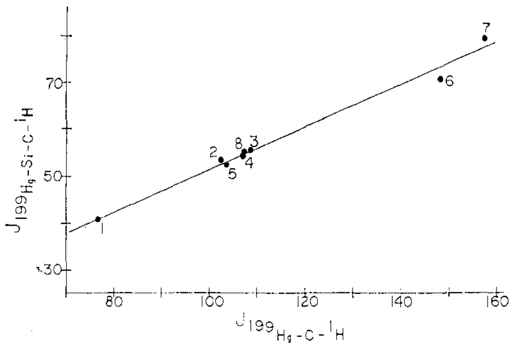

Figure 1.—Plot of $J_{^{199}Hg-Si-C-^1H}$ in $(CH_3)_3SiHgR$ *vs.* $J_{^{199}Hg-C-^1H}$ in CH_3HgR. R = (1) trimethylsilyl, (2) methyl, (3) phenyl, (4) vinyl, (5) cyclopropyl, (6) 1-propynal, (7) bis(trimethylsilyl)-amido, and (8) benzyl.

In Figure 1, $J_{^{199}Hg-Si-C-^1H}$ is plotted against $J_{^{199}Hg-C-^1H}$. The points fall on a line described by

$$0.453|J_{^{199}Hg-C-^1H}| + 6.0 = |J_{^{199}Hg-Si-C-^1H}| \qquad (3)$$

This linear relationship indicates that the mechanism of coupling is basically the same in both series of compounds.

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Preparation and Characterization of Some Mixed Halo-Nitrile Complexes of Rhodium(III)[1]

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A number of nitrile complexes of rhodium(III) have been reported and characterized by spectroscopic methods.[2] In all cases the complexes have been prepared using rhodium trichloride hydrate or the hexachlororhodate anion as the starting material. A search for new preparative methods for these complexes and an interest in the corresponding bromide complexes resulted in the study of the reactions of various nitriles with rhodium tribromide hydrate and tetraethylammonium nonachlorodirhodate. The increased solubility of this latter compound in warm nitriles facilitated the preparation of the respective monosubstituted and disubstituted complexes (especially those of the higher nitriles). The spectral properties of the new complexes were investigated in some detail to further our understanding of the donor properties of nitriles when they are coordinated to a non-first-row transition metal and to contrast the properties of the bromo complexes with the corresponding chloro species.

During the course of the study outlined above, the utility of proton nmr spectra in determining the structure of certain of these nitrile complexes was demonstrated. Thus the confirmation of the structure of the previously reported[2b] *trans*-$RhCl_3(C_2H_5CN)_3$ by proton nmr is also reported.

Experimental Section

Preparation of Tetraethylammonium Tetrabromodiacetonitrilerhodate(III).—$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$ was prepared in a manner similar to that used for the analogous chloro complex.[2c] Upon mixing equimolar amounts of rhodium tribromide (hydrate) and tetraethylammonium bromide in acetonitrile, a green species was formed, possibly $((C_2H_5)_4N)_3RhBr_6$. This green product decomposed upon heating and the solution became red-brown. This green intermediate could be avoided by mixing the reactants directly in hot acetonitrile: rhodium tribromide dihydrate (0.195 g, 0.515 mmol) was dissolved in 25 ml of boiling acetonitrile and tetraethylammonium bromide (0.108 g or 0.515 mmol dissolved in a minimum amount of acetonitrile) was slowly added. The solution turned dark red. Upon standing overnight in the freezer some brown precipitate was obtained which was filtered and washed with ether. Addition of an equal amount of ether to the filtrate yielded additional brown precipitate. The two samples had identical infrared spectra. The final product was recrystallized from acetonitrile, washed with anhydrous ether, and dried under vacuum over P_2O_5. *Anal.* Calcd for $C_{12}H_{26}N_3RhBr_4$: C, 22.70; H, 4.13; N, 6.62. Found: C, 22.99; H, 4.01; N, 6.90.

Preparation of Aquotribromodiacetonitrilerhodium(III).—The complex $RhBr_3(H_2O)(CH_3CN)_2$ was prepared by dissolving rhodium tribromide dihydrate (0.20 g) in acetonitrile and refluxing the solution for 7 hr, during which time the solution changed from very dark brown to wine red. Removal of the solvent by means of a rotary evaporator produced dark brown crystals, which were recrystallized, washed, and dried as above. *Anal.* Calcd for $C_4H_8N_2ORhBr_3$: C, 10.85; H, 1.82; N, 6.33. Found: C, 11.66; H, 1.93; N, 6.37.

Preparation of *trans*-Trichlorotris(propionitrile)rhodium(III).—The *trans*-$RhCl_3(CH_3CH_2CN)_3$ complex was prepared in a fashion similar to the one used for the analogous acetonitrile complex.[2c] One gram of rhodium trichloride trihydrate was dissolved in 20 ml of absolute ethanol and propionitrile (10 ml) was added. The solution was refluxed until a yellow precipitate was obtained. Complete precipitation was accomplished by means of ether addition. The final product was recrystallized from propionitrile and washed and dried as above. The presence of the $RhCl_3(CH_3CH_2CN)_3$ species was verified by its visible and infrared spectra.[2b]

Preparation of Tetraethylammonium Tetrachlorobis(benzonitrile)rhodate(III).—$((C_2H_5)_4N)[RhCl_4(C_6H_5CN)_2]\cdot H_2O$ was prepared from $((C_2H_5)_4N)_3Rh_2Cl_9$. The starting material was stirred slowly with warming in benzonitrile until all of it had been dissolved leaving a reddish orange solution. The hot solution was filtered and the desired compound was obtained by slow addition of anhydrous ether. The pale orange (apricot) complex was washed and dried as above. *Anal.* Calcd for $C_{22}H_{32}N_3ORhCl_4$: C, 44.10; H, 5.38; N, 7.01. Found: C, 43.74; H, 5.01; N, 6.86.

Visible, Infrared, and Proton Nmr Spectra.—The visible spectra were obtained on a Perkin-Elmer Model 450 spectrophotometer or a Cary Model 15 spectrophotometer. The infrared spectra in the 4000–650-cm^{-1} region were taken on a Beckman Model IR-5A instrument and those in the 500–700-cm^{-1} region were recorded on a Beckman Model IR-11 or Perkin-Elmer FIS-3 spectrophotometer. All proton nmr spectra were obtained on a Varian Model A-60 high-resolution spectrometer at 60 Mc.

Results and Discussion

Infrared Spectra.—Since the mixed complexes prepared in this investigation contained nitriles and halides coordinated to the metal, it seemed feasible to determine their infrared spectra in the normal infrared range and in the far-infrared region to observe both the spectra of the coordinated nitriles and the coordinated halides. The values observed for the C≡N stretching frequencies in the various rhodium–nitrile

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[1] Taken in part from the thesis presented by B. D. C. for the Ph.D. degree from Louisiana State University in New Orleans.

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TABLE I

C≡N STRETCHING FREQUENCY IN RHODIUM–NITRILE COMPLEXES[a]

Compd	ν(C≡N), cm^{-1}	$\Delta\nu$, cm^{-1}
CH_3CN	2254	. . .
$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$	2315	61
$RhBr_3(CH_3CN)_2H_2O$	2315	61
C_6H_5CN	2227	. . .
$((C_2H_5)_4N)[RhCl_4(C_6H_5CN)_2]$	2283	56

[a] The spectra of the ligands were obtained as films between KBr plates and those of the complexes were obtained as KBr pellets. All spectra obtained on the Beckman Model IR-5A were calibrated using the standard polystyrene wavelength calibrator furnished with the spectrometer. The sharp polystyrene band at 1944.5 cm^{-1} was recorded on each spectrum and the bands reported are expected to be accurate to better than ±5 cm^{-1}. Repetitive spectra were superimposable.

complexes are presented in Table I. An increase in frequency upon coordination was observed in all cases. This behavior is indicative of complexation through the lone pair of electrons localized on the nitrogen.[3]

The identification of the metal–ligand infrared bands associated with the Rh–Br bonds was hampered by the lack of literature values for similar complexes. Clark and coworkers,[4] in a study of the spectra of complexes of the type RhX_3L_3, where L was $P(C_2H_5)_3$ or $As(C_2H_5)_3$, could not locate with certainty any Rh–Br bands in the region 460–200-cm^{-1}. It appears that the only report of such stretching bands is that of Brooks and Shaw,[5] who tentatively reported values of 277 and 276 cm^{-1} for the trisubstituted complexes of rhodium tribromide with dimethylphenylphosphine and triphenylphosphine, respectively.

To provide further comparative information on the character and position of fundamental Rh–Br frequencies, the spectra of the bridged $Rh_2Br_9^{3-}$ species and the octahedral $RhBr_6^{3-}$ were obtained.[6] The two bands shown in Table II for $Rh_2Br_9^{3-}$ can be assigned to the Rh–Br stretching frequency of the terminal (259 cm^{-1}) and the bridging (174 cm^{-1}) bromides. The assignment can be made with some certainty by analogy to the corresponding $Rh_2Cl_9^{3-}$.[7] The strong, symmetrical band observed for $RhBr_6^{3-}$ can be assigned to ν_3, the Rh–Br stretching frequency. The far-infrared data obtained for the complexes prepared during this investigation are shown in Table II.

TABLE II

FAR-INFRARED SPECTRA OF THE NITRILE COMPLEXES[a]

Complex	M–X str, cm^{-1}	Other bands, cm^{-1}
$((C_2H_5)_4N)[RhCl_4(C_6H_5CN)_2]$	346 s, 312 s	39 w, 289 m, 277 sh
$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$	307 s, 286 s	486 vw, 267 sh, 234 m, 208 s
$RhBr_3(CH_3CN)_2H_2O$	321 s, 304 s, 296 s	483 w, 460 w, 217 s, 186 w
$K_3[Rh_2Br_9]$	259 s, 174 m	. . .
$((C_2H_5)_4N)_3[RhBr_6]$	252 s	. . .

[a] Samples were run as Nujol mulls. The far-infrared spectrometer was calibrated with atmospheric water vapor according to the assignments of Randall and coworkers: H. M. Randall, D. M. Dennison, N. Ginsberg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937). All frequencies reported for sharp bands are expected to be accurate to better than ±3 cm^{-1}. Repetitive spectra were superimposable.

TABLE III

PROTON NMR SPECTRA OF RHODIUM(III)–NITRILE COMPLEXES

Compd	Chem shift,[a] ppm (rel intens)	Solvent
CH_3CN	2.00 s	. . .
$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$	2.61 s (3)	D_2O
	3.17 q (4)	
	1.17 t (6)	
$RhBr_3(CH_3CN)_2H_2O$	2.58 s (1)	CD_3CN
	2.55 s (1)	
CH_3CH_2CN	2.34 q (2)	. . .
	1.18 t (3)	
$RhCl_3(CH_3CH_2CN)_3$	2.96 q (2)	CD_3CN
	2.90 q	
	1.32 t (3)	

[a] Chemical shifts in heavy water with respect to HOD and in CD_3CN and neat liquids with respect to internal TMS: s, singlet; t, triplet; q, quartet.

TABLE IV

ELECTRONIC SPECTRA OF RHODIUM(III)–NITRILE COMPLEXES

Complex	Absorption max, mμ	ε	Assignment	Conditions
$((C_2H_5)_4N)[RhCl_4(C_6H_5CN)_2]$	490	65	$^1A_{1g} \rightarrow {}^1T_{1g}$	Nitromethane
	418	194	$\rightarrow {}^1T_{2g}$	
$((C_2H_5)_4N)[RhBr_4(CH_3CN)_2]$	490 sh	167	$^1A_{1g} \rightarrow {}^1T_{1g}$	Acetonitrile
	450 sh	620	$\rightarrow {}^1T_{2g}$	
	344	6,200	Charge transfer	
	304 sh	9,000	Charge transfer	
	260	34,000	Charge transfer	
$RhBr_3(CH_3CN)_2H_2O$	465 sh	317	$^1A_{1g} \rightarrow {}^1T_{1g}$ or $^1T_{2g}$	Acetonitrile
	334	2,960	Charge transfer	
	266	4,370	Charge transfer	

Nuclear Magnetic Resonance Spectra.—Proton studies of rhodium–acetonitrile complexes proved very helpful in assigning the configuration of the geometrical isomers of the $RhCl_3(CH_3CN)_3$ complexes.[2c] Johnson and Walton[2b] had reported the preparation of an analogous propionitrile complex to which they assigned the trans configuration on the basis of the similarity of its visible and far-infrared spectra to those of the trans rhodium-trisubstituted pyridine complex. This compound was prepared and its spectral properties were determined. The trans isomer should contain two equivalent and one distinct propionitrile molecules, which would result in two separate sets of signals in the nmr spectrum. Pure ethyl cyanide exhibited a quartet at 2.34 ppm (δ) and a triplet at 1.18 ppm corresponding

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(3) J. Reedijk, A. P. Zuur, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **86**, 1103 (1967), and references cited therein.

(4) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(5) P. R. Brooks and B. L. Shaw, *J. Chem. Soc. A*, 1079 (1967).

(6) The $Rh_2Br_9^{3-}$ ion was prepared as the potassium salt by a procedure outlined by P. Poulenc, *Ann. Chim.*, **4**, 579 (1935), and $RhBr_6^{3-}$ was obtained from the immediate reaction of tetraethylammonium bromide and rhodium tribromide dihydrate in acetonitrile. Both compounds gave metal analysis within ±0.2% of the calculated value.

(7) R. A. Work, III, and M. L. Good, *Inorg. Chem.*, **9**, 956 (1970).

to the methylene and methyl protons, respectively (Table III). The complex *trans*-$RhCl_3(CH_3CH_2CN)_3$ in CD_3CN exhibited a set of two quartets centered at 2.96 and 2.90 ppm in a ratio of approximately 2:1 and a lone triplet centered at 1.32 ppm. The ratio of the quartets to the lone triplet was 2:3 as in the free ligand. Thus the assignment of the trans structure to this species on the basis of its optical spectra is confirmed. It is interesting to observe that the difference in ligands does not extend to the nitrile methyl group or that the difference is very small and cannot be resolved, since a single triplet is observed for the terminal methyl group. However, the triplet has been shifted downfield by 0.14 ppm from its position in the free ligand as compared to 0.62 and 0.56 ppm for the two methylene quartets, respectively.

The proton nmr spectrum of $RhBr_3(CH_3CN)_2H_2O$ contained two peaks of equal intensity from the coordinated acetonitrile, thus indicating that this complex could have only an even number of bonded nitriles. Again the nmr spectrum confirms the proposed stoichiometry for this species.

Electronic Spectra.—The electronic spectra of the rhodium–nitrile complexes reported in this study are presented in Table IV. The various assignments were made with the aid of previous reports.[8] The assignment of the transitions in the bromide complexes is not completely clear, because of the large magnitude of the molar absorptivities of some of the d–d bands. Schmidtke assigned such bands with molar absorptivities as high as 1000 to d–d transitions, which are spin allowed and Laporte forbidden.[8b] The unusually high values are probably due to the overlap of these transitions with strong charge-transfer bands.

Conclusion

A final word is needed with regard to the geometric configurations of the complexes in this report. The complexes $RhX_4(RCN)_2^-$ can be assigned the trans configuration on the basis of their visible spectra by comparison with the spectra of the geometrical isomers of the analogous pyridine complexes.[18a] This assignment is further substantiated by the number of Rh–X stretching bands observed in their far-infrared spectra since theoretically four such stretches would be expected for the less symmetrical cis configuration.[2c] The trans assignment for the $RhCl_4(C_6H_5CN)_2^-$ species would indicate that in the reaction of the bridged species $Rh_2Cl_9^{3-}$ with benzonitrile, the size of the ligand necessitates a rearrangement.

The formation and structure of the complex $RhBr_3(CH_3CN)_2H_2O$ is of interest. The infrared spectrum of the complex indicated the presence of coordinated water and suggested a low symmetry, and the nmr spectrum confirmed the presence of an even number of nonequivalent acetonitrile molecules. On the basis of this information the two nitrile ligands cannot be bonded trans to each other and in addition one nitrile would have to be bonded across a bromide ion, whereas the other nitrile would lie across the lone water molecule.

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Synthesis of *N*-Trialkylborazines from Phenyl Borate, Aluminum, Hydrogen, and Primary Amines

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N-Trialkylborazines have received considerable attention in recent years and presently are utilized as synthetic intermediates[2,3] and as reducing agents.[4] Previously reported synthetic procedures involve reaction of diborane with primary amines[5] (eq 1), diborane with alkyl cyanides[6] (eq 2), and reaction of lithium borohydride and the appropriate monoalkylammonium halide[7] (eq 3).

$$B_2H_6 + 2H_2NR \xrightarrow{\Delta} {}^2/_3(HBNR)_3 + 4H_2 \tag{1}$$

$$B_2H_6 + 2RCN \xrightarrow{\Delta} {}^2/_3(HBNCH_2R)_3 \tag{2}$$

$$LiBH_4 + RNH_3{}^+Cl^- \xrightarrow{\Delta} LiCl + {}^1/_3(HBNR)_3 + 3H_2 \tag{3}$$

We have previously reported on the preparation of B–H compounds by the reduction of borate esters with aluminum and hydrogen. In this way amine–boranes[8] (eq 4) and aminoboranes[9] (equation 5) have been prepared in high yield. By analogy it would appear that reduction of phenyl borate with aluminum and hydrogen in the presence of a primary amine might produce borazines according to eq 6. In order to test this

$$B(OC_6H_5)_3 + Al + R_3N \xrightarrow[\Delta,\text{pressure}]{H_2} H_3BNR_3 + Al(OC_6H_5)_3 \tag{4}$$

$$B(OC_6H_5)_3 + Al + R_2NH \xrightarrow[\Delta,\text{pressure}]{H_2} HB(NR_2)_2 + Al(OC_6H_5)_3 \tag{5}$$

$$B(OC_6H_5)_3 + Al + RNH_2 \xrightarrow[\Delta,\text{pressure}]{H_2} {}^1/_3(HBNR)_3 + Al(OC_6H_5)_3 \tag{6}$$

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