atmosphere at 125° for 1 hr. After cooling to room temperature, the crude product was recrystallized from *n*-pentane. The yield was 0.03 g (20%).

Trichlorosilyltetrakis(**trifluorophosphine**)rhodium(**−I**), **$Cl_3SiRh(PF_3)_4$**.—A solution of $Rh_2(PF_3)_8$ (0.30 g, 0.33 mmol) in 10 ml of *n*-pentane was stirred with trichlorosilane (0.09 g, 0.66 mmol) at room temperature for 20 hr. The solution was evaporated in a stream of nitrogen, and the residual oil was sublimed twice at 25° (10^{-3} mm) onto a −80° cold finger. A yield of 0.25 g (64%) of pale yellow liquid was obtained. It turned red reversibly below −50°.

Triethoxysilyltetrakis(**trifluorophosphine**)rhodium(**−I**), **$(C_2H_5O)_3SiRh(PF_3)_4$**.—A solution of $Rh_2(PF_3)_8$ (0.55 mmol) in 10 ml of *n*-pentane was stirred at room temperature and a solution of triethoxysilane (0.18 g, 1.10 mmol) in 10 ml of *n*-pentane was added slowly. The course of the reaction was monitored by infrared spectroscopy (see below) in an effort to avoid the presence of excess triethoxysilane, and addition was stopped when there was still some $HRh(PF_3)_4$ in the solution. After being stirred for 30 min at room temperature, *n*-pentane was removed in a stream of nitrogen. The dark oily residue was sublimed at 25° (10^{-3} mm) onto a −80° probe to give white crystals which melted at ∼−20° to a yellow liquid. Analytical data suggested that the product was contaminated with triethoxysilane, but it could not be purified further.

Triphenylgermyltetrakis(**trifluorophosphine**)**rhodium**(**−I**), **$(C_6H_5)_3GeRh(PF_3)_4$**.—This was prepared similarly to $(C_6H_5)_3SiRh(PF_3)_4$, from $Rh_2(PF_3)_8$ (0.2 g, 0.22 mmol) and triphenylgermane (0.13 g, 0.43 mmol) in 5 ml of *n*-pentane for 24 hr. The yield was 0.24 g (73%) after one recrystallization from *n*-pentane at −80°. Though more stable than $(C_6H_5)_3SiRh(PF_3)_4$, the compound decomposes slowly in solution.

Triphenylstannyltetrakis(**trifluorophosphine**)**rhodium**(**−I**), **$(C_6H_5)_3SnRh(PF_3)_4$**.—A solution of $K[Rh(PF_3)_4]$ (0.20 g, 0.40 mmol) in 10 ml of ether was treated with triphenyltin chloride (0.16 g, 0.42 mmol) and the mixture was stirred at room temperature for 10 min. The solvent was removed at 15 mm and the residue was extracted with 20 ml of *n*-pentane. The extract was evaporated to ∼0.5 ml and cooled to −78°, yielding 0.18 g (55%) of crude product, which was purified by another crystallization from *n*-pentane at −78°.

The following were prepared similarly: **$(C_6H_5)_3SnIr(PF_3)_4$**, from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3SnCl$ (yield 57%); **$(C_6H_5)_3PbIr(PF_3)_4$** from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3PbCl$ (yield 80%); **$(C_6H_5)_3PAuRh(PF_3)_4$** from $K[Rh(PF_3)_4]$ and $(C_6H_5)_3PAuCl$ (yield 60%); **$(C_6H_5)_3PAuIr(PF_3)_4$** from $K[Ir(PF_3)_4]$ and $(C_6H_5)_3PAuCl$ (yield 50%, after three recrystallizations from *n*-pentane at −80°).

Kinetics.—The kinetics of the reactions of triphenylsilane and triphenylgermane with $M_2(PF_3)_8$ in *n*-hexane were studied by mixing known concentrations of the reactants (∼0.03–0.07 *M*) and transferring the solution rapidly to a 1-mm path length infrared liquid cell with KBr windows. The peak heights of the bands due to ν(Si–H) at 2140 cm^{-1}, ν(Ge–H) at 2055 cm^{-1}, ν(Rh–H) at 1960 cm^{-1}, and ν(Ir–H) at 2090 cm^{-1} were then followed as a function of time using the PE 457 spectrometer; the cell temperature was 30°. The peak heights were converted to concentrations by means of calibration curves obtained from standard solutions of the compounds.

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Charge-Transfer Spectra of Ruthenium(II) Complexes

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The charge-transfer spectra of four series of ruthenium(II) complexes—$(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2{}^{2+}$, where L represents a nitrogen heterocycle—have been analyzed. The molecular orbital parameters thus obtained allow back-bonding, metal to ligand, in these compounds to be quantitatively assessed.

Ford, Rudd, Gaunder, and Taube[1] have reported the syntheses and spectra of pentaammineruthenium(II) complexes containing aromatic nitrogen heterocycles such as pyridine and pyrazine. They found that, in addition to essentially unperturbed internal ligand transitions at *ca.* 40 kK (250 nm), these compounds shown an intense (ϵ *ca.* 10^4) band at roughly 20 kK (400–500 nm). This band, analogous to Jørgensen's iridium–pyridine bands,[2] was assigned to metal–ligand charge transfer.

They reported[1] that the basicity of the pyrazine complex is some 2 powers of 10 greater than that of free ligand, thus proving that back-bonding, metal to π^*, is significant in these species. The charge-transfer band gives information about the states involved in this interaction, and it is therefore of interest to evaluate the relevant molecular orbital parameters.

To do so, we analyze the spectra of the complexes $(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2{}^{2+}$, where L represents a nitrogen heterocycle—pyridine, isonicotinamide, methyl isonicotinate, or pyrazine. This series allows us to evaluate semiempirically the various interactions without recourse to assumed matrix elements. We shall proceed to show, first, that symmetry and/or overlap arguments exclude all but one metal 5d orbital and one π^* ligand orbital from consideration and, next, that a simple molecular orbital treatment using only these states can give semiquantitative agreement with experiment (each of our four series of compounds has four spectral bands, two of which serve to fix our two parameters leaving two bands as tests) We then show that one additional small interaction parameter for all compounds suffices to bring all the data into agreement. Using these parameters, we compute back-bonding energies.

Experimental Section

cis-$(NH_3)_4(NC_4H_4N)_2{}^{2+}$, *trans*-$(NH_3)_4Ru(NC_5H_4CO_2CH_3)_2{}^{2+}$, and *trans*-$(NH_3)_4Ru(NC_5H_4CONH_2)_2{}^{2+}$.—These ions were pre-

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

[2] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1966 (1957).

pared in solution by the following procedure. A solution 10^{-3} *M* in the appropriate ruthenium(III) ammine chloride salt (*cis*[3] or *trans*-$(NH_3)_4RuCl_3$[4]) and *ca.* *M* 10^{-3} in acid was reduced for 0.5 hr over freshly prepared amalgamated zinc under a stream of argon scrubbed through Cr^{2+}(aq). Portions of the reduced solution were syringed into a deaerated solution of the ligand of interest (0.1–0.5 *M*, at pH 5–7), the Ru(II) being diluted tenfold to *ca.* 10^{-4} *M*. The band maxima as reported were recorded when the spectra showed the formation reactions to be complete. Ford and Sutton[5] have shown that the Ru(II) ions maintain their stereochemistry under these conditions.

trans-$(NH_3)_4Ru(NC_4H_4N)_2(ClO_4)_2 \cdot 1.5H_2O$ was prepared by Gaunder's procedure.[6] *Anal.* Calcd: N, 20.6; H, 4.15; Cl, 12.6; C, 17.3. Found: N, 20.3; H, 4.16; Cl, 12.7; C, 17.1. (Microanalyses were performed by the Microanalytical Laboratory, Stanford University.)

Results

The pentaammineruthenium(II) complexes of the aromatic nitrogen bases studied here show one absorption band in the visible spectrum (Table I). Because of that band's intensity, that asymmetry characteristic of charge-transfer bands, and, most convincing, its absence in species such as hexaammineruthenium(II) in which low-lying ligand orbitals are not availabe, we agree with the assignment of Ford, *et al.*,[1] of this band to a metal-to-ligand charge-transfer process. While it is true that this non-Gaussian band can be resolved into a sum of Gaussians, we agree with Ford that such resolution is not significant; therefore, only band maxima will be considered here, band shapes being disregarded.

TABLE I

BAND MAXIMA IN Ru(II) COMPLEXES (kK)

Ligand	$(NH_3)_5RuL^{2+}$	*cis*-$(NH_3)_4RuL_2^{2+}$	*trans*-$(NH_3)_4RuL_2^{2+}$
Pyridine	24.5[a]	24.4, 26.6[b]	23.6[b]
Isonicotinamide	20.8[a]	21.0, 24.2[c]	20.4[d]
Methyl isonicotinate	20.2[a]	20.3, 23.6[c]	19.5[d]
Pyrazine	21.3[a]	21.3, 25.1[d]	20.6[d]

[a] Reference 1. [b] Reference 5. [c] Reference 6. [d] This work.

In the cis tetraammine complexes, there are two bands in the visible spectrum which, for the same reasons as in the pentaammines, can be ascribed to charge-transfer processes. One of these bands is found at an energy not dissimilar to that in the pentaammine species, and the other occurs several kilokaisers higher in energy (Table I). The trans tetraammine compounds show only one band which can be assigned to charge transfer, that at somewhat lower energy than the cis or pentaammine analogs containing the same heterocycle.

As Ford, *et al.*,[1] have pointed out, there are many more symmetry-allowed transitions in these compounds than are experimentally observed, even in the pentaammine species. If, as Ford,[1] we disregard transitions to that orbital which transforms like A_2 under C_{2v} symmetry, that is, the ligand orbital having a node at the nitrogen attached to the metal, then there are still three metal orbitals of different symmetry which can provide the optical electron, and more transitions are predicted still than are observed. If, however, we make the additional assumption that only the metal 4d orbital oriented so as to overlap the ligand π system efficiently is of spectroscopic importance, then only one charge-transfer band is predicted—the transition from that 4d level to the ligand B_2 antibonding π level. We neglect the highest lying B_2 ligand level, since transitions to it should lie very much higher in energy[7,8] and are outside the spectral range considered here.

These assumptions reduce the problem to a two-orbital case in the pentaammines and a three-orbital problem in the cis and trans tetraammine complexes, the relevant orbitals being that 4d metal orbital which uniquely overlaps the ligand π system and the ligand antibonding π orbital of relatively low energy without a node at the metal center. Using elementary methods, these problems are readily solved if molecular geometries are known. In the pentaammines this presents no problem; regardless of the orientation of the ligand, linear combinations of the metal orbitals can be chosen that will rotate the zeroth-order wave functions to yield an equivalent problem. The cis and trans tetraammines require more detailed consideration.

In the absence of structural evidence, we assume that the rings in the trans compounds are coplanar. Were they not so, these complexes would be expected to show the same spectra as the parent pentaammine species, since there could be no π interaction between rings located in perpendicular planes.[9] Because the trans tetraammines are experimentally different from the pentaammines, we assume coplanarity.

Again lacking structural evidence, we assume that cis tetraammines have the ring systems in planes which can be taken as *xz* and *yz*. This choice is stereochemically reasonable and permits interactions not possible in the pentaammines, in agreement with experiment.

A naive molecular orbital treatment can now be carried out. The results are summarized in Figure 1. It must be clearly noted that the wave functions written are nothing more than symmetry orbitals; the lowest level is predominantly metal in character and the higher levels predominantly ligand, as will be shown.

Of the transitions possible under the above scheme, that at higher energy in the trans compounds is parity forbidden and thus only vibronically allowed; all others are allowed. The two transitions in the cis species are predicted to have orthogonal polarizations, and in a polarizing microscope, the compounds are strongly dichroic. Thus, we rationalize two bands in the cis species and one each in the trans and the pentaammine, in agreement with experiment.

Because the naivete of our model does not warrant a more sophisticated treatment, we assume that β and δ

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[3] K. Gleu and W. Breuel, *Z. Anorg. Allg. Chem.*, **237**, 197 (1938).

[4] We are indebted to P. C. Ford, who provided a workable procedure for the preparation of *trans*-$(NH_3)_4RuCl_3$ based on Gleu's procedure.[3]

[5] P. C. Ford and C. Sutton, *Inorg. Chem.*, **8**, 1544 (1969).

[6] R. Gaunder, Ph.D. Thesis, Stanford University, Stanford, Calif., 1969.

[7] For pyridine the higher antibonding level of proper symmetry to interact with the metal t_{2g} level lies about 29 kK above the first.[8] Adding to this 24 kK observed for the metal-to-ligand charge transfer assuming it derives from the lower antibonding level, 47 kK (212 nm) is calculated to be the energy of the second metal-to-ligand charge-transfer band. For pyrazine as the ligand, the second metal-to-ligand charge transfer (calculated in the same manner) should lie at 61 kK (164 nm).

[8] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 366.

[9] A reviewer has suggested that the trans species should differ from the mono because of the different ligand set. Were this the origin of the observed difference, we would expect the shift to be in the opposite direction. Pyridine, etc., by back-bonding, should increase the effective nuclear charge of the ruthenium, thus making it harder photochemically to oxidize and shifting the band in the trans species to higher energy rather than to lower, the effective nuclear charge in the trans species being presumably greater than in the mono.

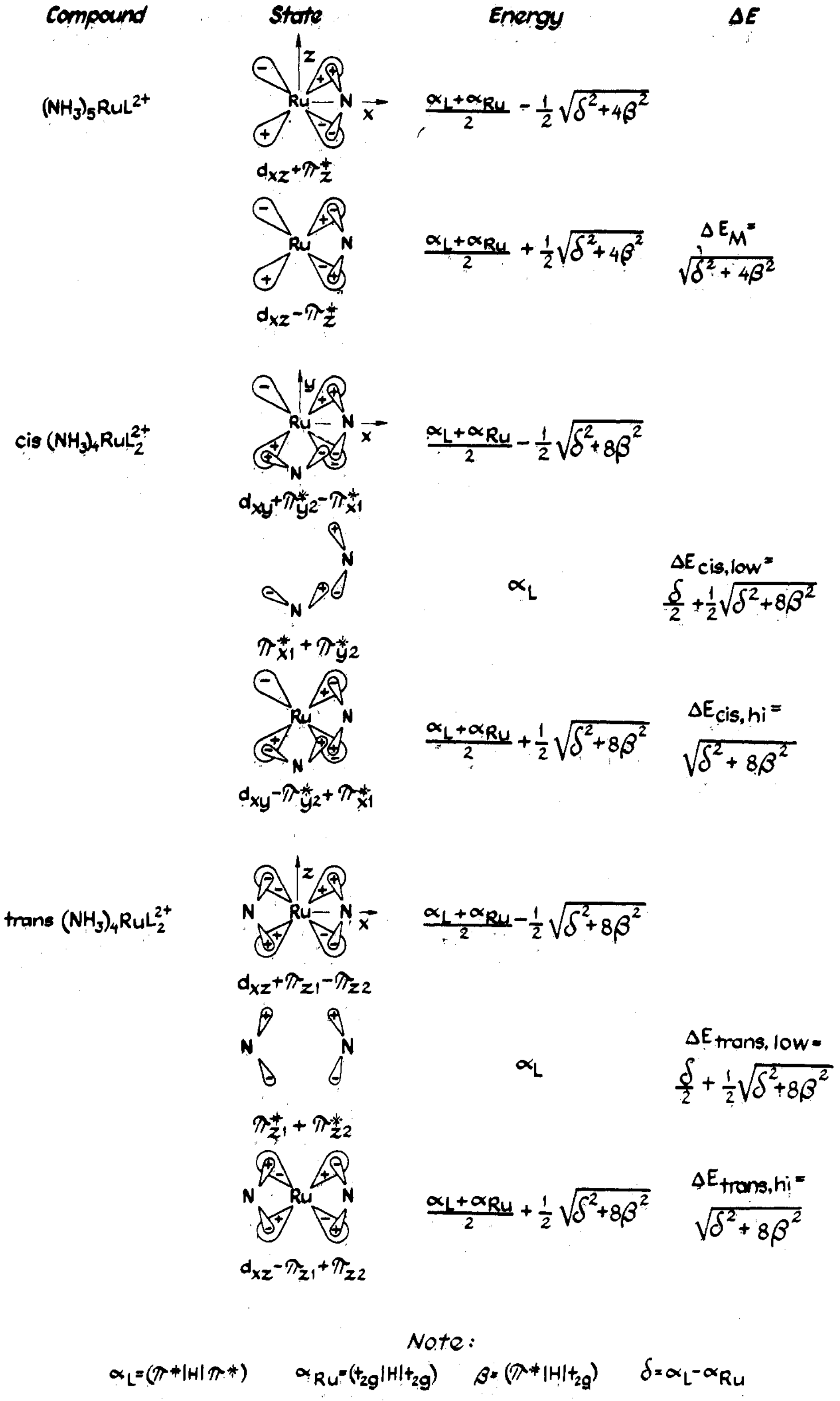

Figure 1.—Molecular orbital calculation for $(NH_3)_5RuL^{2+}$ and *cis*- and *trans*-$(NH_3)_4RuL_2^{2+}$.

are constant for a given heterocycle. Although there are surely synergistic effects, we assume that they represent higher order terms and neglect them in this treatment; the proximity of pyridine and ammonia in the spectrochemical series supports this assumption. With this assumption the data for the pentaammines and the higher energy band of the cis tetraammines allow us to evaluate the parameters β and δ. We can then predict the energy of the lower cis band and that of the trans; the two are predicted to lie at the same energy to this degree of approximation, a point to which we shall return. The results of these calculations are shown in Table II.

Corresponding to the ground states implied by Table II are the wave functions for the pentaammines shown in Table III. These results demonstrate that the

TABLE II

CALCULATED PARAMETERS AND CALCULATED AND EXPERIMENTAL SPECTRA (kK)

Ligand	β	δ	Calcd $\Delta E_{\mathrm{cis,low}}$	Exptl $\Delta E_{\mathrm{cis,low}}$ or $\Delta E_{\mathrm{trans}}$	Exptl $\Delta E_{\mathrm{trans}}$
Pyridine	5.2	22.2	24.4	24.4	23.6
Isonicotinamide	6.2	16.8	20.5	21.0	20.4
Methyl isonicotinate	6.1	16.1	19.8	20.3	19.5
Pyrazine	6.6	16.7	20.9	21.3	20.6

TABLE III

FIRST-ORDER WAVE FUNCTIONS FOR $(NH_3)_5RuL^{2+}$

Ligand	
Pyridine	$\psi = 0.97\psi_{\mathrm{Ru}} + 0.23\psi_{\mathrm{L}}$
Isonicotinamide	$\psi = 0.96\psi_{\mathrm{Ru}} + 0.28\psi_{\mathrm{L}}$
Methyl isonicotinate	$\psi = 0.96\psi_{\mathrm{Ru}} + 0.28\psi_{\mathrm{L}}$
Pyrazine	$\psi = 0.95\psi_{\mathrm{Ru}} + 0.33\psi_{\mathrm{L}}$

ground states are indeed mainly metal, and it follows that the excited states are mainly ligand in character. However, significant transfer of electron density from metal to ligand (back-bonding) is evident, amounting to roughly 0.05 electron in the pentaamminepyridine complex, 0.075 electron in the isonicotines, and 0.10 electron in the pyrazine moiety. These numbers, arrived at by neglecting overlap and disregarding excited states, are admittedly speculative, but taken qualitatively they do agree with intuition.

We note in Table II a mild inverse dependence between δ and β, as might be expected: the closer the states in energy, the greater their interaction. We also note that the predicted transition energies to the lower excited state in the cis complexes average *ca.* 0.4 kK lower than the experimental values and that the predicted energies for the trans compounds average *ca.* 0.4 kK higher than experimentally found.

To remove these discrepancies in what is otherwise at least a qualitatively satisfactory scheme, we invoke interaction with higher excited states. We note that there are zeroth-order orbitals springing from metal 5p levels of symmetry appropriate for interaction with some of the levels hitherto considered; under octahedral symmetry these are t_{1u}^*. These empty levels are not spectroscopically observable in aqueous solution, and thus must lie high in energy. Admixture of them will therefore depress the levels with which they interact. The symmetry of the first trans excited state, but not the ground state, is appropriate to admixture with these t_{1u}^*-like states; we therefore expect, and find, a calculated transition energy that is too high when this interaction is neglected, the excited states but not the ground state being depressed. In the cis compounds, the converse situation obtains—the ground and second excited states, but not the first excited states, have the right symmetry to interact with t_{1u}^*. We thus predict that the higher energy cis transition should be relatively unaffected by interaction of the states with the t_{1u}^* level and that our paramaterization should therefore also be unaffected but that the lower energy transition should be predicted at too low an energy, the ground but not the excited states being depressed by the interaction.

It is interesting to note that the t_{1u}^*-like state appropriate to interaction with the cis species is of the form $(P_x^* + P_y^*)/\sqrt{2}$, while that appropriate to the trans species is the t_{1u}^*-like state itself. One therefore predicts a first-order correction $\sqrt{2}$ larger in the trans than in the cis compounds. Taking, then, the average of the sum of the deviations of cis and trans predictions from experiment, 0.7 kK, as a measure of this interaction β', we find $2(1 + \sqrt{2})\beta' = 0.7$ kK, whence β' is 0.1–0.2 kK. Thus the effect is to stabilize the cis ground states by approximately 0.1–0.2 kK, a term of the order of thermal energies and thus not readily seen in equilibrium measurements.

A quantitative estimate of the back-bonding in these compounds follows easily from the above. Neglecting the admixture of the t_{1u}^* excited state as a second-order term, it is simply the difference in energy between an orbital assumed purely metal and the molecular ground states. For the cis, this is

$$\frac{-\delta}{2} + \frac{1}{2}\sqrt{\delta^2 + 8\beta^2} = \frac{-\delta}{2} + \frac{1}{2}\Delta E_{\mathrm{cis,hi}}$$

and for the pentaammine

$$\frac{-\delta}{2} + \frac{1}{2}\sqrt{\delta^2 + 4\beta^2} = \frac{-\delta}{2} + \frac{1}{2}\Delta E_{\mathrm{M}}$$

Using the values of δ in Table II, the results of Tables IV and V are obtained.

TABLE IV

CALCULATED BACK-BONDING (kK)

Ligands	$(NH_3)_5RuL^{2+}$	*cis*-$(NH_3)_4RuL_2^{2+}$
Pyridine	1.2	2.2
Isonicotinamide	2.1	3.8
Methyl isonicotinate	2.0	3.7
Pyrazine	2.3	4.2

TABLE V

BACK-BONDING CALCULATED FROM SPECTRA AND ELECTROCHEMICAL DATA (V)

Ligand	E_π from spectra	from $E°$[a]		
	Pentaammine		*cis*-Tetraammine	
Pyridine	0.15	0.29[b]		
Isonicotinamide	0.26	0.31	0.47	0.57
Methyl isonicotinate	0.25	0.33	0.45	0.61

[a] Reference 6. [b] Dr. M. Abe, from the University of Tokyo (Postdoctoral Fellow at Stanford), by spectrophotometric determinations of the compositions of solutions at equilibrium, has recently estimated that the difference between $E°$'s for isonicotinamide or methyl isonicotinate and pyridine complexes is on the order of 0.1 V (rather than, as previously measured[6] electrochemically, 0.02–0.04 V). This brings the equilibrium data into line with our prediction that pyridine and isonicotine complexes should differ in stability by about 0.1 V.

An independent estimate of the stabilization due to back-bonding in these Ru(II) complexes can be extracted from the electrochemical potentials of a number of ruthenium(II) and -(III) ammines. If the average of the potentials for the aquopentaammine (−0.16 V) and the hexaammine (−0.10 V) couples is used as a measure of the level of the zeroth-order (no back-bonding) Ru(II) state, the π stabilization for the other complexes can be estimated by subtraction, assuming it to be zero for the higher oxidation state (see Table V). That is, $E_\pi = E_{\mathrm{L}}° - 0.13$. In general, the spectral data indicate less back-bonding than do the potential data. If this trend is real, we feel its origin may lie in a σ interaction in the Ru(II) complexes which is detectable by electrochemical but not spectral measurements: back-bonding increases the effective charge on Ru(II), indirectly tightening all the metal–ligand bonds slightly *via* the σ system. This ground-state σ stabilization effect would not be observable in the spectral measurements, however, because the energy of the excited state is lowered as well, the photochemically formed Ru(III) having slightly more appropriate bond lengths than would otherwise be the case since the Franck–Condon principle applies. To the contrary, this difficulty should not arise with the equilibrium measurements, since the Ru(III) is formed in this case with its equilibrium metal–ligand bond lengths. Whether or not this added σ interaction plays an important role, the back-bonding values calculated from the two kinds of data are gratifyingly consistent and demonstrate the validity of our model for the Ru(II) back-bonding interaction and spectra for this class of compounds.

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The Relative Importance of σ and π Bonding of Molecular Nitrogen and Carbonyl in Osmium(II) Complexes as Determined by Infrared Intensities of the Molecular Nitrogen and Carbonyl Stretching Vibrations

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Integrated infrared intensity data are presented here for a series of complexes of the type $Os(N_2)X_2[PR_2C_6H_5]_3$ as well as for their carbonyl analogs. Dipole moment derivatives were calculated which involve both OsN or OsC and NN or CO stretching motions. The effective group dipole moment derivatives were found to be substantially larger for the carbonyl compounds as compared to the molecular nitrogen analogs and to vary within the dinitrogen series systematically with the nature of the phosphine and halide bound to the osmium. It is concluded on the basis of these results that CO is a better σ-donor and π-acceptor ligand than N_2.

Introduction

Along with the progress in synthetic routes to novel molecular nitrogen–transition metal complexes much interest in recent years has developed in the electronic and structural properties of the metal–nitrogen bond. In particular the question of the π-acceptor and σ-donor abilities of molecular nitrogen as compared with the isoelectronic carbon monoxide ligand has stimulated much discussion.

Answers to this question of the relative σ-donor and π-acceptor abilities of N_2 and CO have been put forth based on infrared frequency studies,[1-3] Mössbauer measurements,[4,5] rates of molecular nitrogen substitution reactions,[6] and comprehensive molecular orbital calculations.[7,8] These methods generally conclude CO to be an appreciably better σ donor and/or π acceptor than N_2. However, the most commonly employed technique of infrared frequency shifts has led to some conclusions which are disputable.

As part of a continuing study of the properties of metal–molecular nitrogen and metal–carbon monoxide bonds we have attempted to answer this question *via* infrared intensity measurements. Previously we demonstrated the utility of integrated infrared intensity measurements of ν_{N_2} and ν_{CO} vibrations in assessing π-electronic delocalization in transition metal–molecular nitrogen and –carbon monoxide compounds.[9-12] In order to obtain accurate intensity measurements it is necessary to have available pure, stable molecular nitrogen complexes. It would also be advantageous to have a series of complexes in which systematic changes in the metal's electronic character, as determined by the other affixed ligands, is also present. Such a series of complexes of the type $Os(N_2)X_2[PR_2C_6H_5]_3$ has recently been reported by Chatt, Leigh, and Richards[13] and by Maples, Basolo, and Pearson.[6] In addition the latter researchers have prepared several of their carbonyl analogs.

The purpose of the present study was to determine in more detail the usefulness of infrared intensity measurements by studying the variations in the intensity of the dinitrogen stretching frequency as the nature of the other ligands attached to the metal is varied. It is then

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