Nuclear Magnetic Resonance Studies of Organonitrile Ligands Coordinated to Rhodium(III) and to Ruthenium(II). A Demonstration of Metal π-Orbital Electron Density Delocalization into Unsaturated Ligands Having Extended π Conjugation[1]

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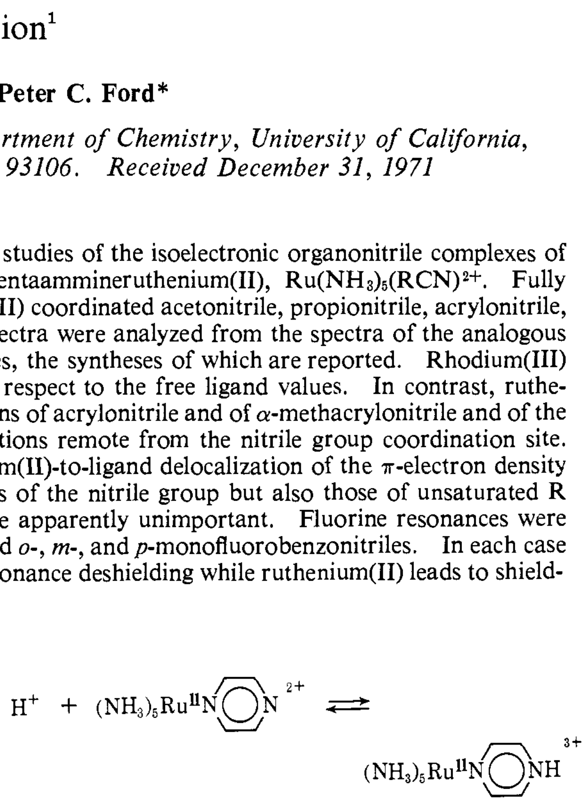
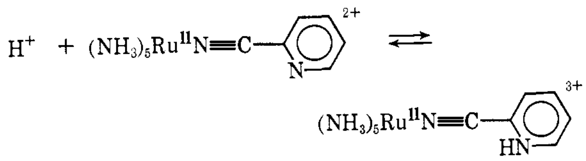
Abstract: Reported are proton and fluorine nmr spectral studies of the isoelectronic organonitrile complexes of pentaamminerhodium(III), Rh(NH$_3$)$_5$(RCN),$^{3+}$ and of pentaammineruthenium(II), Ru(NH$_3$)$_5$(RCN)$^{2+}$. Fully analyzed proton spectra were obtained for Ru(II) and Rh(III) coordinated acetonitrile, propionitrile, acrylonitrile, α-methacrylonitrile, and benzonitrile. The benzonitrile spectra were analyzed from the spectra of the analogous 4-deuteriobenzonitrile and 3,5-dideuteriobenzonitrile species, the syntheses of which are reported. Rhodium(III) coordination leads to deshielding of all ligand protons with respect to the free ligand values. In contrast, ruthenium(II) coordination leads to shielding of the geminal protons of acrylonitrile and of α-methacrylonitrile and of the meta and para protons of benzonitrile, each of these positions remote from the nitrile group coordination site. These observations are interpreted as indicating a ruthenium(II)-to-ligand delocalization of the π-electron density (back-bonding) involving not only the π-symmetry orbitals of the nitrile group but also those of unsaturated R groups of RCN. Similar interactions for rhodium(III) are apparently unimportant. Fluorine resonances were obtained for the ruthenium(II) and rhodium(III) coordinated *o*-, *m*-, and *p*-monofluorobenzonitriles. In each case rhodium(III) coordination at the nitrile leads to fluorine resonance deshielding while ruthenium(II) leads to shielding.

The chemistry of pentaammineruthenium(II) complexes having a π acceptor as the sixth ligand, Ru^{II}(NH$_3$)$_5$L, has received considerable attention in recent years.[2] Among others, these include complexes with L as nitrosyl, carbon monoxide, dinitrogen, hydrogen cyanide,[3] various aromatic nitrogen heterocycles, and various alkyl and aromatic organonitriles. Electronic and infrared spectral data, as well as the relative chemical stabilities of these complexes, indicate considerable interaction between the d$_\pi$ electrons of the low spin 4d^6 ruthenium(II) and the unfilled π-symmetry orbitals on these ligands. These data have a number of times been interpreted as indicating π "back-bonding" between metal atoms and ligand. In addition, particularly interesting chemical phenomena observed for several of these systems are the acid–base properties of pyrazine[4] and of the nitrile coordinated *o*-, *m*-, and *p*-cyanopyridines.[5] Each of these pentaammineruthenium(II) complexes is substantially *more basic* than the corresponding free ligand, despite the fact that the complexes are positively charged (*e.g.*, eq 1 and 2). In addition, it was observed that the basicity enhancement of the cyanopyridine complexes was largest for the ortho and para isomers and smallest for the meta isomer, a pattern of alternation about the aromatic ring typical of a π-resonance substituent effect on the properties of the ring positions.


(1)


(2)

One interpretation of the enhanced basicity at aromatic ring nitrogen atoms remote from the coordination site is that π back-bonding from Ru(II) into the unfilled π orbitals of the nitrogen heterocycles serves to delocalize the positive charge of the protonated ligand. These results do not imply necessarily that Ru(II) electron density is delocalized into the aromatic heterocycle of the unprotonated complex, since both the magnitude of the back-bonding and the extent of delocalization into the aromatic ring very likely will differ between the protonated and unprotonated complexes. Indeed, this possibility is indicated by the infrared spectra of the free and complexed cyanopyridines and cyanopyridinium ions.[5] For example, protonation of 4-cyanopyridine has negligible effect on the nitrile group stretching frequency, ν(CN); however, protonation of pentaammine(4-cyanopyridine)ruthenium(II) lowers its ν(CN) 29 cm^{-1}. Since the unprotonated complex already displays a ν(CN) 64 cm^{-1} lower than the free ligand (presumably because of π back-bonding into the N-coordinated nitrile group), this further decrease suggests that protonation of the pyridine increases the π-interaction between the ruthenium(II) and the nitrile group.

The present study was initiated to investigate the extent of π delocalization into unsaturated and uncharged R groups of Ru(NH$_3$)$_5$$^{2+}$ coordinated organo-

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[1] Taken in part from the Ph.D. Dissertation of R. D. F., University of California, Santa Barbara, 1971. This work has been presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

[2] P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

[3] P. C. Ford, *Chem. Commun.*, 7 (1971).

[4] P. Ford, DeF. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

[5] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 495 (1970).

nitriles, RCN. Nuclear magnetic resonance was chosen as a nondestructive technique potentially capable of distinguishing (by chemical shift or coupling constant effects) small perturbations in the electron density in the vicinity of magnetically active nuclei at various locations of the coordinated ligand. Organonitriles both with saturated and with unsaturated R groups were studied and spectra were obtained for complexes both of pentaammineruthenium(II) and of pentaamminerhodium(III). The rhodium(III) complexes, which are isoelectronic to the 4d^6 ruthenium(II) complexes, provide comparative examples where π backbonding is apparently unimportant. In addition, comparisons of these two sets of complexes is consistent with a program in these laboratories to study the similarities and differences in the properties of electronically and structurally analogous complexes.

Experimental Section

Nuclear Magnetic Resonance Spectra. Proton magnetic resonance spectra were recorded on a Varian HA-100 nmr spectrometer, operating in frequency sweep mode at 100 MHz, and with a Jeolco C60-H, 60-MHz nmr spectrometer. Fluorine magnetic resonance spectra were measured with a Varian HA-100 spectrometer operating at 94.1 MHz. All spectra recorded on the HA-100 nmr spectrometer were calibrated in 2.0-Hz increments by measuring the frequencies of the sweep and manual frequency oscillators with a Varian V-4315 frequency counter and subtracting to obtain the difference in hertz from the internal lock signal. The spectrum of each sample was recorded at least four times, with an equal number of upfield and downfield sweeps. The chemical shift of the lock signals relative to tetramethylsilane was determined from separate solutions of the reference material with TMS present.

Ruthenium and rhodium samples were prepared by placing the recrystallized bromide salt in a 10-ml beaker, adding deuterium oxide (or 33% *N*,*N*-dimethylacetamide–D_2O) until the sample dissolved, and filtering through a sintered glass filter into a 9-in. Wilmad Imperial nmr tube. The sample was then passed through several "freeze–thaw" degassing cycles and sealed under vacuum. Bromide salt solutions of rhodium complexes were generated from their less soluble perchlorate salts by adding a 3-mol excess of potassium bromide to the rhodium complex in a D_2O solution and filtering off the potassium perchlorate precipitate.

Nmr spectra of benzonitrile and benzonitrile metal complexes were recorded in a solvent of 33% *N*,*N*-dimethylacetamide–deuterium oxide (volume to volume). The use of this solvent was dictated by the solubilities of the benzonitrile and the benzonitrile complex. The use of a single solvent minimizes possible solution differences in the spectra. A mixture of 33% *N*,*N*-dimethylacetamide–water (volume to volume) was used for all fluorine-19 nmr samples.

A Varian C-1024 time averaging computer was used to improve the signal-to-noise ratio of dilute samples.[6] Homonuclear spin–spin decoupling experiments were conducted in the usual manner. Spin–spin decoupling of deuterium and fluorine from proton spectra was accomplished by irradiating the sample at 15.4 or 94.1 MHz,[7] respectively, with a Nmr Specialties HD-60 heteronuclear decoupler. It was necessary to use a broad band decoupling technique to obtain the completely deuterium decoupled proton spectrum of 3,5-dideuteriobenzonitrile.

Computer refinement of nmr spectral parameters was accomplished with the Magnetic Equilavence Factoring (MEF) program of Ferguson and Marquardt[8] and with the LAOCOON III program of Bothner-By and Castellano.[9] The experimental frequencies used in the iterative portion of the analyses reflect the average value obtained from an equal number of upfield and downfield sweeps. The decision to accept or reject a given analysis was based on the magnitude of the root mean square (rms) error between the experimental and calculated frequencies and on a visual comparison of the theoretical and experimental spectra. The maximum acceptable rms error was 0.05 Hz for all analyses. Spectral parameters thus obtained are considered accurate to ±0.05 Hz.

Syntheses of Metal Complexes. Pentaammineruthenium(II) complexes of the various organonitriles used in this study were prepared from $[Ru(NH_3)_5Cl]Cl_2$ by the method described[10] previously for the syntheses of the benzonitrile complex, $[Ru(NH_3)_5C_6H_5CN][ClO_4]_2$. In all cases, however, the more soluble bromide salts were prepared. The analogous rhodium(III) complexes were synthesized from $[Rh(NH_3)_5H_2O][ClO_4]_3$ in the manner described[11] previously for the preparation of the acetonitrile complex, $[Rh(NH_3)_5CH_3CN][ClO_4]_3$. The organonitrile ligands used here are available commercially, with the exception of the 3,5-dideuterio- and 4-deuteriobenzonitriles, whose syntheses are described below.

Syntheses of Deuterated Benzonitriles. The specifically labeled 4-deuteriobenzonitrile and 3,5-dideuteriobenzonitrile were prepared from 1,4-dibromobenzene and 1,3,5-tribromobenzene, respectively. The method involves the serial preparations of Grignard reagents (RMgBr, where R is a substituted phenyl group), quenching with D_2O to deuterate the phenyl ring, or quenching (the final Grignard reagent) with CO_2 to form the benzoic acids. The deuteriobenzamides, prepared from the deuteriobenzoic acids, were dehydrated to deuteriobenzonitrile by treatment with phosphorous pentoxide.[12] Specific details follow. The procedure described here was used to generate all Grignard reagents. A three-necked, 500-ml Morton stirring flask containing a Teflon-coated stirring bar was fitted with a reflux condenser and addition funnel and connected to a vacuum pump. Magnesium metal turnings (Mallinckrodt, dried overnight at 150°) were weighed into the flask. The flask was purged with dry argon gas, heated with a hot air gun while evacuated, and then filled with argon. The organic substrate was placed in the addition funnel and dissolved in tetrahydrofuran distilled from lithium aluminum hydride directly onto the substrate. The apparatus was flushed with dry argon gas during the transfer of all reagents. The reaction commenced upon addition of the THF solution to the magnesium. On several occasions, the flask was packed in ice to slow the reaction.

5-Deuterio-1,3-dibromobenzene. 1,3,5-Tribromobenzene (31.4 g, 0.100 mol) was dissolved in freshly distilled tetrahydrofuran (150 ml), added to magnesium metal turnings (4.86 g, 0.200 g-atom), and allowed to reflux overnight. The reaction was quenched with deuterium oxide (20 ml, 1.1 mol), separated from organic material by ether extraction, and purified by fractional distillation at atmospheric pressure: yield, 10.8 g (45.7%); bp 217° (lit.[13] for 1,3-dibromobenzene 217–219°).

3,5-Dideuteriobromobenzene. This was prepared by dissolving 5-deuterio-1,3-dibromobenzene (27.6 g, 0.116 mol) in freshly distilled tetrahydrofuran (75 ml) and slowly adding the resulting solution to magnesium metal turnings (2.87 g, 0.116 g-atom). The reaction was quenched with D_2O after refluxing 1 hr and purified by fractional distillation: yield, 13.9 g (75.4%); bp 157° (lit.[13] for bromobenzene 155–156°).

3,5-Dideuteriobenzoic Acid. 3,5-Dideuteriobromobenzene (21.0 g, 0.132 mol) was dissolved in freshly distilled THF (50 ml) and added to magnesium metal turnings (3.3 g, 0.135 g-atom). This mixture was stirred for 45 min after bromobenzene addition was completed and then rapidly poured into a finely ground suspension of fresh Dry Ice in tetrahydrofuran. After warming to room temperature, the crude reaction mixture was washed with 3 *M* HCl and mixed with ether, and the deuterated benzoic acid was extracted into a 10% sodium bicarbonate solution. The volume of the $NaHCO_3$ extract was reduced to 50 ml by heating, and concentrated HCl was added to precipitate 3,5-dideuteriobenzoic acid from solution. The product was recrystallized from hot water with decolorizing carbon present: yield, 7.05 g (43%); mp 118–122° (lit.[13] for benzoic acid 122°).

3,5-Dideuteriobenzamide. 3,5-Dideuteriobenzoic acid (1.01 g, 8.0 mmol) was dissolved in thionyl chloride (15.0 ml) and refluxed for 30 min. Excess $SOCl_2$ was removed from the reaction flask by distillation. The reaction mixture was then cooled in ice and carefully added to ice-cold, concentrated ammonium hydroxide (40 ml). The amide precipitate was collected on a sintered glass

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[6] T. W. Emsley, T. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1965, p 230.

[7] Reference 6, p 456.

[8] R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).

[9] S. Castellano and A. A. Bothner-By, *ibid.*, **41**, 3863 (1964).

[10] R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970).

[11] R. D. Foust, Jr., and P. C. Ford, *ibid.*, **11**, 899 (1972).

[12] B. Rickborn and F. R. Jensen, *J. Org. Chem.*, **27**, 4608 (1962).

[13] "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.

filter and recrystallized from 95% ethanol: yield, 0.58 g (57%); mp 124–126° (lit.[13] for benzamide 125–126°).

3,5-Dideuteriobenzonitrile. 3,5-Dideuteriobenzamide (0.58 g, 4.7 mmol) was mixed with a phosphorus pentoxide (1.0 g) and placed into a microdistillation apparatus. Benzonitrile began forming immediately after the flask was immersed in a preheated oil bath (*ca.* 250°). A slow stream of argon was used to assist movement of the product through the apparatus to the receiving flask (immersed in Dry Ice–acetone). Reaction was complete in about 15 min. The product was redistilled at reduced pressure before use: yield, 0.235 g (44%); bp 78° (118 mm) [lit.[13] for benzonitrile 190.7° (760 mm)]. The mass spectrum of this product was recorded on a Finnegan 1015 quadrapole mass spectrometer. After correcting for natural isotopic abundances the spectrum showed peaks corresponding to C_7H_5N (0.9%), C_7H_4DN (10.0%), and $C_7H_3D_2N$ (89.1%).

4-Deuteriobromobenzene. 1,4-Dibromobenzene (75.0 g, 0.318 mol) was dissolved in freshly distilled THF (200 ml) and added to magnesium metal turnings (7.8 g, 0.32 g-atom). The reaction was refluxed for 1 hr and then was treated with D_2O (20 ml, 1.1 mol) to give, after work-up, 4-deuteriobromobenzene: yield, 24.7 g (49%); bp 160°.

4-Deuteriobenzoic Acid. Deuteriobromobenzene (24.7 g, 0.157 mol) was dissolved in freshly distilled THF (100 ml) and the resulting solution was added slowly to the magnesium metal turnings (3.90 g, 0.165 mol). After stirring the mixture for 45 min, it was rapidly poured into a finely ground suspension of Dry Ice in tetrahydrofuran. The work-up and purification procedures were those described for 3,5-dideuteriobenzoic acid: yield, 7.1 g (37%); mp 114–119°.

4-Deuteriobenzamide. 4-Deuteriobenzoic acid (0.988 g, 8.04 mmol) was dissolved in freshly distilled thionyl chloride (15 ml) and refluxed for 2 hr. Excess thionyl chloride was then removed by distillation. After cooling, the benzoyl chloride was slowly added to ice-cold concentrated ammonium hydroxide (5.0 ml). The crude amide product was collected on a sintered glass filter and recrystallized from hot water: yield, 0.610 g (61.7%); mp 125–126° (lit.[13] 125–126°).

4-Deuteriobenzonitrile. This was prepared by dehydration of the benzamide as described. 4-Deuteriobenzamide (0.503 g, 3.4 mmol) was mixed with phosphorus pentoxide (1.0 g) to give, after work-up, 4-deuteriobenzonitrile: yield, 0.328 g (65.5%); bp 82° (20 mm).

A mass spectrum of the product, corrected for naturally occurring isotope abundances, showed peaks corresponding to C_7H_5N (3.5%) and C_7H_4DN (96.5%).

Results

The synthesis and spectral properties (electronic and infrared) of the pentaamminerhodium(III) organonitrile complexes, $Rh(NH_3)_5(RCN)^{3+}$, studied here are being reported separately.[11] In brief summary, the ir spectra of the salts of these ions each display a carbon–nitrogen triple bond stretching frequency ν(CN) increased over the free ligand value 50–70 cm^{-1}. Such an increase is commonly observed for organonitriles coordinated through the nitrogen lone pair electrons. The electronic spectra appears to be essentially a simple superposition of the ligand uv absorptions with those d–d bands of the pentaamminerhodium(III) moiety. The synthesis and spectral properties of the pentaammineruthenium(II) complexes of benzonitrile,[10] of acetonitrile,[10] and of acrylonitrile[14] have been reported previously. New complexes prepared for this nmr study are those of propionitrile, of α-methacrylonitrile, and of the three monofluorobenzonitriles (ortho, meta, and para). The ir and electronic spectral properties of each are directly analogous to the above previously described ruthenium(II) complexes.[10,14] Namely, in the ir spectrum of each, ν(CN) is decreased from the respective free ligand value, and metal-to-ligand charge-transfer bands are prominent in the electronic spectrum. The results of some preliminary pmr studies of the ruthenium(II) acrylonitrile complex have been reported.[14]

Proton Magnetic Resonance Spectra. Free Ligands. The pmr spectra of all of the organonitriles studied here were recorded and analyzed under the same conditions (*i.e.*, solvent, concentration, and temperature) used to obtain spectra for the metal complexes. The spectral parameters of the organonitriles, obtained by iterative computer analysis of estimated values, are listed in subsequent tables. All of the analyses compare favorably with accepted literature values[15–17] and were rather straightforward, except for α-methacrylonitrile, where assignment of the chemical shifts of the geminal protons is somewhat ambiguous. The trans coupling constant is usually larger than the cis coupling constant in monosubstituted olefins;[18–20] in this case the higher field geminal proton is coupled more strongly to the CH_3 group, suggesting that it is trans to the α-methyl function. However, Reddy, *et al.*,[15] have shown by deuterium substitution studies that the higher field geminal proton is cis to the methyl group. The assignment of Reddy and coworkers was used in the present work and the changes observed in the pmr spectra of α-methacrylonitrile metal complexes closely parallel those of acrylonitrile, where the chemical shift assignments are less ambiguous.[16] The pmr spectrum of benzonitrile is very complicated, consisting of 110 theoretical transitions, of which 75 have observable intensities.[17] For this reason, two deuterium-substituted compounds (4-deuteriobenzonitrile and 3,5-dideuteriobenzonitrile) were prepared to facilitate the analysis of the pmr spectra of coordinated benzonitriles. The use of deuterated compounds unequivocally established the chemical shifts of the benzonitrile protons and the quality of the pmr spectra of the deuteriobenzonitrile complexes, obtained by decoupling of deuterium, permitted complete analysis of the proton–proton coupling constants of the ring hydrogens. Spectral parameters computed for spectra of the two deuterated benzonitriles were then combined to give a set of parameters for (perhydro) benzonitrile. The spectrum calculated from these values, after a slight correction[21] for deuterium substitution on the chemical shift (*ca.* 1.0 Hz), is a good match with the experimental spectrum.

Acetonitrile and Propionitrile Complexes. Proton magnetic resonance spectra of acetonitrile and propionitrile coordinated to pentaamminerhodium(III) are characterized by a decrease in chemical shielding for all ligand protons (relative to the free ligand) and by spin–spin coupling of ligand protons to the rhodium nucleus (^{103}Rh, $I = {}^1/_2$, 100% abundant[13]). The pmr spectrum of $Rh(NH_3)_5(CH_3CN)^{3+}$ shows a doublet for the methyl group ($J_{Rh-CH_3} = 0.4$ Hz) appearing 0.576 ppm (parts per million equals value in hertz divided by 100 MHz) downfield from the uncoordinated acetonitrile

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(14) P. C. Ford, R. D. Foust, Jr., and R. E. Clarke, *Inorg. Chem.*, **9**, 1933 (1970).

(15) G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **83**, 1300 (1961).

(16) R. T. Hobgood, Jr., R. E. Mayo, and J. H. Goldstein, *J. Chem. Phys.*, **39**, 2501 (1963).

(17) K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **25**, 422 (1968).

(18) M. Karplus, *J. Chem. Phys.*, **30**, 15 (1959).

(19) H. G. Hecht and B. L. Victor, *J. Amer. Chem. Soc.*, **90**, 3333 (1968).

(20) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 278.

(21) A. L. Allred and W. D. Wilk, *Chem. Commun.*, 273 (1969).

Table I. Chemical Shift Data for Pentaammineruthenium(II) and Pentaamminerhodium(III) Complexes of Acetonitrile and Propionitrile in D_2O

Complex or free ligand	Proton	Chemical shift[b]	Difference from free ligand[c]
CH_3CN	$-CH_3$	197.0	
$[(NH_3)_5RuN{\equiv}CCH_3{}^{2+}]^a$	$-CH_3$	240.3	+43.3
$[(NH_3)_5RhN{\equiv}CCH_3{}^{3+}]^a$	$-CH_3$	254.6[d]	+57.6
CH_3CH_2CN	$-CH_2-$	241.3	
	$-CH_3$	120.6	
$[(NH_3)_5RuN{\equiv}CCH_2CH_3{}^{2+}]^a$	$-CH_2-$	282.3	+41.0
	$-CH_3$	125.1	+4.5
$[(NH_3)_5RhN{\equiv}CCH_2CH_3{}^{3+}]^a$	$-CH_2-$	298.1[e]	+56.8
	$-CH_3$	126.4	+5.8

[a] Bromide salt. [b] Frequencies in hertz, downfield from TMS at 100 MHz. [c] In hertz, difference equals chemical shift (complex) − chemical shift (free ligand); a positive value represents a deshielding effect (downfield from free ligand). [d] Doublet, $J_{Rh-CH_3} = 0.4$ Hz. [e] Octet, $J_{Rh-CH_2} = 0.4$ Hz.

(Table I). The downfield shift is expected for coordination to a transition metal cation[22,23] and suggests reduced electron density at the acetonitrile methyl protons after coordination to rhodium(III). The magnitude of the deshielding is similar for the methylene group of coordinated propionitrile (Table I) but much smaller for the methyl protons (0.568 and 0.058 ppm, respectively). This trend is consistent with the interpretation that the deshielding is the result of a σ donation of the nitrile electrons to the 3+ cation. The methylene carbon insulates the methyl carbon from the effects of coordination.

Rhodium–proton spin–spin coupling is observed for the protons of acetonitrile and for the methylene protons of propionitrile ($J_{Rh-H} = 0.4$ Hz in both cases). However, it was not possible to detect any rhodium coupling to the methyl protons of coordinated propionitrile.

Pmr spectra of acetonitrile and propionitrile coordinated to pentaammineruthenium(II) are distinguished by deshielding of the protons relative to the free ligands and by broadening of the proton resonances. The methyl group of $Ru(NH_3)_5(CH_3CN)^{2+}$ appears as a broadened singlet 0.433 ppm downfield from uncoordinated acetonitrile (Table I). The deshielding from ruthenium(II) coordination is less than that observed for the rhodium(III) complexes, a fact consistent with the suggestion that an inductive mechanism is responsible for this effect. The tripositive cation $Rh(NH_3)_5{}^{3+}$ would be expected to perturb the ligand properties more than would the dipositive $Ru(NH_3)_5{}^{2+}$. The methyl protons of propionitrile coordinated to ruthenium(II) are deshielded much less than the methylene protons (0.045 and 0.433 ppm, respectively), which parallels the changes observed for the rhodium(III) complex (Table I).

The broadening of the pmr resonances of ligands coordinated to ruthenium(II) is very likely due to the coupling of various ruthenium nuclei (^{99}Ru, $I = {}^5/_2$, 12.81% abundant; ^{101}Ru, $I = {}^5/_2$, 16.9% abundant[13]) to the protons of the nitrile. The greatest broadening is observed for protons on the carbon directly adjacent to the nitrile group.

Acrylonitrile and α-Methylacrylonitrile. The changes in the pmr spectra of acrylonitrile and α-methacrylonitrile that result from coordination to pentaamminerhodium(III) are similar to those described above for the acetonitrile and propionitrile complexes. Each proton of acrylonitrile is shifted downfield after coordination to rhodium(III) (Table II), the geminal proton cis to the nitrile group showing the greatest change (0.428 ppm). Analogous changes are observed for the geminal protons of α-methacrylonitrile, but the methyl group is deshielded only 0.127 ppm.

Spin–spin coupling is observed between the α proton of acrylonitrile and rhodium ($J_{Rh-H} = 0.32$ Hz). However, no coupling is observed between the methyl group of α-methacrylonitrile and rhodium or to the geminal protons of acrylonitrile. There is some evidence for a weak spin–spin coupling between rhodium and the geminal proton of α-methacrylonitrile cis to the nitrile group, but the coupling can be no larger than 0.15 Hz. This very small coupling is suggested by the fact that a computer simulated spectrum more closely fits the experimental spectrum if ^{103}Rh-geminal coupling is included.

The cis and trans coupling constants of acrylonitrile and α-methacrylonitrile remain unchanged after coordination to pentaamminerhodium(III). The geminal coupling constant decreases significantly in both cases, however.

The changes in the pmr spectra of acrylonitrile derivatives that result from coordination to pentaammineruthenium(II) are summarized in Table II. The hydrogens of groups on the carbon adjacent to the nitrile function of coordinated acrylonitrile appear downfield from their free ligand counterparts. This deshielding is much larger for the proton of acrylonitrile than for the methyl protons of α-methacrylonitrile (0.241 compared to 0.038 ppm) and parallels the changes observed in the nmr spectra of rhodium(III) complexes (see Figure 1).

The geminal protons of acrylonitrile and α-methacrylonitrile coordinated to pentaammineruthenium(II) exhibit a major digression from the trend set by the complexes discussed above. Whereas all protons of ligands coordinated to $[Rh(NH_3)_5]^{3+}$, and of the acetonitrile and propionitrile complexes of ruthenium(II), are deshielded after coordination, the *geminal proton resonances of acrylonitrile complexes of pentaammineruthenium(II) are shifted upfield.* The largest increase in shielding occurs at the proton trans to the nitrile function (0.274 ppm for acrylonitrile and 0.211 ppm for α-methacrylonitrile) indicating an *increase* in the electron density at that position resulting from coordination to $[Ru(NH_3)_5]^{2+}$.

The tendency of ruthenium(II) to *increase* shielding at the geminal carbon and of rhodium(III) to *decrease* the shielding is illustrated by the spectra of the methacrylonitrile complexes (Figure 1). The geminal protons of the pentaammineruthenium(II) complex appear at higher field after coordination in contrast to those of the rhodium(III) complex which are deshielded relative to the free ligand resonances.

The cis and trans coupling constants of the ruthenium(II) coordinated acrylonitriles remain unchanged, a fact also noted for coordination to $[Rh(NH_3)_5]^{3+}$. However, the geminal coupling constants, J_{gem}, of the

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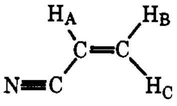
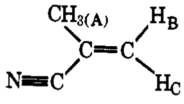
(22) (a) B. Catsikis and M. L. Good, *Inorg. Nucl. Chem. Lett.*, **4**, 529 (1968); (b) *Inorg. Chem.*, **8**, 1095 (1969); (c) *ibid.*, **10**, 1522 (1971).
(23) C. D. Schmulbach and I. Y. Ahmed, *ibid.*, **10**, 1902 (1971).

Table II. Proton Magnetic Resonance Spectral Parameters for the Acrylonitrile and α-Methacrylonitrile Complexes of Pentaammineruthenium(II) and of Pentaamminerhodium(III) in D_2O



Acrylonitrile



α-Methacrylonitrile

Proton or coupling constant	Free ligand	$[(NH_3)_5RuL^{2+}]$[a]	Difference from free ligand[c]	$[(NH_3)_5RhL^{3+}]$[a]	Difference from free ligand[c]
			Acrylonitrile		
H_A	574.0	598.1[b]	+24.1[b]	614.1[b]	+40.1[b]
H_B	612.9	585.5	−27.4	649.6	+36.7
H_C	626.7	610.9	−15.8	669.5	+42.8
J_{AB}	11.62	11.53	−0.09	12.22	+0.60
J_{AC}	17.68	17.61	−0.08	17.85	+0.17
J_{BC}	0.75	0.94	+0.19	0.24	−0.51
$J_{H_A\text{-}Rh}$				0.32	
			α-Methacrylonitrile		
H_A	194.0[b]	197.8[b]	+3.8[b]	206.7[b]	+12.7[b]
H_B	587.6	566.5	−21.1	622.7	+35.1
H_C	590.5	580.6	−9.9	636.4	+45.9
J_{AB}	1.70	1.68	−0.02	1.71	+0.01
J_{AC}	1.25	1.10	−0.15	1.22	−0.03
J_{BC}	0.50	0.75	+0.25	0.16	−0.44

[a] Bromide salt. [b] Frequencies in hertz, downfield from TMS at 100 MHz. [c] Difference equals chemical shift (complex) − chemical shift (free ligand).

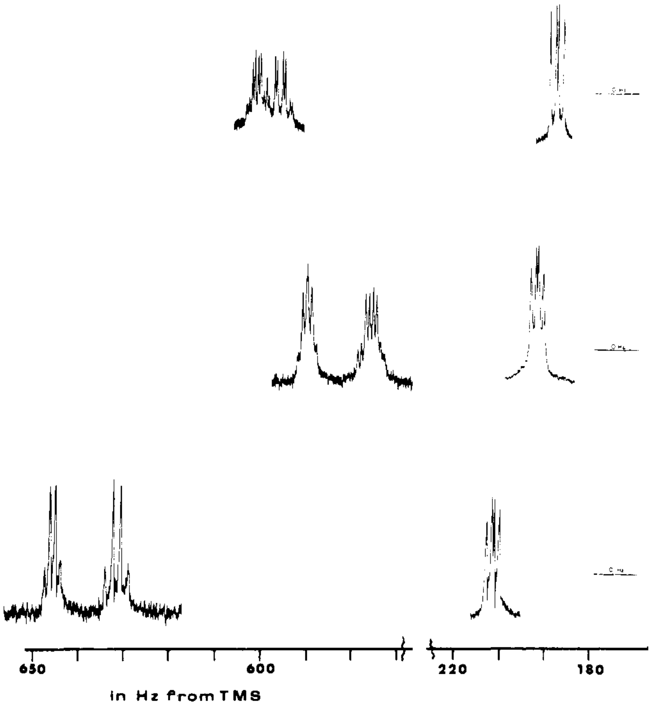


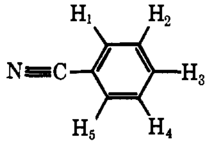
Figure 1. Pmr absorption spectrum of α-methacrylonitrile (top), pentaammine(α-methacrylonitrile)ruthenium(II) bromide (center), and pentaammine(α-methacrylonitrile)rhodium(III) bromide (bottom).

ruthenium(II)-coordinated acrylonitriles increase (Table II) in contrast to the rhodium(III) complexes where a decrease in the value of J_{gem} is observed. The changes in the geminal coupling are responsible for the apparent differences in the splitting pattern of the geminal protons of coordinated α-methacrylonitrile. The pmr resonance of the geminal protons consists of 16 lines (Figure 1) that arise from coupling to the methyl group (J = 1.25 and 1.70 Hz), affording a pair of quartets. The quartets are then split into octets by geminal coupling (J = 0.50 Hz). The spectrum of α-methacrylonitrile coordinated to ruthenium(II) consists of an octet and a quintet. The quintet arises from three upper field lines of a quartet overlapping with three lower field lines of another quartet. The two sets of quartets overlap in this manner because the geminal coupling constant is 0.75 Hz, exactly half the value of the coupling to the methyl group. A decrease in the value of J_{gem} for α-methacrylonitrile coordinated to rhodium(III) causes the two octets to appear as quartets.

Benzonitrile Complexes. Coordination to pentaamminerhodium(III) leads to proton deshielding relative to the free ligand at each position of this aromatic ring (Table III). The chemical shift difference is greatest for the ortho protons (0.332 ppm), half as large at the para position (0.158 ppm), and quite small for the meta resonance (0.046 ppm). None of the proton–proton coupling constants are perturbed by coordination to rhodium(III), and no ^{103}Rh–^{1}H coupling is observed.

Coordination of benzonitrile to pentaammineruthenium(II) results in a major redistribution of the electron density in the aromatic ring, as it evidenced by comparison of the pmr spectra of 3,5-dideuteriobenzonitrile and 4-deuteriobenzonitrile with the spectra of the coordinated compounds (see Figures 2 and 3 and Table III). The ortho and para proton resonances of benzonitrile have very similar chemical shifts, as shown in the spectrum of 3,5-dideuteriobenzonitrile (Figure 2). However, coordination of 3,5-dideuteriobenzonitrile to ruthenium(II) separates the ortho and para signals by moving the para proton resonance to a higher field (an *increase* in chemical shielding of 0.13 ppm), while the ortho proton absorptions are shifted downfield 0.055 ppm. As a comparison, the spectrum of 3,5-dideuteriobenzonitrile complexed to rhodium(III) is shown at the bottom of Figure 2, where the overall deshielding of the aromatic ring protons caused by coordination to rhodium(III) can be seen.

Table III. Proton Magnetic Resonance Spectral Parameters for the Benzonitrile Complexes of Pentaammineruthenium(II) and of Pentaamminerhodium(III)[a,b]



Proton or coupling constant	Free ligand	$[Ru(NH_3)_5L]^{3+}$ [c]	Difference from free ligand[e]	$[Rh(NH_3)_5Li]^{3+}$ [c]	Difference from free ligand[e]
H_1, H_5	775.5[d]	780.5[d]	+5.5[d]	808.2[d]	+33.2[d]
H_2, H_4	757.7	751.5	−6.2	762.3	+4.6
H_3	771.0	758.0	−13.0	786.8	+15.8
$J_{1,2} = J_{4,5}$	7.66	7.84	+0.18	7.81	+0.15
$J_{1,3} = J_{3,5}$	1.35	1.35	0.0	1.35	0.0
$J_{1,4} = J_{2,5}$	0.63	0.78	+0.15	0.63	0.0
$J_{1,5}$	1.78	1.78	0.0	1.76	−0.02
$J_{2,4}$	1.29	1.17	−0.12	1.23	−0.06

[a] Computer calculated values based upon spectra of the 4-deuteriobenzonitrile and of the 3,5-dideuteriobenzonitrile complexes. [b] All spectra were run in 33% *N,N*-dimethylacetamide–D_2O. [c] Bromide salt. [d] Frequencies in hertz, chemical shift values are downfield from TMS at 100 MHz. [e] Difference equals chemical shift (complex) − chemical shift (free ligand).

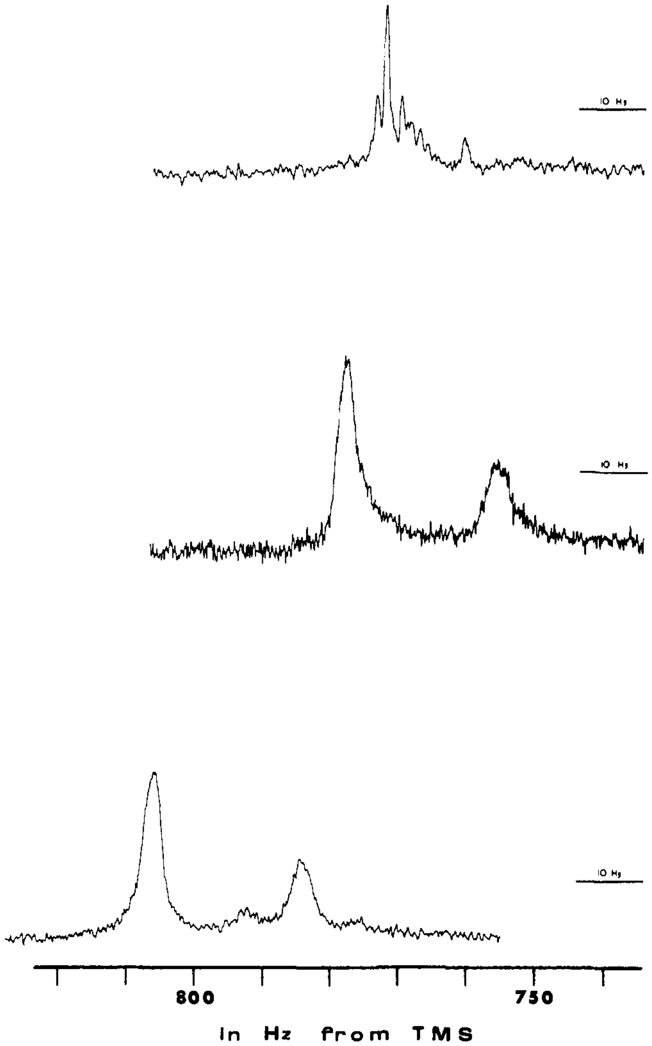


Figure 2. Deuterium decoupled pmr spectrum of 3,5-dideuteriobenzonitrile (top), pentaammine(3,5-dideuteriobenzonitrile)-ruthenium(II) bromide (center), and pentaammine(3,5-dideuteriobenzonitrile)rhodium(III) bromide (bottom).

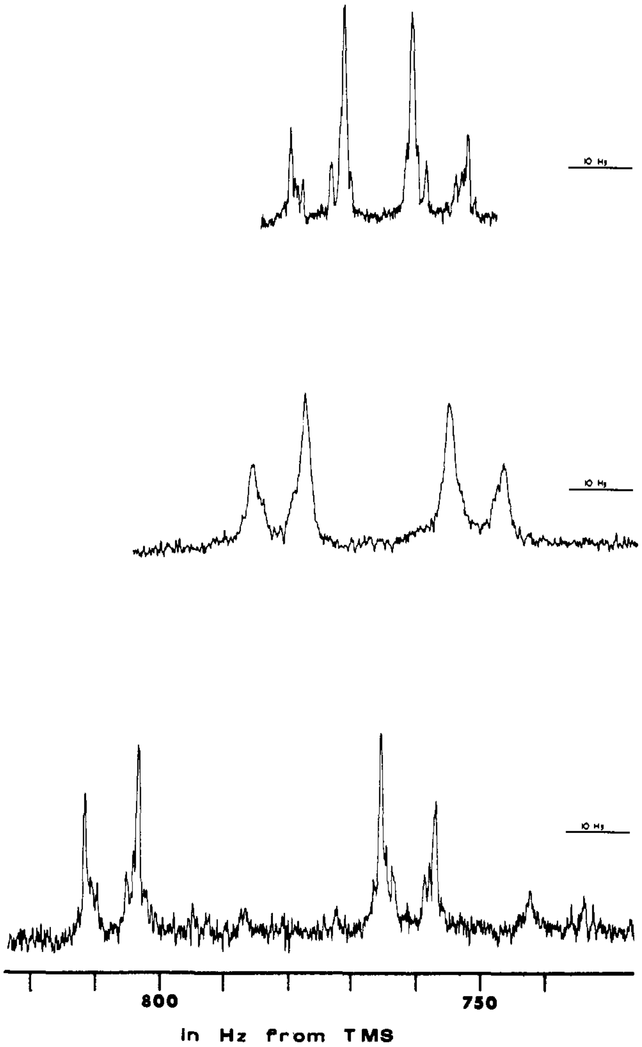
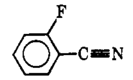
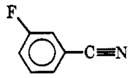
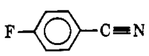


Figure 3. Deuterium decoupled pmr absorption spectrum of 4-deuteriobenzonitrile (top), pentaammine(4-deuteriobenzonitrile)-ruthenium(II) bromide (center), and pentaammine(4-deuteriobenzonitrile)rhodium(III) bromide (bottom).

The effect of coordination to ruthenium(II) on the benzonitrile meta protons can be determined from the 4-deuteriobenzonitrile spectrum (Figure 3). The pmr spectrum of 4-deuteriobenzonitrile is an AA′BB′ type, the meta proton resonances appearing at a higher field than the ortho proton absorptions. Coordination to

Table IV. Fluorine-19 Chemical Shift Data for Fluorobenzonitrile Complexes of Pentaamminerhodium(III) and of Pentaammineruthenium(II)[a]

L	Free ligand[c]	$(NH_3)_5RhL^{2+}$ [b,c]	Difference from free ligand[d]	$(NH_3)_5RuL^{2+}$ [b,c]	Difference from free ligand[c,d]
	2788.1	2395.9	−392.2	2867.0	+78.9
	3015.7	2929.0	−86.7	3086.5	+70.8
	2264.5	1817.7	−446.8	2489.1	+224.6

[a] All spectra were run in 33% *N*,*N*-dimethylacetamide-deuterium oxide. [b] Bromide salt. [c] Chemical shift reported in hertz, upfield from an external capillary of trifluoroacetic acid, at 94.1 MHz. [d] Note that for the fluorine chemical shifts, which are relative to the internal lock of trifluoroacetic acid, a positive chemical shift charge is shielding (upfield from free ligand) and a negative chemical shift charge is deshielding (downfield).

ruthenium(II) increases the shielding at the meta position 0.062 ppm while the ortho protons are deshielded relative to the uncoordinated ligand. The rhodium(III) complex, shown for comparison, exhibits deshielding at both the ortho and meta positions.

Analysis of the nmr spectrum of benzonitrile coordinated to ruthenium(II) shows that the spin–spin coupling constants between protons on the aromatic ring are unaffected by coordination within experimental error (see Table III). The upfield shifts of the meta and para proton absorptions are not as large as those seen for the geminal protons of ruthenium(II) acrylonitrile complexes.

Fluorine Magnetic Resonance Spectra. Fluorobenzonitrile Complexes. The ^{19}F chemical shift data for the *o*-, *m*-, and *p*-fluorobenzonitrile complexes of pentaamminerhodium(III) are summarized in Table IV. The fluorine resonance is shifted downfield for each of the fluorobenzonitrile rhodium(III) complexes relative to the free ligand values (Table IV). The largest deshielding occurs for the ortho and para isomers of fluorobenzonitrile (4.16 and 4.74 ppm, respectively; parts per million for fluorine frequencies equals value in hertz divided by 94.1 MHz). The *m*-fluorobenzonitrile fluorine resonance is shifted downfield 0.92 ppm after coordination to $[Rh(NH_3)_5]^{3+}$.

The chemical shift data for the fluorobenzonitrile complexes of pentaammineruthenium(II) are given in Table IV. Relative to the free ligand values, shielding is increased for the fluorine-19 resonance at each position in the ring, the largest increase coming at the para position (+2.39 ppm).

Discussion

The results from the nuclear magnetic resonance (nmr) study of organonitriles coordinated to pentaammineruthenium(II) or to pentaamminerhodium(III) are summarized in Tables I–IV. The proton chemical shift differences of coordinated *vs.* free ligands are not large (less than 0.60 ppm) but definite trends in the magnitude and direction of these effects are evident. The proton resonances of saturated organonitriles coordinated to either $Rh(NH_3)_5^{3+}$ or to $Ru(NH_3)_5^{2+}$ appear downfield from their free ligand values. Deshielding is greater for coordination of these organonitriles to rhodium(III) than to ruthenium(II) (0.576 and 0.433 ppm for $Rh(NH_3)_5(CH_3CN)^{3+}$ and $Ru(NH_3)_5(CH_3CN)^{2+}$, respectively). Unsaturated ligands show decreased shielding at all positions after coordination to rhodium(III) and for protons adjacent to the nitrile in ruthenium(II) complexes. The para and meta protons of benzonitrile and the geminal protons of acrylonitrile and α-methacrylonitrile show *increased* shielding (0.062–0.274 ppm) when these unsaturated ligands are coordinated to pentaammineruthenium(II). The ^{19}F nmr results for the *o*-, *m*-, and *p*-fluorobenzonitrile complexes of $Rh(NH_3)_5^{3+}$ and $Ru(NH_3)_5^{2+}$ parallel the proton magnetic resonance studies. These data are interpreted as indicating that changes in the nmr chemical shifts of the compounds studied are related to changes of the electron density distributions in these compounds. A discussion of the validity of this interpretation follows.

Studies of the proton magnetic resonance of substituted hydrocarbons have demonstrated a correlation between the electronegativity of the substituent and the observed chemical shifts of the paraffin protons. This correlation has been offered as evidence for a linear relationship between the chemical shift and the electron density of the nucleus under investigation.[24–26] Spiesecke and Schneider[27] have shown a correlation between the chemical shifts of the para protons of substituted benzenes and the Hammett σ_p constants of the substituents, implying a relationship to π-electron density. Hückel molecular orbital calculations (HMO) by Wu and Dailey[28] verified the relationship between π-electron density and the chemical shift of para protons of monosubstituted benzenes and demonstrated a similar relationship for the ortho protons of several phenyl derivatives. However, the meta proton chemical shifts of substituted benzenes could not be correlated to changes in π-electron density at the meta carbon, nor could the ortho protons of halogenated benzenes be related to π-electron density.

In more recent work, Figeys and Flammang[29] have revised the calculations of Wu and Dailey to give a better correlation between the calculated and experimental shifts of para protons on aromatic rings, and

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(24) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(25) A. L. Allred and E. G. Rochow, *J. Amer. Chem. Soc.*, **79**, 5361 (1957).

(26) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1009 (1961).

(27) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 731 (1961).

(28) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796 (1964).

(29) H. P. Figeys and R. Flammang, *Mol. Phys.*, **12**, 581 (1967).

Schug[30] has been able to account for the chemical shifts of the meta protons in phenyl rings on a qualitative basis using modified Hückel MO calculations. The dependence of the proton chemical shift on electron density at the nucleus under investigation, for both saturated and aromatic systems, is thus well established, and chemical shifts may justifiably be used to measure changes of electron density within a limited set of analogous examples.

If the relatively small chemical shift differences resulting from coordination of the organonitrile is to be used to assess electron density perturbation in these ligands, other factors which may affect the proton shielding must be considered. Some of these are (1) solution effects[31] resulting either from specific solvent substrate interactions or from changes in substrate concentration, (2) changes in the magnetic anisotropy of the CN group, (3) the paramagnetic anisotropy resulting from the temperature-independent paramagnetic moment of the metal atom, (4) possible anisotropic effects in the metal–ligand bond, and (5) interaction of the ligand protons with the nuclear quadrupole of the metal nucleus. Point 1 can be largely discounted, since solvent effects were minimized in this study by comparing only the spectral parameters obtained from compounds dissolved in the same solvent. In addition, dilution studies were run on all compounds reported in this work, but the "corrected" chemical shifts were, within experimental error, identical with the uncorrected values. Point 2: the anisotropic shielding associated with the nitrile triple bond arises from the flow of electrons in a "loop" around the CN bond axis. The circulating π electrons generate an induced magnetic field which opposes the external magnetic field of the spectrometer, causing protons in the vicinity of the triple bond to appear more "shielded" than protons away from the induced magnetic field. Reddy, Goldstein, and Mandell[15] have shown that the anomalous chemical shifts of the protons of acrylonitrile are caused by a diamagnetic anisotropic contribution to the proton chemical shielding from the nitrile group. These workers were able to calculate "corrected" chemical shifts for the acrylonitrile protons using the point–dipole approximation.[32,33] The shielding contribution to the chemical shift for protons near the nitrile triple bond would then be

$$\Delta\sigma = (1/3)R^{-3}\Delta\chi(3\cos^2\theta - 1) \qquad (3)$$

where $\Delta\chi$ is the anisotropy in the molecular magnetic susceptibility of the nitrile group measured along the C–N bond axis, θ is the angle between the C–N bond axis and a line drawn from the center of the C–N bond and the proton under consideration, and R is the distance between the center of the nitrile group and the proton. These workers showed that the proton resonances of acrylonitrile would be located 0.288 to 1.13 ppm further downfield than observed in the absence of diamagnetic anisotropic shielding. Clearly, perturbation of the diamagnetic anisotropy of the nitrile triple bond might be expected to change the chemical shift of the organonitrile protons.

The anisotropic shielding due to the nitrile function may be perturbed upon coordination to a transition metal by moving the electron "loop" that surrounds the triple bond along the C–N bond axis or by retarding the flow of electrons through the loop. Either perturbation would be expected to effect all of the organonitrile protons in the same way. However, for the pentaammineruthenium(II) complexes, the pmr resonances of the methyl protons of coordinated propionitrile are shifted downfield 0.058 ppm from the free ligand value while the geminal proton resonances of acrylonitrile show increased shielding of 0.274 and 0.158 ppm after coordination. The propionitrile methyl protons and the acrylonitrile geminal protons are in similar spatial environments in relation of the nitrile group. Consequently, the opposite direction of the shifts observed for the protons of propionitrile and of acrylonitrile argues against a change in the nitrile group's anisotropic shielding as being solely responsible for these coordination effects.

Point 3: magnetic susceptibility studies[34] of d^6 transition metal ions have shown that the spin-paired complexes are not diamagnetic as expected but have small paramagnetic moments of 0.2–0.4 BM, apparently a result of mixing of the spin-paired electronic ground state with low-lying excited states.[32] Paramagnetic contributions have large effects on the chemical shielding,[35] and these should be considered when interpreting the nmr spectra of d^6 complexes.

The temperature-independent paramagnetism of ruthenium(II) and rhodium(III) has been used to rationalize[36] the very high field proton chemical shifts ($\tau \sim 17.0$–20.0 ppm) observed for rhodium and ruthenium hydride complexes. Buckingham and Stephens[36] demonstrated that the paramagnetic contributions from low-spin d^6 metals to the chemical shielding of ligand protons is a function of R^{-3} where R is the distance from the metal atom. Thus, paramagnetism is the dominating factor in the chemical shielding of metal hydrides (M–H bond length $\simeq$2.0 Å), but the effect falls off very rapidly with increasing distance from the metal atom. Bramley, *et al.*,[33] have observed the ^{14}N magnetic resonance spectra of hexaamminerhodium(III) chloride and hexaammineruthenium(II) chloride. These workers have shown that the small paramagnetism of ruthenium(II) and rhodium(III) leads to upfield shifts in the nitrogen resonances. In contrast, the chemical shifts of *all* protons adjacent to the nitrile function of coordinated organonitriles reported in this study were *deshielded* relative to the free ligand resonances, a fact which demonstrates that paramagnetic contributions to the chemical shifts of the organonitrile protons are more than counterbalanced by other effects.

Point 4: a nitrile group coordinated to a metal atom can form a weak "triple" bond by the overlap of two sets of metal d orbitals, in perpendicular planes, with the nitrile antibonding orbitals. The diamagnetic anisotropy associated with the d–π^* triple bond could then shield protons on the organonitrile, causing an upfield shift in the observed resonance of the ligand

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[30] J. C. Schug, *J. Chem. Phys.*, **46**, 2447 (1967).

[31] Reference 20, p 104.

[32] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

[33] R. Bramley, B. N. Figgis, and R. S. Nyholm, *J. Chem. Soc. A*, 861 (1967).

[34] (a) B. Cabrera, *Atti Congr. Int. Fis.*, **95** (1927); (b) D. M. Bose, *Z. Phys.*, **48**, 716 (1928); (c) A. N. Guthrie and L. T. Bourlard, *Phys. Rev.*, **37**, 303 (1931).

[35] N. F. Ramsey, *ibid.*, **78**, 699 (1950).

[36] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747 (1964).

protons after coordination to the metal. However, this can be at most a very small factor in the chemical shifts of coordinated organonitrile protons since the resonances of protons on carbons directly adjacent to the coordinated nitrile all appear downfield from the free ligand values.

Point 5: broadening of nmr signals is seen for the resonances of nuclei having strong interactions with atoms which have nuclear quadrupole moments. For example, double resonance experiments have shown that the ortho proton resonances in the pmr spectrum of pyridine are considerably broadened by coupling to the ^{14}N nuclear quadrupole.[37] Two ruthenium nuclei (^{99}Ru and ^{101}Ru, total natural abundance = 29.8%) have nuclear quadrupole moments although the quadrupole magnitudes have not been measured.[38] Lavallee and Fleischer[39] have studied the nmr properties of pyridine coordinated to pentaammineruthenium(II) and have observed that the intensity of the ortho proton resonance decreases about 30%, relative to the meta and para protons. The loss in signal intensity for the pyridine ortho protons was attributed to coupling between the ortho protons and the nuclei of ^{99}Ru and ^{101}Ru to give sextuplets, which are broadened beyond recognition by the nuclear quadrupoles of ruthenium and of the pyridine nitrogen. However, these workers did not detect any interaction between the nuclear quadrupoles of ruthenium nuclei and the meta or para protons of coordinated pyridine. Since none of the organonitriles examined in this work contained protons any closer to the ruthenium atom than the meta proton of pyridine, it is unlikely that the ruthenium quadrupoles affected the pmr spectra markedly.

Acetonitrile and Propionitrile Complexes. The methyl pmr absorption of coordinated acetonitrile appears downfield from the uncoordinated acetonitrile resonance in both pentaammineruthenium(II) and pentaamminerhodium(III) complexes (Table I). The downfield shift of the acetonitrile resonance is larger for the rhodium(III) complex (0.576 ppm) than for the ruthenium(II) complex (0.433 ppm) and indicates that there is less electron density at the acetonitrile protons after coordination to the metal. Similar deshielding of about 0.6 ppm has previously been noted[40] for other rhodium(III) acetonitrile complexes of the type $RhX_n(CH_3CN)_{6-n}{}^{(n-3)-}$ where X is Cl^- or Br^- and n is 4, 5, or 6. In these cases, however, ^{103}Rh–methyl group proton spin–spin coupling was not reported (Table I). The decreased shielding of the methyl protons on coordination of CH_3CN to Ru(II) or Rh(III) potentially may be attributable either to a perturbation of the diamagnetic anisotropy of the nitrile group or to an inductive mechanism decreasing the electron density at the methyl carbon. Either mechanism is consistent with the observation that the more highly charged $Rh(NH_3)_5{}^{3+}$ leads to greater deshielding (0.576 ppm) than does $Ru(NH_3)_5{}^{2+}$ (0.433 ppm). Both are also consistent with the spectral results for the propionitrile complexes where the deshielding of the methylene hydrogens relative to the free ligand is of a magnitude (0.568 and 0.410 ppm for the Rh(III) and Ru(II) complexes, respectively) comparable to those observed for acetonitrile while the deshielding of the methyl hydrogens, one bond further removed, is an order of magnitude less (0.058 and 0.045 ppm for the Rh(III) and Ru(II) complexes, respectively). Since, according to the point-dipole model (above), the diamagnetic anisotropic effect of the nitrile group falls off as a function of R^{-3} (where R is the distance from the nitrile to the proton) the result of any perturbation would also fall off with distance in a comparable manner. However, the proton deshielding of the acrylonitrile- and benzonitrile–rhodium(III) complexes does not fall off comparably with distance (Tables II and III, and below), a fact which suggests that perturbation of the nitrile group's diamagnetic anisotropy is not the principal deshielding mechanism at work.

The inductive mechanism which acts by coordination of the nitrile nitrogen lone electron pair and subsequent electron-withdrawing polarization of σ bonds is also consistent with the propionitrile complex data. The small deshielding of the methyl protons results from the rather low polarization of a sp^3 carbon,[41] *i.e.*, the methylene group, hence insulating the methyl group from the inductive electron withdrawal.

Acrylonitrile and α-Methylacrylonitrile Complexes. The protons adjacent to the nitrile function in the acrylonitrile complexes and of the α-methyl groups in the α-methacrylonitrile complexes are deshielded relative to their uncoordinated resonance (Table II). The deshielding is greater for the rhodium(III) compounds (0.401 ppm for acrylonitrile and 0.127 ppm for the α-methacrylonitrile methyl group) than for the corresponding ruthenium(II) compounds (0.241 ppm for acrylonitrile and 0.038 ppm for the α-methacrylonitrile methyl group). These changes parallel those observed in the corresponding acetonitrile and propionitrile complexes where an inductive mechanism was credited with decreasing electron density at positions adjacent to the coordinated nitrile group (*vide supra*).

Although a sp^2 hybridized carbon atom transmits inductive effects more efficiently than does a sp^3 hybridized carbon,[41] the inductive polarization of σ bonds alone cannot account for the magnitude of the deshielding observed for the geminal proton resonances of the acrylonitrile and α-methacrylonitrile complexes of rhodium(III) (0.351 and 0.459 ppm for $Rh(NH_3)_5(\alpha\text{-methacrylonitrile})^{3+}$). For example, the methyl protons of α-methacrylonitrile which occupy a similar spacial environment to the geminal protons are deshielded only 0.127 ppm. The greater deshielding of the geminal protons is very likely the result of π-bond polarization, *i.e.*, a resonance redistribution of the occupied π orbitals resulting in deshielding of the geminal protons of acrylonitrile coordinated to rhodium(III).

The geminal proton resonance from acrylonitrile and α-methacrylonitrile coordinated to pentaammineruthenium(II) is shifted upfield (shielded) relative to the free ligands, *indicating an increase in electron density at the geminal carbon after coordination.* Notably, for the

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(37) J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

(38) (a) E. H. Carlson, *Phys. Lett. A*, **29**, 696 (1969); (b) P. Machmer, *Z. Naturforsch., B*, **24**, 193 (1969).

(39) D. K. Lavallee and E. B. Fleischer, *J. Amer. Chem. Soc.*, **94**, 2583 (1972).

(40) (a) B. F. G. Johnson and R. A. Walton, *J. Inorg. Nucl. Chem.*, **28**, 1901 (1966); (b) B. D. Catsikis and M. L. Good, *Inorg. Chem.*, **8**, 1095 (1969); (c) B. D. Catsikis and M. L. Good, *ibid.*, **10**, 1522 (1971).

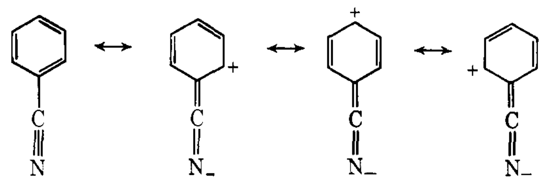
(41) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt Rinehart and Winston, New York, N. Y., 1959, p 212.

same complexes deshielding is observed for the α hydrogen of Ru(II)-coordinated acrylonitrile and for the methyl hydrogens of Ru(II)-coordinated α-methacrylonitrile (Table II). Consequently, an electron-withdrawing inductive mechanism is still operable in these Ru(II) complexes, but another effect must be superimposed to lead to shielding of the geminal position.

We interpret this shielding as being the result of d_π–p_π back-bonding involving delocalization of electron density from the ruthenium(II) into unfilled π (antibonding) orbitals of the unsaturated ligand. Such back-bonding is undoubtedly responsible for the decreases in the nitrile stretching frequencies ν(CN) (above) observed[14] for these ligands. That such geminal proton shielding effects are not the result simply of back-bonding repolarization of the nitrile group is apparent when one considers that (1) the α proton of the acrylonitrile complex and the methyl protons of the α-methacrylonitrile complex are deshielded and (2) all protons of the Ru(II) acetonitrile and propionitrile complexes are deshielded, despite the fact that in these complexes ν(CN) decreases are also observed.[10]

Spin–spin coupling constants of substituted olefins are a function of the substituents on the alkene[42] and of the intramolecular bond angles between the protons.[43] The cis and trans coupling constants of the metal complexes of acrylonitrile and α-methacrylonitrile were (within experimental error) identical with the coupling constants of the free ligands (Table II). In contrast, the geminal coupling constants J_{gem} are perturbed by coordination, with J_{gem} values for the $Ru(NH_3)_5{}^{2+}$ complexes greater than the free ligand values and J_{gem} for the $Rh(NH_3)_5{}^{3+}$ complexes smaller. The fact that J_{cis} and J_{trans} are little changed by coordination suggests that there has been no major change in the geometry of the protons with respect to each other. Electron-withdrawing substituents (X) on vinyl compounds ($XCH{=}CH_2$) decrease J_{gem} while electron-donating substituents increase J_{gem}, an observation suggesting that J_{gem} is related to the electron density of the methylene carbon.[42] It is an interesting correlation that J_{gem} *increases* for the acrylonitrile and α-methacrylonitrile complexes of $Ru(NH_3)_5{}^{2+}$, complexes for which increased shielding relative to the free ligands is observed for the geminal hydrogen chemical shifts. Similarly, a J_{gem} *decrease* and deshielding are both noted for the rhodium(III) complexes.

Benzonitrile Complexes. The chemical shift data for the $Ru(NH_3)_5{}^{2+}$ and $Rh(NH_3)_5{}^{3+}$ complexes of benzonitrile qualitatively parallel the observations for the acrylonitrile and α-methacrylonitrile complexes. The aromatic ring protons of the rhodium(III) complex are each deshielded relative to free benzonitrile (Table III). The ortho protons of the ruthenium(II) complex are deshielded somewhat but the chemical shifts of the meta and para protons are observed to be upfield from the free ligand values. For $Rh(NH_3)_5(C_6H_5CN)^{3+}$, deshielding is greatest at the ortho (0.332 ppm) and para (0.158 ppm) positions and relatively small for the meta protons (0.046 ppm). These data can be explained on the basis of two superimposed effects: an electron-withdrawing inductive mechanism and a π-orbital (bonding) polarization of the type suggested by the mesomers.



The ortho position being closest to the coordination site feels the brunt of the inductive effect as well as a major contribution from the π polarization. The meta position apparently is affected largely by the inductive mechanism which is somewhat weakened by the greater distance from the coordination site, while the major contribution to the deshielding of the para hydrogen must be from the π-polarization mechanism.

The pmr data from benzonitrile coordinated to pentaammineruthenium(II) shows that the ortho protons are deshielded in the metal complex (0.055 ppm) in contrast to the meta and para protons which appear upfield from the free ligand values (0.062 and 0.130 ppm, respectively). The chemical shift changes for the coordinated benzonitrile protons can be interpreted to reflect overall changes in electron density owing to competitive π back-bonding from the metal ion and inductive polarization toward the metal ion. The inductive effect decreases with distance from the coordination site, while the increase in electron density from π back-bonding is expected to be greatest at the para position of the coordinated benzonitrile (*vide infra*). A combination of these competitive effects rationalize the observed proton chemical shift changes. The deshielding of the ortho protons is probably due to the inductive effect being only partially counterbalanced by metal-to-ligand π back-bonding. The shielding of the meta and para protons indicates that the enhanced electron density at these sites from back-bonding overwhelms the weak inductive effects. Lavallee and Fleischer[39] have attempted to observe similar effects for the coordinated pyridine of $Ru(NH_3)_5py^{2+}$; however, these workers determined that the *m*- and *p*-pyridine protons were deshielded relative to uncoordinated pyridine. Apparently, in this case, the inductive effect on the nmr parameters was greater than any back-bonding contribution. Our success with the unsaturated organonitriles may be because the sites showing π back-bonding induced increased shielding for the benzonitriles are further from the coordination site. (The para position of pyridine is equivalent to the ortho position of benzonitrile in distance from the coordination site.)

Presumably the metal-to-ligand π back-bonding involves interaction between the d_π metal orbitals and the lowest unfilled π-symmetry (antibonding) ligand orbital. The character of this orbital is illustrated by the spin density distribution for the benzonitrile radical anion (Table V). The LCAO-MO calculated spin densities from the two methods employed (Hückel and SCF) are in good agreement with one another, and the predictions have been verified by epr studies.[44] Examination of

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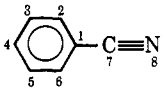
[42] C. N. Banwell and N. Sheppard, *Discuss. Faraday Soc*, 34, 115 (1962); (b) T. Schaefer, *Can. J. Chem.*, 40, 1 (1962); (c) N. Sheppard and C. N. Banwell, *Proc. Roy. Soc., Ser. A*, 263, 136 (1961); (d) W. W. Lee, A. Benitez, C. D. Anderson, L. Goodman, and B. R. Baker, *J. Amer. Chem. Soc.*, 83, 1906 (1961).

[43] (a) H. S. Gutowsky and A. L. Porte, *J. Chem. Phys.*, 35, 839 (1961); (b) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, 31, 1278 (1959).

[44] A. Carrington and P. F. Todd, *Mol. Phys.*, 6, 161 (1963).

Table V. Calculated LCAO–MO Spin Densities in the Benzonitrile Radical Anion



Position	—Spin densities, P_i^{π}— Hückel[a]	SCF[b]	Back-bonding contribution to the chemical shift[c]
4	0.2515	0.2450	−0.235
3,5	0.0419	0.0444	−0.093
2,6	0.1119	0.1067	−0.167
1	0.2282	0.2508	
7	0.0962	0.0615	
8	0.1166	0.1423	

[a] P. H. Reiger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962). [b] T. E. Peacock and P. T. Wilkinson, *Proc. Phys. Soc.*, 79, 105 (1962). [c] In parts per million, for the complex $Ru(NH_3)_5(C_6H_5CN)^{2+}$. Calculation described in text.

Table V shows that the increase in electron density at the para position of benzonitrile is six times larger than the increase in electron density at the meta position when an electron is placed into the lowest unfilled orbital of benzonitrile. Qualitatively, the observation that the coordination of benzonitrile to ruthenium(II) leads to a greater upfield shift of the para proton than of the meta proton suggests that this ligand orbital is involved. Unfortunately the opposing deshielding effects cloud the question. However, an artificial way to separate the relative contributions of the shielding and deshielding mechanisms is to assume that pentaamminerhodium(III) does not participate meaningfully in any back-bonding. This latter assumption is supported by the fact that $Rh(NH_3)_5^{3+}$ complexes of the various organonitriles all show substantial *increases* in the CN triple bond stretching frequencies.[11] A second assumption would be that deshielding contributions from coordination to $Ru(NH_3)_5^{2+}$ in the absence of back-bonding is equal to two-thirds (*i.e.*, the ratio of the cationic charges) the deshielding resulting from coordination to $Rh(NH_3)_5^{3+}$. The back-bonding contribution then would be equal to the difference between the observed proton resonances and the "expected" resonance for a deshielding mechanism only. The validity of the second assumption can be examined by comparing the extent of deshielding of the acetonitrile and propionitrile complexes (Table I) where coordination to ruthenium(II) led to deshielding approximately 70% that resulting from coordination to rhodium(III). The back-bonding contributions calculated on the basis of the two assumptions are listed for the Ru(II) benzonitrile complex in Table V. Comparison to the spin densities calculated for the benzonitrile radical anion shows a good qualitative correlation.

Fluorobenzonitrile Complexes. Fluorine nmr has proved to be a valuable and sensitive tool for the investigation of the electronic character of aromatic rings.[45,46] Parshall,[46] for example, has examined the inductive and resonance interactions between fluorophenyl derivations and platinum(II) in complexes of the type *m*- or *p*-$FC_6H_4PtX(PEt_3)_2$. In these studies, he noted that the group $-PtX(PEt_3)_2$, when bound to fluorobenzene, is an electron donor in both the resonance and inductive senses. There was also a strong dependence of the ^{19}F shielding parameter on the nature of X. Examination of Parshall's data shows that $PtX(PEt_3)_2$ is an electron donor (*i.e.*, it is shielding) when compared to a hydrogen atom occupying that position in fluorobenzene, not when compared to the free ligand, the anion $FC_6H_4^-$. In contrast, the $Ru(NH_3)_5^{2+}$ complexes of the fluorobenzonitriles show resonances shielded in comparison to the free ligands.

An *increase in electron density* at the fluorine nucleus is observed for all of the fluorobenzonitrile complexes of pentaammineruthenium(II) in contrast to the *decreased electron density* that is seen for each of the fluorobenzonitrile complexes of $[Rh(NH_3)_5]^{3+}$ (Table IV). The chemical shift changes are larger than those observed for the protons of coordinated benzonitrile, which is expected for fluorine magnetic resonance studies.[47] The increased shielding for the ruthenium(II) complexes can be attributed to metal-to-ligand π back-bonding (*vide supra*). The deshielding observed for the rhodium(III) compounds is most likely due to the inductive and resonance redistribution of the phenyl electron density toward the coordination site (*vide supra*).

The fluorine-19 resonance of *o*-fluorobenzonitrile coordinated to pentaammineruthenium(II) occurs at a higher field than for the free ligand, in contrast to the ortho proton resonance of coordinated benzonitrile where deshielding is seen. This apparent discrepancy can be explained by differences in the electronic structure and electronegativity of the fluorine and hydrogen nuclei. Fluorine is more electronegative than hydrogen and contains a p orbital capable of overlapping with the aromatic π system. Thus any perturbation of the electron density in the π system of benzonitrile can be directly felt at the fluorine nucleus, while a proton on the benzonitrile ring reflects changes of π-electron density by more indirect means. In addition, the symmetry of the lowest unoccupied molecular orbital of fluorobenzonitrile changes with the position of the fluorine substitution on the aromatic ring. An increase in electron density at the nitrile group may then be directed toward the ortho position in *o*-fluorobenzonitrile instead of toward the para position (as predicted from consideration of the symmetry of the lowest excited molecular orbital of nonfluorinated benzonitrile).

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(45) M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 283 (1969).

(46) G. W. Parshall, *ibid.*, **88**, 704 (1966).

(47) Reference 6, Chapter 11.