir) + B_1(R, ir) + B_2(R, ir)$$

The infrared spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$ in the cyanide stretching region exhibits bands from both the TBP and SQP structures. Upon dehydration to $[Cr(en)_3][Ni(CN)_5]$, only those bands attributed to the SQP structure are apparent at 2116, 2105, 2096, and 2078 cm^{-1}.[4]

Figure 1 illustrates the ambient and nonambient temperature and pressure infrared spectra for $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$. It was found that dehydration of the compound resulted during the recording of spectra if some precautions were not taken. This, presumably, was a result of localized heating of the sample by the 6X beam condenser. This dehydration was prevented by cooling the sample prior to and during pressure application to nearly liquid nitrogen temperatures. No appreciable change occurred in the OH stretching region during our pressure experiments. The 3-μm region was recorded at ambient and nonambient pressures. It can be concluded from these results that the waters of crystalliza-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Resident Associate under ANL-AUA Fellowship from Marquette University, Milwaukee, Wis. 53233.

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