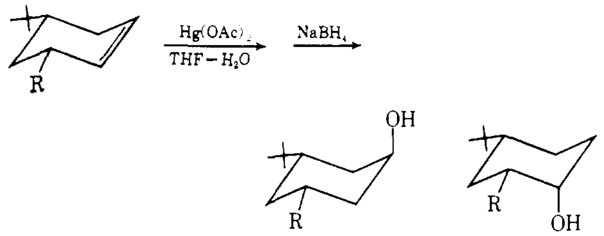
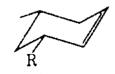
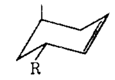
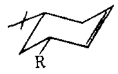
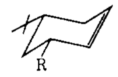
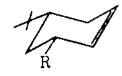
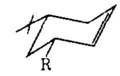
these olefins. The results are given in Scheme I. Changing the nucleophile from water to acetic acid (acetoxymercuration) does not significantly change the steric course of the reaction. The size of the 3-alkyl group has a rather profound effect on the steric course of the reaction. As the products are formed in competitive reactions it is possible to calculate the difference in activation energies ($\Delta\Delta G^{\ddagger}$) of the competitive reaction pathways. These values are given in Table I along with the corresponding A values for the alkyl groups.[19] The results are nicely rationalized by invoking torsional angle effects in the transition state for the rate-determining attack by solvent on the mercurinium ion intermediates as illustrated in Scheme II. In the attack by solvent at C_1 in **13** the C_1–H bond moves past the C_6–H_e bond as indicated by the arrow in transition state **14**. In contrast, attack at C_2 in **15** forces the C_2–H bond toward the C_3–R_e bond as indicated in **16**. As the eclipsing strain energy in **16** will be considerably greater than in **14**, reaction *via* **13** will be favored. The results are not consistent with reaction proceeding *via* an AdE3-type transition state. In the AdE3 transition states the C_1–H and C_2–H bonds continuously remain between the C_6–H bonds and the C_3–R_e and C_3–H_a bonds. The present results represent the first quantitative measurement of torsional angle effects.

Scheme I. Results of Oxymercuration of *cis*-3-Alkyl-5-*tert*-butylcyclohexenes

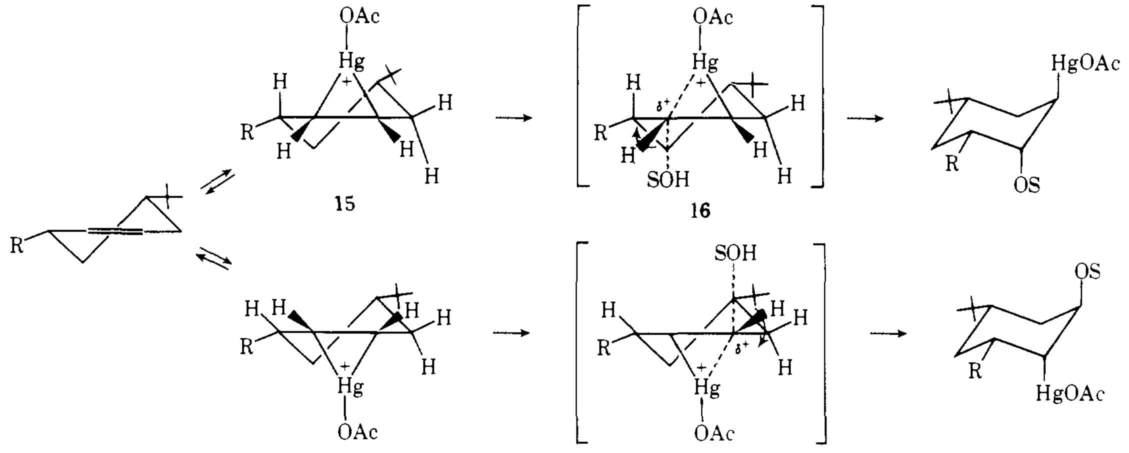


12a, R = $-CH_3$	89.8%	10.2%
b, R = CH_2CH_3	90.5%	9.5%
c, R = $-CH(CH_3)_2$	94.2%	5.8%
d, R = $-C(CH_3)_3$	99.06%	0.94%

Table I. $\Delta\Delta G^{\ddagger}$ Values for Competitive Pathways in the Oxymercuration of 3-Substituted Cyclohexenes

Olefin	R	$\Delta\Delta G^{\ddagger}$	A_R
	CH_3	0.95	1.7
	CH_3	0.85	1.7
	CH_3	1.28	1.7
	C_2H_5	1.33	1.8
	$CH(CH_3)_2$	1.65	2.1
	$C(CH_3)_3$	2.75	~5

Scheme II

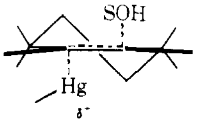


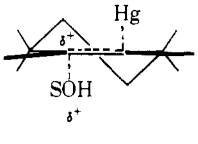
15

16

13

14





Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (PRF-1225-A1,3), and to the Alfred P. Sloan Foundation for partial support of this work.

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A Mössbauer Study of the Bonding in Ruthenium(II) Compounds

Sir:

Extensive reports of the utilization of Mössbauer spectroscopy in the elucidation of the structure and

Table I. Mössbauer Parameters of Ruthenium Compounds at 4.2°K

Compound	δ, mm/sec[a]	ΔE, mm/sec	Γ, mm/sec[b]	I_1[c]	I_2[d]	d, mg/cm^2 [e]
$K_2[Ru(CN)_5NO]\cdot 2H_2O$	$+0.03 \pm 0.03$	0.49 ± 0.03	0.50 ± 0.05	0.83	0.62	183
$K_4[Ru(CN)_6]$	-0.25 ± 0.03		0.24 ± 0.05	1.96		196
$K_4[Ru(CN)_5NO_2]\cdot 2H_2O$	-0.40 ± 0.03	0.35 ± 0.03	0.24 ± 0.05	0.22	0.65	119

[a] Expressed relative to ruthenium metal. [b] Line width at half maximum peak height. [c] Per cent dip of low-velocity peak. [d] Per cent dip of high-velocity peak. [e] Absorber thickness d, in mg/cm^2 of natural Ru.

bonding of coordination compounds can be found in the literature. Most of these reports have been concerned with compounds of iron and tin. However, recent studies on other Mössbauer nuclides have indicated that it may be possible to obtain chemical information from the Mössbauer spectra of a number of other elements. One possible Mössbauer nuclide of considerable chemical interest is ruthenium. This element is particularly exciting because it falls in the iron periodic group and its chemistry is particularly complex. Thus if extensive Mössbauer studies are possible with this element, comparisons can be made between similar compounds formed with both a first- and second-row transition element and possibly some of the unique problems of ruthenium chemistry, such as compounds with mixed metal oxidation states, can be solved. This communication reports the results of a Mössbauer study of the series of compounds $K_2[Ru(CN)_5NO]\cdot 2H_2O$, $K_4[Ru(CN)_6]$, and $K_4[Ru(CN)_5NO_2]$. Correlations are made between these results and those previously reported for the chemically similar iron species.

Previous studies have shown that ^{99}Ru is a suitable Mössbauer nuclide,[1-3] although it has been necessary to carry out the experiments at liquid helium temperatures. The Mössbauer parameters for the ruthenium cyano complexes (Table I) were determined on the solid (powdered) compounds in the conventional transmission geometry using an Austin Science Associates' Mössbauer effect spectrometer. Both source and absorber were cooled to 4.2°K in a liquid helium cryostat. The source consisted of approximately 5 mCi of 16-day ^{99}Rh contained in a host lattice of ruthenium metal, prepared by New England Nuclear Corp., Boston, Mass. The absorber compounds were prepared according to procedures reported in the literature[4-6] and all of them contained the natural abundance of ^{99}Ru. All Mössbauer spectra (Figure 1) were computer analyzed by a least-squares fit to a Lorentzian line shape.

The results of the hyperfine interactions of these compounds show that the isomer shift decreases in the order of ligand substitution as $NO^+ > CN^- > NO_2^-$ and the quadrupole splitting is greater for NO^+ than it is for NO_2^-. A similar trend has been observed in the analogous iron(II) complexes where the ordering has been correlated with the tendency of the ligand to delocalize the t_{2g} electrons into a metal–ligand π bond.[7] This delocalization decreases the d-electron density and increases the s-electron density at the metal nucleus. In $K_4[Ru(CN)_6]$, the cyano groups are attached to the central ruthenium atom by σ bonds with partial π-bond character. This electron delocalization or "back-donation" inhibits a buildup of negative charge on the ruthenium. If a cyanide is replaced by a ligand such as NO^+ which can delocalize the electrons even more, then the electron density of the 4d orbital at the metal nucleus should be reduced still further and the effective 4s-electron density should increase because of the reduced d-electron shielding. An increase in the s-electron density at the ^{99}Ru nucleus results in a more positive isomer shift,[2,3] so that the increase in the isomer shift of $K_2[Ru(CN)_5NO]$ with respect to $K_4[Ru(CN)_6]$ can be rationalized. The opposite effect should be predicted if a cyano group is replaced by a ligand such as NO_2^- which is incapable of forming π bonds. The isomer-shift value reported here for $K_4[Ru(CN)_5NO_2]$ is in line with this prediction. Thus the isomer shifts for this series of compounds can be correlated with known ligand properties.

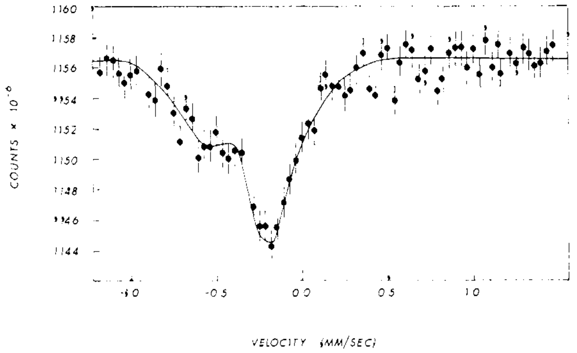

Figure 1. Mössbauer spectra of $K_4[Ru(CN)_5NO_2]\cdot 2H_2O$ at 4.2°K.

Ruthenium(II) in an octahedral field has a $t_{2g}{}^6e_g{}^0$ electronic configuration. The six paired electrons in the t_{2g} orbitals possess cubic symmetry and make no contribution to the electronic field gradient (EFG) at the nucleus. Thus $K_4[Ru(CN)_6]$ shows no quadrupole splitting, as would be expected. A lowering of the symmetry about the ruthenium nucleus in $K_2[Ru(CN)_5NO]$ and $K_4[Ru(CN)_5NO_2]$ is indicated by the appearance of quadrupole splitting in the Mössbauer spectra.[8] It seems reasonable to assume that the quadrupole splitting observed in these compounds is a result of the EFG induced at the ruthenium nucleus because of the asymmetric expansion of the t_{2g} electrons toward the ligands. The imbalance of the d electrons

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(8) The quadrupole splitting in these compounds exists in the form of a doublet, although ^{99}Ru has a ground-state spin of $^5/_2$ and an excited state spin of $^3/_2$, which should result in a fully resolved quadrupole splitting of six lines.[1] This doublet is characteristic when the quadrupole splitting of the excited $^3/_2$ state dominates, each member of the doublet consisting of an unresolved triplet.

would be expected to contribute more to the EFG than the imbalance in the p electrons. Thus the formation of a stronger metal–ligand π bond with the sixth ligand in $[Ru(CN)_5X]^{-n}$ should result in a positive EFG, and a weaker π bond should result in a negative EFG. The EFG for $K_2[Ru(CN)_5NO]$ would be expected to be positive and that for $K_4[Ru(CN)_5NO_2]$ would be expected to be negative. The EFG for the analogous $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ has been found to be positive.[9] Additional studies will need to be made to actually determine the sign of the V_{zz} element of the EFG tensor in these complexes.

While the trend in the quadrupole splittings for these ruthenium complexes is the same as that reported for the analogous iron complexes, the splitting parameters are much smaller, *e.g.*, ΔE for $K_2[Fe(CN)_5NO]\cdot 2H_2O$ is 1.72 mm/sec and ΔE for $Na_4[Fe(CN)_5NO]$ is 0.89 mm/sec. Another striking difference between the Mössbauer spectra for the two sets of compounds is the asymmetric quadrupole split spectra for the ruthenium complexes. Since the samples were analyzed as polycrystalline samples, the asymmetry could be a consequence of the Goldanskii effect.[10] Additional studies are being carried out on the correlation of these asymmetric spectra with the sign of the EFG.

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Nucleophilic Displacement Reactions in the Gas Phase

Sir:

In recent publications we have utilized ion cyclotron resonance spectroscopy (icr) to examine the gas-phase ion chemistry and thermochemical properties of organic molecules.[1-6] Not surprisingly, analogies to processes common to solution chemistry have been found. For example, we recently reported the gas-phase ionic dehydration of aliphatic alcohols, a reaction which has the character of an acid-catalyzed *elimination* process.[1-3] We report here the factors governing the occurrence of another gas-phase ionic process which has the character of a *nucleophilic displacement* reaction.

As part of our continuing program of determining proton affinities (basicities) in the gas phase,[4-6] we had occasion to examine a 1:3.5 mixture of CH_3F and HCl. The results obtained at low electron energy (14.9 eV) are illustrated in Figure 1. At low pressures the parent ions $HCl\cdot^+$ and $CH_3F\cdot^+$ are the major species present. With increasing pressure both ions react to form the protonated species H_2Cl^+ and CH_3FH^+. Careful examination of the pressure dependence of these latter two species in conjunction with ion cyclotron double-resonance experiments indicate the proton affinity of CH_3F to be greater than HCl. At the highest pressures employed both CH_3FH^+ and H_2Cl^+ are observed to decrease and disappear, reacting to generate $(CH_3)_2F^+$ and CH_3ClH^+. The formation of protonated methyl chloride is especially intriguing and indicates the occurrence of the nucleophilic displacement reaction[7]

$$HCl + CH_3FH^+ \longrightarrow CH_3ClH^+ + HF \tag{1}$$

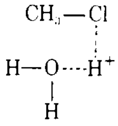
Double-resonance experiments indicate that CH_3FH^+ and ions such as H_2Cl^+, $HCl\cdot^+$, and $CH_3F\cdot^+$, which form CH_3FH^+, are the ionic precursors to CH_3ClH^+.[10] The second-order rate constant associated with reaction 1 was determined to be $3.1 \pm 0.3 \times 10^{-10}$ cm^3 molecule^{-1} sec^{-1} ($2 \times 10^{11}\ M^{-1}$ sec^{-1}).

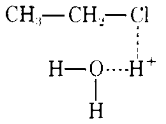
To test the generality of the nucleophilic displacement process mixtures of H_2O with CH_3Cl and C_2H_5Cl were investigated. While reaction 3 is observed, reaction 2 does not occur. The reason for this difference

$$CH_3ClH^+ + H_2O \not\longrightarrow CH_3OH_2^+ + HCl \tag{2}$$

$$C_2H_5ClH^+ + H_2O \longrightarrow C_2H_5OH_2^+ + HCl \tag{3}$$

follows directly from a consideration of the probable reaction mechanism. A reasonable representation of the intimate reaction complex for processes 2 and 3 in which the labile proton is shared between the two polar reactants is illustrated by I and II. The proton affinity (basicity) of H_2O (164 kcal/mol)[4] lies between the proton affinity of CH_3Cl (160 kcal/mol)[8] and that of C_2H_5Cl (167 kcal/mol).[8] Thus, in I the proton is transferred to H_2O, destroying the nucleophilicity of water and inhibiting the displacement reaction. As a result reaction 2 does not occur, even though it is calculated to be exothermic. Instead, the simple proton-transfer reaction 4 is observed. In II however,


I


II

$$CH_3ClH^+ + H_2O \longrightarrow H_3O^+ + CH_3Cl \tag{4}$$

the proton remains bound to chlorine and HCl is displaced by H_2O. It appears that gas-phase displacement reactions occur provided two criteria are met: (1) *the reaction is exothermic* (a general requirement for ion–molecule reactions);[11-14] and (2)

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(7) It is to be noted that $(CH_3)_2F^+$ also forms by a nucleophilic displacement process: $CH_3FH^+ + CH_3F \rightarrow (CH_3)_2F^+ + HF$. All of the dialkylhalonium ions can be similarly generated in the gas phase[3] and have recently been generated in solution, isolated, and characterized.[9]

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(10) Some CH_3ClH^+ may be generated directly from H_2Cl^+ in the reaction $H_2Cl^+ + CH_3F \rightarrow CH_3ClH^+ + HF$.