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The Preparation and Spectral Properties of Some Organonitrile Complexes of Pentaamminerhodium(III)[1]

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Recent efforts in these laboratories have been directed toward the interpretation of ligand–metal interactions between organic ligands and cationic metal–ammine complexes of the second transition row. Of particular interest are comparisons of ligand properties and reactions between different complexes of the structurally analogous series $M(NH_3)_5L$, where M = Ru(II), Ru(III), or Rh(III) and L is the organic ligand under study. Previously, we have reported the syntheses and some spectroscopic and chemical properties of the spin-paired $4d^6$ $Ru(NH_3)_5{}^{2+}$ and low-spin $4d^5$ $Ru(NH_3)_5{}^{3+}$ complexes of nitrile-coordinated acetonitrile,[2] acrylonitrile,[3] and benzonitrile.[2] Here we report the synthesis and ir, electronic, and some nmr spectral properties of the spin-paired $4d^6$ rhodium(III) analogs. These complexes provide direct comparisons with the isoelectronic Ru(II) complexes for which significant $d\pi$–$p\pi$ back-bonding has been described[2,3] and with the analogously 3+ charged Ru(III) complexes. In a subsequent publication, we will report the detailed high-resolution nmr spectra of the rhodium(III)- and ruthenium(II)–organonitrile complexes.[4]

The complexes reported here are the first examples of pentaamminerhodium(III)–organonitrile complexes. However, organonitrile–rhodium(III) complexes of the type $RhX_n(RCN)_{6-n}{}^{(n-3)-}$ have been previously reported[5,6] for $X^- = Cl^-$ or Br^-; RCN = CH_3CN, C_2H_5CN, C_6H_5CN, or $MeOCH_2CH_2CN$; and n = 5, 4, or 3. In addition, the inorganic nitrile complex ions isothiocyanatopentaamminerhodium(III),[7] $Rh(NH_3)_5(NCS)^{2+}$, and isocyanatopentaamminerhodium(III),[8] $Rh(NH_3)_5(NCO)^{2+}$, have been synthesized.

Experimental Section

Syntheses. $[Rh(NH_3)_5H_2O][ClO_4]_3$.—Chloropentaamminerhodium(III) chloride was prepared from rhodium trichloride (Engelhard Industries) by the method of Anderson and Basolo.[9] The aquo complex $[Rh(NH_3)_5H_2O][ClO_4]_3$ was prepared by heating at reflux the aqueous mixture (5 ml) of $[Rh(NH_3)_5Cl]Cl_2$ (0.105 g, 0.36 mmol) and silver(I) perchlorate (1.07 mmol, prepared by dissolution of Ag_2O in a minimum of aqueous perchloric acid) for 1 hr. Filtration of the hot reaction solution followed by addition of saturated aqueous $NaClO_4$ solution (several milliliters) to the filtrate leads to precipitation of the white solid $[Rh(NH_3)_5H_2O][ClO_4]_3$ (0.168 g, 93%). The uv spectrum of this material displayed two absorption bands with λ_{max} 316 and 263 nm and extinction coefficients agreeing with the literature values.[10]

$[Rh(NH_3)_5(CH_3CN)][ClO_4]_3$.—Syntheses of various organonitrile complexes $[Rh(NH_3)_5L][ClO_4]_3$ with L = acetonitrile, benzonitrile, acrylonitrile, etc., were all carried out using the procedure described here for the acetonitrile complex. A mixture of $[Rh(NH_3)_5H_2O][ClO_4]_3$ (0.10 g, 0.20 mmol), acetonitrile (1 g, 24 mmol), dry *N,N*-dimethylacetamide (5 g), and dry, Type 3A molecular sieves (0.5 g) was placed in a glass tube and sealed under a slight vacuum. The sealed tube was then heated in an oil bath at 110° for 5 hr. After this step, the hot tube was opened and the solution was filtered through a preheated sintered-glass crucible to remove the molecular sieves and other solids. Chloroform (30 ml) was added to the filtrate to give a white flocculent precipitate which after cooling was collected by filtration, washed with 95% ethanol and then anhydrous ether, and air-dried (yield 0.70 g, 60%). This material was recrystallized with small loss by dissolution in ambient-temperature water followed by addition of 1 drop of saturated aqueous $NaClO_4$ and cooling to 0°. *Anal.* Calcd for $C_2H_{18}O_{12}N_6Cl_3Rh$: C, 4.6; H, 3.5; N, 15.9. Found: C, 4.7; H, 3.9; N, 15.4. The benzonitrile complex $[Rh(NH_3)_5(C_6H_5CN)][ClO_4]_3$ was prepared similarly. *Anal.* Calcd for $C_7H_{20}O_{12}N_6Cl_3Rh$: C, 14.3; H, 3.4; N, 14.3. Found: C, 14.4; H, 3.9; N, 13.8.

Spectra.—All uv-visible spectra were recorded on a Cary 14 spectrophotometer in aqueous solution, 25°. Extinction coefficients were determined from duplicate solutions prepared gravimetrically. Infrared spectra were obtained as KBr disks on a Perkin-Elmer Model 225 recording spectrophotometer. Proton nmr spectra were obtained using deoxygenated D_2O solutions on a Varian HA-100 high-resolution spectrometer at 100 MHz.

Results and Discussion

Infrared Spectra.—The spectrum of each organonitrile complex, $[Rh(NH_3)_5L][ClO_4]_3$, displayed a medium to strong nitrile stretching band, $\nu(CN)$, at a frequency 50–70 cm^{-1} greater than the corresponding free ligand (Table I). The acetonitrile complex showed two absorptions in the $\nu(CN)$ region (2323 (m) and 2300 cm^{-1} (w)). The more intense band was assigned to the C≡N stretch and the weaker band to the combination $\delta(CH_3) + \nu(CC)$.[11] Other bands observed included those group frequencies characteristic of the $Rh(NH_3)_5{}^{3+}$ moiety {$\nu(NH)$ [~3400 (s, b) and ~3200 cm^{-1} (vs, b)], $\delta(NH_3)_{deg}$ [~1620 cm^{-1} (s, b)], $\delta(NH_3)_{sym}$ [1310 cm^{-1} (vs)], $\rho(NH_3)_{rock}$ [860 cm^{-1} (s, b)], and $\nu(Rh–NH_3)$ [475 cm^{-1} (m)]}; those characteristic of the ClO_4^- ion [~1100 (vs, b), 938 (m), ~630 cm^{-1} (vs)]; and those characteristic of the individual ligand L.

TABLE I

NITRILE STRETCHING FREQUENCIES[a] [$\nu(CN)$] FOR THE COMPLEXES $[Rh(NH_3)_5(RCN)][ClO_4]_3$

RCN	Free ligand	Coordinated[b]	$\Delta\nu(CN)$
CH_3CN	2254[c]	2323	+69
CD_3CN	2263[c]	2318	+55
CH_3CH_2CN	2248[e]	2312	+64
$CH_2=CHCN$	2228[d]	2288	+60
$CH_2=C(CH_3)CN$	2229[e]	2284	+55
C_6H_5CN	2231[c]	2287	+56
o-FC_6H_4CN	2238[e]	2291	+53
m-FC_6H_4CN	2236[e]	2295	+59
p-FC_6H_4CN	2232[e]	2290	+58

[a] In cm^{-1}. [b] All complex spectra taken in KBr pellets. [c] Reference 2. [d] Reference 3. [e] Neat.

The 50–70-cm^{-1} increase in the nitrile stretching frequency upon coordination to $Rh(NH_3)_5{}^{3+}$ is of the

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same magnitude as that observed for the halogenoacetonitrile- and -benzonitrilerhodium(III) complexes first reported by Johnson and Walton.[5] Similar ν(CN) increases are normally observed for nitrile coordination through the nitrogen lone-pair electrons[12] and have been observed for the analogous pentaammineruthenium(III) complexes (Table II). Consequently, the ν(CN) increases on coordination of acrylonitrile (+60 cm^{-1}) and of methacrylonitrile (+55 cm^{-1}) clearly denote the nitrile nitrogen as the coordination site for these potentially ambident ligands. This conclusion is confirmed by the complete analysis of the high-resolution nmr spectrum.[4] It is especially interesting, however, to note that among the few exceptions to the rule that nitrogen lone-pair coordination increases ν(CN) are the Ru(II) complexes $Ru(NH_3)_5(NCR)^{2+}$, where RCN is any organonitrile. The Ru(II) complexes, which are isoelectronic ($4d^6$) and isostructural to the Rh(III) complexes reported here, display significant ν(CN) decreases (Table II) with frequencies ranging from 13 to 93 cm^{-1} below the free-ligand values.[2,3] The decreases have been attributed to metal $d\pi$ to ligand $p\pi^*$ back-bonding sufficient to override the normal Lewis acid coordination effect which should increase ν(CN).[2] Similar back-bonding clearly is not indicated for the Rh(III) complexes. The ν(CN) frequency order for the species types reported in Table II is as follows: $Ru(NH_3)_5{}^{2+}$ complexes < free ligand < $Ru(NH_3)_5{}^{3+}$ complexes < $Rh(NH_3)_5{}^{3+}$ complexes. The fact that the ν(CN) values for the Ru(III) complexes average 20 cm^{-1} less than those for the Rh(III) complexes may be interpretable in terms of two potential effects. Rhodium(III) may be a stronger Lewis acid than ruthenium(III) owing to a greater nuclear charge not completely shielded by the additional t_{2g} electron. On the other hand, the low-spin $4d^5$ electronic configuration of Ru(III) allows some $p\pi \rightarrow d\pi$ bonding between the filled C≡N bonding orbitals and the incomplete t_{2g} subshell. The net result might be a modest decrease in the C—N bond order with respect to that in the Rh(III) complex. The π-bonding argument is supported by the observation that the aquo complex ion $M(NH_3)_5H_2O^{3+}$ is more acidic[8] in aqueous solution for M = Ru(III) than for M = Rh(III) despite the potentially greater Lewis acidity of Rh(III). The inorganic nitrile complex[8] $[Ru(NH_3)_5(NCO)][ClO_4]_2$ also shows a ν(CN) 40 cm^{-1} less than that of $[Rh(NH_3)_5(NCO)][ClO_4]_2$.

TABLE II

COMPARISON OF ν(CN) VALUES (cm^{-1}) OBSERVED FOR RUTHENIUM(II)-, RUTHENIUM(III)-, AND RHODIUM(III)-ORGANONITRILE COMPLEXES OF THE TYPE $M(NH_3)_5(RCN)$

Complex[a]	L	
	CH_3CN	C_6H_5CN
L	2254	2231
$Rh(NH_3)_5L^{3+}$	2323 m	2287 m
$Ru(NH_3)_5L^{3+}$	2286 m[b]	2267 m[b]
$Ru(NH_3)_5L^{2+}$	2239 s[b]	2188 s[b]

[a] Free ligand neat; complexes as ClO_4^- salts in KBr pellets. [b] Reference 2.

Visible-Uv Spectra.—The electronic spectra for the $Rh(NH_3)_5(RCN)^{3+}$ complex ions are listed in Table III. The spectra of the complexes having unsaturated R groups are dominated by very intense uv absorptions which apparently are internal π–π^* ligand transitions perturbed somewhat by coordination. In contrast to the unsaturated organonitrile complexes, the acetonitrile complex displays only two relatively low intensity bands (λ_{max} 300 and 253 nm) which are apparently the d–d transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (octahedral point group notation used, low spin $4d^6$), often observable for $Rh^{III}(NH_3)_5X$ complexes[8,10] (see Experimental Section for spectrum of $Rh(NH_3)_5H_2O^{3+}$). The lower energy band is evident for each of the other $Rh(NH_3)_5(RCN)^{3+}$ complexes (Table III); however, the exact intensities and positions of these bands are less certain owing to their appearance as shoulders on the trailing edges of the stronger uv bands. The similarity of the energies of this first band in the various complexes does suggest, however, that there are no marked differences in the ligand field strengths of the several organonitriles in their interactions with Rh(III). Osborn, Gillard, and Wilkinson[10] have used the energy of the longer wavelength transition to organize the ligands X into a spectrochemical series for $Rh^{III}(NH_3)_5X$ and this series recently has been amplified with additional ligands.[8] The ligand CH_3CN (λ_{max} 301 nm) occupies a position high in this spectroscopic series, falling between NH_3 (306 nm) and $-NO_2^-$ (296 nm).[10] Whether this series reflects the strength of the Rh(III)–ligand interactions is a matter of conjecture. However, the ir data indicate that the high position of CH_3CN cannot result from π-back-bonding effects, and therefore any strong interaction must be due to the polarizability of the CH_3CN coordination site.

TABLE III

VISIBLE-UV SPECTRA OF THE Rh(III) COMPLEX IONS $Rh(NH_3)_5(RCN)^{3+}$ IN AQUEOUS SOLUTION[a]

Complex ion	$\lambda_{max}{}^b$ (log ϵ)
$Rh(NH_3)_5(CH_3CN)^{3+}$	301 (2.20), 253 (2.10)
$Rh(NH_3)_5(CH_2{=}CHCN)^{3+}$	300 (2.58), 210 (3.92)
$Rh(NH_3)_5(CH_2{=}C(CH_3)CN)^{3+}$	301 (2.28), 213 (3.92)
$Rh(NH_3)_5(C_6H_5CN)^{3+}$	301 sh (2.51), 282 sh (3.15), 275 (3.23), 268 sh (3.22), 245 sh (4.20), 234 (4.30)
$Rh(NH_3)_5(o\text{-}FC_4H_6CN)^{3+}$	305 sh (2.50), 288 sh (3,39), 281 (3.41), 243 sh (4.16), 235 (4.26)
$Rh(NH_3)_5(m\text{-}FC_4H_6CN)^{3+}$	300 sh (2.44), 288 sh (3.23), 280 (3.30), 273 sh (3.27), 242 sh (4.04), 233 (4.12)
$Rh(NH_3)_5(p\text{-}FC_4H_6CN)^{3+}$	304 sh (2.35), 276 sh (2.61), 265 sh (2.91), 237 (3.924)

[a] 25°; ClO_4^- salts. [b] In nanometers.

Nmr Spectra.—The proton magnetic resonance spectrum of the acetonitrile complex $[Rh(NH_3)_5(CH_3CN)][ClO_4]_3$ in D_2O displays a doublet centered at δ 2.546 (ppm downfield from TMS), which can be assigned to the acetonitrile methyl hydrogens. The doublet splitting is 0.4 Hz and is due to coupling between the CH_3 hydrogens and the rhodium-103 nucleus (spin $^1/_2$, natural abundance 100%). Complexation to $Rh(NH_3)_5{}^{3+}$ shifts the methyl resonance frequency 0.576 ppm downfield from the free-ligand value (δ_{CH_3CN} 1.970 ppm), a deshielding effect which would be expected from coordination to a metal cation. The pmr spectrum of the isoelectronic Ru(II) species, $Ru(NH_3)_5(CH_3CN)^{2+}$, displays a methyl singlet (δ_{CH_3} 2.403 ppm) shifted 0.433 ppm downfield from the free-ligand value. Catsikis and Good[6] have reported pmr spectra for several

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halogenoacetonitrilerhodium(III) complexes with coordinated acetonitrile resonances all falling in the range δ 2.55–2.64 ppm, in agreement with our observations. No rhodium–hydrogen coupling was reported for their complexes which were studied on a lower resolution instrument.

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The Synthesis of Bis-μ-difluorophosphido-diiron Hexacarbonyl

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Although phosphorus trifluoride closely resembles carbon monoxide in many of its properties toward low-valent transition metals, it has not been observed to act as a bridging group. Instead, in only one example a PF_2 moiety has been found to bridge two metals. The compound $[Co(PF_3)_3PF_2]_2$ was prepared by Kruck and Lang[2] using forcing conditions (*e.g.*, cobalt(II) iodide, excess copper, and phosphorus trifluoride at 400 atm and temperatures above 170°). By use of nickel carbonyl, PF_2 bridging groups can be formed by a halogen-abstraction reaction. Thus with $BrPF_2Fe(CO)_4$,[3] $Ni(CO)_4$ affords the complex $[PF_2Fe(CO)_3]_2$. Criegee and Schroeder used a similar technique in the preparation of dichlorotetramethylcyclobutadienenickel dimer, $[(CH_3C)_4NiCl_2]_2$.[4]

Experimental Section

Materials.—Nickel carbonyl was used as obtained from J. T. Baker. $BrPF_2Fe(CO)_4$ was prepared according to the literature.[3]

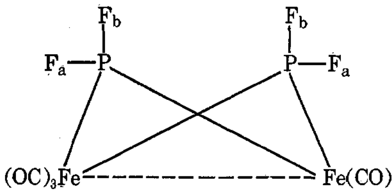
Analysis and Spectroscopic Measurements.—The mass, infrared, and nmr spectra were recorded on AEI MS-902, Perkin-Elmer 621, and Hitachi Perkin-Elmer R-20 spectrometers, respectively. Elemental analysis was obtained from Galbraith Laboratories, Knoxville, Tenn.

The Preparation of Bis-μ-difluorophosphido-diiron Hexacarbonyl.—A 9.51-g (30-mmol) sample of $BrPF_2Fe(CO)_4$ was added to 350 ml of deoxygenated hexane in a 500-ml flask. After degassing at −196°, nickel carbonyl (17.1 g, 100 mmol) was condensed into the flask. The flask was allowed to warm to ambient temperature under a nitrogen atmosphere and then fitted with a dewar condenser cooled to −78°. After refluxing until a metallic deposit was observed, the reaction mixture was allowed to cool to room temperature, and then the mixture was filtered through filter-aid. The solvent was removed *in vacuo*. The residue was extracted with four 50-ml portions of methylene chloride and the extracts were filtered. The filtrate was stripped dry, extracted with three 10-ml portions of pentane, and filtered again. The volume of the solution was then reduced to *ca.* 10 ml with a stream of dry nitrogen, and after cooling to −78°, orange-red to red crystals were obtained. Final purification was accomplished by sublimation (40–45° (0.1 mm)), yield 0.4 g (6.3%). *Anal.* Calcd for $P_2F_4Fe_2C_6O_6$: C, 17.21; H, 0.00; P, 14.85; F, 18.20; mol wt 418. Found: C, 17.44; H, 0.09; P, 14.85; F, 18.27; mol wt 418 (mass spectroscopy).

Results and Discussion

Nickel carbonyl has been found to react with $BrPF_2Fe(CO)_4$ in refluxing hexane to give the bis-μ-difluorophosphido complex $[F_2PFe(CO)_3]_2$. The new complex is an orange-red crystalline material, soluble in organic solvents, and easily sublimable. Though indefinitely stable under nitrogen, the complex decomposes upon exposure to the atmosphere.

Since the complex $[F_2PFe(CO)_3]_2$ is formally similar to the known complexes $[R_2PFe(CO)_3]_2$[5] ($R = CH_3$, C_6H_5), $[CH_3PC_6H_5Fe(CO)_3]_2$,[6,7] and $[C_2H_5SFe(CO)_3]_2$,[8,9] it is probable that it possesses the same generalized geometry. The complex $[C_2H_5SFe(CO)_3]_2$ has been shown by Dahl and Wei[9] to have a folded structure consisting of two octahedra sharing a common face whose three points of intersection consist of two bridging C_2H_5S units and a metal–metal bond. A recent structural determination of *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$[7] (II) has shown it to be isostructural with $[C_2H_5SFe(CO)_3]_2$, in which the $CH_3PC_6H_5$ moiety replaces the C_2H_5S units. Hence it is likely that $[FePFe(CO)_3]_2$ possesses a similar structure as shown in I.



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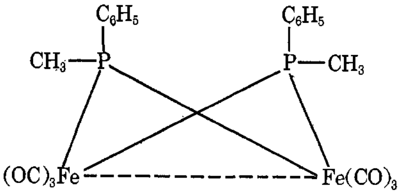

II

The fluorine-19 nmr spectrum of $[F_2PFe(CO)_3]_2$ is consistent with the proposed structure. The observed spectrum consists of two sets of doublets, δ_a +46 ppm, $J_{F_aP} = 1260$ Hz, and δ_b +55 ppm, $J_{F_bP} = 1375$ Hz (*vs.* CCl_3F), whose areas integrate in a 1:1 ratio. Each member of the doublets is further split into a doublet by the adjacent fluorine atom, $J_{F_aF_b} = 285$ Hz. While it is not possible to assign the chemical shift values definitively, it is felt that the F_b fluorines [parallel to the principal (C_2) axis] are shifted upfield by a through-space interaction. This assignment is based on the relative shielding of the methyl groups in the complexes $[(CH_3)_2PFe(CO)_3]_2$[5] and *sym*-$[CH_3PC_6H_5Fe(CO)_3]_2$.[6] The proton nmr spectra of these complexes

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