Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850, and the Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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

E. L. Muetterties*

Received August 23, 1973

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.

Acknowledgment. The part of this work done at Cornell University was sponsored by the National Science Foundation (Grant No. GP-39306X).

Registry No. $Rh[CNC(CH_3)_3]_4^+PF_6^-$, 42744-96-7; $[(C_2H_4)_2RhCl]_2$, 12081-16-2.

---

* Address correspondence to Cornell University.

[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).

[2] C. A. Tolman, *Chem. Soc. Rev.*, 1, 337 (1972).

[3] L. Malatesta, "Isocyanide Complexes of Metals," Wiley, New York, N. Y., 1969, p 28.

[4] E. L. Muetterties, *J. Chem. Soc., Chem. Commun.*, 221 (1973).

[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°.

[6] L. M. Haines, *Inorg. Chem.*, 10, 1685 (1971).

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