

The only variable, of those changed within the limits given in the Experimental Section, that affected any of the equilibrium results in Tables I-III within experimental error was the NaClO_4 concentration.

The kinetic and other NMR parameters are shown in Table IV. The entries correspond in the order listed to those solution compositions given in Table III in the same order. The last entry is again for Ni-cyclam. Figures 1 and 2 show the typical T_{2p}^* and Q data obtained and the calculated lines based on the fitted parameters.

Discussion

Some four species can be present in the Ni-2,3,2-tet solutions: cis- α , cis- β , trans, and planar. As far as the water-exchange data are concerned, the behavior is consistent with only two forms, NiL and $\text{NiL}(\text{H}_2\text{O})_2$. The slow cis-trans conversion is not evidenced in the water-exchange rate, and it appears that all $\text{NiL}(\text{H}_2\text{O})_2$ species exchange with similar rates. It would be difficult to specify the limits of detection for unequal rates, but certainly factors of 10 would easily be seen and perhaps even factors of 2.

The equilibrium parameters are necessarily rather imprecise; thus, the agreement among the various studies and methods is quite reasonable. For the Ni-2,3,2 tet system, where the high-spin-low-spin equilibrium $\text{NiL}(\text{H}_2\text{O})_x \rightleftharpoons \text{NiL} + x\text{H}_2\text{O}$ is described by the concentration quotient K , the value of x is found to be 2 on the basis of the ^{17}O NMR results. The argument is that the high-temperature limit of Q_{inner} should be ca. 4.0 per H_2O bound to Ni(II).⁵ The data found all point to a Q_{obsd} of ca. 8.0, thus 2 $\text{H}_2\text{O}/\text{Ni}$ is consistent with our results. As sodium perchlorate concentration increases, K increases, ΔH becomes a bit less positive, and ΔS remains about the same. The ΔS value is roughly what one would expect for the liberation of two water molecules.³ The activity of H_2O does not decrease enough to account for the results, and one must suppose that ClO_4^- plays some more specific role in favoring the low-spin form. Since water appears to be excluded from this form, one seems forced to conclude that

some long "bond" to ClO_4^- in the axial position(s) is involved.

The Ni-cyclam low-spin form has about a 10-fold greater K , than for Ni-2,3,-tet due to a more positive ΔS and in spite of a more positive ΔH . Again the ^{17}O NMR data suggest 2 $\text{H}_2\text{O}/\text{Ni}$ in the high-spin form. The greater stability of cyclic ligand complexes has been discussed by Hinz and Margerum⁶ in terms of ligand solvation.

The water-exchange rate constant at 25 °C (k_1) of $4 \times 10^6 \text{ s}^{-1}$ is about 100-fold greater for $\text{Ni}(2,3,2\text{-tet})(\text{H}_2\text{O})_2^{2+}$ than for $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, showing the usual labilizing effect of amine ligands.⁵ Sodium perchlorate in the concentration range 0.1-4 M has no significant effect on the exchange rate. For Ni-(cyclam) $(\text{H}_2\text{O})_2^{2+}$, $k_1(25 \text{ °C})$ is ca. $2 \times 10^7 \text{ s}^{-1}$, about 5 times larger than for the 2,3,2-tet complex. For Ni(trien) $(\text{H}_2\text{O})_2^{2+}$ $k_1(25 \text{ °C})$ is $6 \times 10^5 \text{ s}^{-1}$, and for Ni(cyclen) $(\text{H}_2\text{O})_2^{2+}$ $k_1(25 \text{ °C})$ is $2 \times 10^7 \text{ s}^{-1}$. The cyclic ligands are more labilizing and remarkably similar in effect, considering the considerably greater strain in the cyclen case. Some discussion of these effects is found in our earlier work.¹

We are planning to study pressure effects on these systems to obtain ΔV^\ddagger values, which may provide new clues to the origin of the differences in ligand effects on water exchange.

In our Ni-cyclen paper¹ we also discussed the relations between τ , the mean lifetime for low-spin-high-spin relaxation, and τ_M , the mean lifetime for water exchange. At that time τ_M for Ni-2,3,2-tet was not known. It is ca. 0.25 μs . This leads to a τ of 0.125 μs compared to 0.28 μs and means that, if only $\text{NiL} + \text{H}_2\text{O} \rightleftharpoons \text{NiL}(\text{H}_2\text{O})$ and $\text{NiL}(\text{H}_2\text{O}) + \text{H}_2\text{O} \rightleftharpoons \text{NiL}(\text{H}_2\text{O})_2$ equilibria are involved in determining both τ 's, then one probably cannot say which process is rate controlling for low-spin to high-spin interconversion.

Acknowledgment. This work was supported by NSF Grant No. CHE-7915792.

Registry No. ^{17}O , 13968-48-1; Ni(2,3,2-tet) $(\text{H}_2\text{O})_2^{2+}$, 36530-71-9; Ni(cyclam) $(\text{H}_2\text{O})_2^{2+}$, 78684-35-2.

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Ruthenium NMR Spectroscopy: A Promising Structural and Analytical Tool. General Trends and Applicability to Organometallic and Inorganic Chemistry¹

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Received March 4, 1982

A comprehensive study of the ruthenium chemical shift scale is presented. The results obtained clearly show the importance of ruthenium NMR for probing the ruthenium environment ($\Delta\delta = 9100$). Moreover, real chemical problems can be tackled via such a technique, for example, aqueous equilibria of ruthenium aqua ions or structural and electronic mapping around the ruthenium liganding site in organometallic ruthenium complexes.

Introduction

Most of the magnetic nuclei of the periodic table have been observed,² and only a few transition-metal isotopes resist NMR detection.³ Very recently^{4,5} both isotopes of Ruthenium (^{99}Ru , ^{101}Ru) were detected, a very important step toward structural

and dynamical studies on ruthenium compounds via Ru NMR owing to the role played by the ruthenium nucleus in or-

- (1) Presented in part at the 5th International Meeting on NMR Spectroscopy, Exeter, England, July 12-17, 1981.
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Table I. NMR Parameters of ^{99}Ru and ^{101}Ru

isotope	% nat abund	spin no. (I)	receptivity rel to ^{13}C	quad-rupole moment, $10^{-28}Q, \text{m}^2 \text{A}$
^{99}Ru	12.72	$5/2$	0.83	0.076
^{101}Ru	17.07	$5/2$	1.56	0.44

ganometallic chemistry and related areas.

Our first paper⁴ presented the NMR parameters of the two ruthenium isotopes, and we would like to introduce now a more comprehensive aspect of Ru NMR, including some interesting chemical applications.

Experimental Section

All spectra have been run on a Bruker WM 250 spectrometer equipped with a multinuclear accessory (10-mm tube). At 5.87 T ^{99}Ru resonates at 11.541 MHz and ^{101}Ru at 12.934 MHz. Spectra were acquired with 90° pulses and a fast pulsing rate (typically 0.1 s), except for very sharp lines, which were recorded under high-resolution conditions and low (1 s) pulsing rate. The sample temperature was stabilized with a BVT 1000 accessory ($\pm 1^\circ\text{C}$). All chemicals were commercially available unless otherwise stated and used without further purification or degassing. A positive δ indicates a high-frequency shift (deshielding) with respect to the reference frequency. Ξ values represent the resonance frequency at a magnetic field value for which the protons of Me_4Si resonate at exactly 100 MHz.

General Features of Ruthenium NMR

Ruthenium has two magnetically active isotopes (Table I). Although the receptivity of ^{99}Ru is only half of that of ^{101}Ru , it is preferable to observe ^{99}Ru due to its lower quadrupole moment, which compensates for the difference in receptivity between the two isotopes.

The Ξ values are⁴

$$\Xi_{99} = 4.614 \text{ MHz} \quad \Xi_{101} = 5.171 \text{ MHz}$$

The relaxation process for both isotopes is essentially quadrupolar. For ^{99}Ru the value of the quadrupole moment is of the same order as for ^{10}B , ^{33}S , ^{35}Cl , ^{37}Cl , or ^{41}K . But, in contrast for example, to covalently bonded chlorine or sulfur atoms, which give in general very broad lines, the coordination number of ruthenium tends to be high (4–6), which implies, a priori, a favorable electronic distribution along the Ru–X bonds and hence sharp lines. These coordination numbers may also help to explain the relative ease with which high-molecular-weight (>1000) organoruthenate compounds give a detectable Ru NMR signal (Table II). Such a situation is observed, for example, in $\text{Ru}(\text{bpy})_3$ -like complexes (vide infra).

Among all the current ruthenium oxidation states (–II to +VIII), the +III state cannot be detected by conventional high-resolution NMR methods because of its paramagnetism. All the other oxidation states are diamagnetic or exhibit a small paramagnetism that depends upon the formal molecular charge at the ruthenium site.

NMR Results

1. Chemical Shift Scale. A chemical shift scale is presented in Figure 1, and comprehensive results are listed in Table II. In our first paper⁴ we suggested RuO_4 1 M in CCl_4 as reference since it gives a sharp line and its temperature coefficient (0.13 ppm/K) is acceptable. But it has been also suggested⁵ that $\text{Ru}(\text{CN})_6^{4-}$ could be a better reference because it is more easily handled. On the other hand, it resonates in the low-frequency range of the ruthenium chemical shift scale, which leads to positive δ values for the majority of Ru resonances.

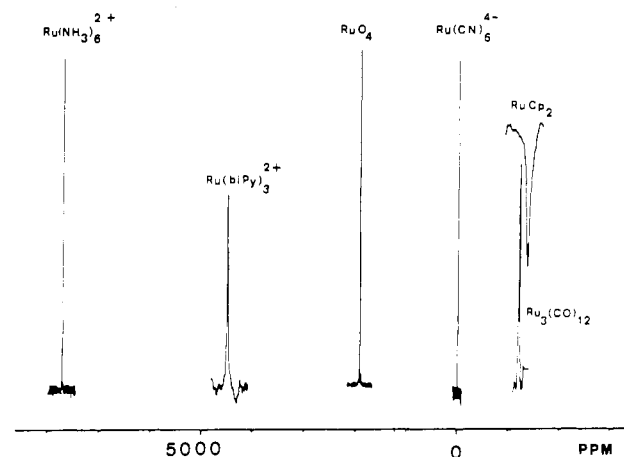


Figure 1. Ruthenium chemical shift scale (^{99}Ru observed). Counterions are indicated in Table II.

Table II. Chemical Shift Values of Chosen Ruthenium Compounds (from ^{99}Ru NMR)

compd	solvent	T, K	δ
RuCp_2	CH_2Cl_2 (satd)	346	–1270
$\text{Ru}_3(\text{CO})_{12}$	C_6H_6 (satd)	297	–1208
$\text{Ru}(\text{CN})_6\text{K}_4$	D_2O (0.3 M)	297	0
$\text{Ru}_2(\text{CO})_6\text{Cl}_4$	acetone (0.3 M)	297	+1204
	EtOH-HCl (0.3 M)		+966
	pyridine (0.3 M)		+806
$\text{Ru}(\text{CO})_3\text{Cl}_3\text{-Cs}^+$	acetone	311	+976
	EtOH	313	+1001
	$\text{D}_2\text{O-HCl}$	296	+1090
	D_2O	223	+1102
		296	+1284
		296	+1094
		333	+1111
			+1272
			+1111
			+1297
$\text{Ru}(\text{SnCl}_3)_2\text{Cl}^-(\text{NEt}_4^+)_4$	CH_3CN (satd)	303	+1554
RuO_4	CCl_4 (1 M)	297	+2021
$\text{Ru}(\text{CO})_2\text{Cl}_4^{2-}(\text{Cs}^+)_2$	D_2O (0.3 M)	333	+2523
	$\text{D}_2\text{O-HCl}$ (0.3 M)	346	+2537
	D_2O (satd)	297	+4518
$\text{Ru}(\text{LL}')_3^{2+}(\text{PF}_6^-)_2^a$	CH_3CN (0.5 M)	297	+5040 (mer) +5003 (fac)
$\text{Ru}(\text{NH}_3)_6^{2+}(\text{Cl}^-)_2$	D_2O (satd)	297	+7821
	D_2O	297	+13.360

^a The compound is tris[1-(2-pyridyl)-3,5-dimethylpyrazole]-ruthenium(II) hexafluorophosphate (see Figure 2).

The only drawback is its large temperature coefficient, greater than 1 ppm/K; the choice of this reference may also allow comparison with other transition metals such as ^{59}Co ,^{2a} for which the hexacyano complex is used as reference. We consequently choose $\text{Ru}(\text{CN})_6^{4-}$ as reference.

Our results show the spread of the Ru chemical shift scale (9100 ppm) from –1270 to +7821 ppm, which compares quite well with other results on heavy transition metals.^{2,3} Solvent effects are difficult to sort out because of the relative width of the resonances (1–50 ppm). On the other hand, some of the compounds studied were structurally solvent dependent. As an example, the $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ dimer gives no signal in EtOH or CCl_4 and a detectable one in acetone or pyridine (see Table II) corresponding to a species known as $[\text{Ru}(\text{CO})_3\text{Cl}_2\text{-solvent}]$.⁶ The only case in which a reasonable conclusion can be drawn is for $\text{Ru}(\text{CO})_3\text{Cl}_3\text{-Cs}^+$, for which a 25-ppm difference is observed from acetone to ethyl alcohol.

2. Chemical Shift Trends. All the general features of the transition-metal family chemical shifts carefully reviewed in

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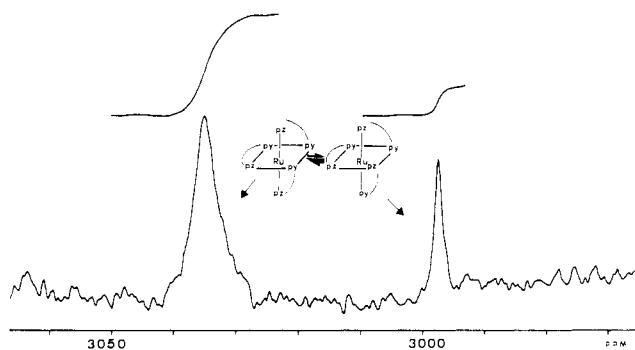


Figure 2. ^{99}Ru spectrum of tris[1-(2-pyridyl)-3,5-dimethylpyrazole]ruthenium(II) hexafluorophosphate showing the *mer-fac* isomerism induced by the ligand (py = pyridine, pz = pyrazole).

ref 3, are found at once in ruthenium NMR (Table II). Thus, the 0 oxidation state lies at the low-frequency end of the scale and there is a definite tendency to go to high frequency with increasing oxidation number. Exciting results are furnished by the ruthenium(+II) oxidation state. In fact, they simply summarize qualitatively the importance of transition-metal NMR, when available, to map out the electronic density around the metal center. The influence of the electronic charge at the ruthenium site is clearly seen from the chemical shift difference (4500 ppm) between $\text{Ru}(\text{bpy})_3^{2+}$ (Ru^{2+} (+II)) and $\text{Ru}(\text{CN})_6^{4-}$ (Ru^{4+} (+II)).

The importance of $\text{Ru}(\text{bpy})_3^{2+}$ type complexes in photochemical catalytic decomposition of water is well-known.⁷ Up to now, very few methods were available to predict the catalytic strength of such complexes or to link unequivocally their chemical properties to some physical observables (e.g., polarographic potential, UV or IR spectra). Ruthenium NMR seems, a priori, to be a very good probe for such a task; as an example, in $\text{Ru}[\text{bis}(\text{N})]_3^{2+}$ compounds, any subtle change in the N moiety (N = heterocyclic ligand) is immediately reflected back into the corresponding ^{99}Ru chemical shift.⁸ Even a *mer-fac* isomerism is detected without difficulty (Figure 2). This sensitivity of ^{99}Ru NMR to both local steric and local electronic environment in such complexes is being actively explored. A word of caution is necessary to end this section on ruthenium chemical shifts. A potassium-39 resonance ($\bar{\nu} = 4.666$ MHz) from any potassium salts of ruthenium compounds will be found around +13.360 ppm. Due to the sensitivity of potassium compared to ruthenium, it is likely that this line will be detected even if the used spectral width will not include the 13.000-ppm region (folding back). We strongly recommend then to avoid ruthenium potassium salts when performing ruthenium NMR.

3. Isotopic Shift Effects on ^{99}Ru Chemical Shift. Table III summarizes the actually measured isotopic shifts. The ^{12}C - ^{13}C isotope shift ($\Delta\delta = 0.37$) parallels the effect found for $\text{Co}(\text{CN})_6^{3-}$, 0.9 ppm.¹⁰

4. Coupling Constants. The measure of $^nJ_{\text{Ru-X}}$ is essentially dependent upon the sharpness of the ruthenium line and hence upon the overall symmetry of the compound under study. The only known values of $^1J_{\text{Ru-X}}$ are listed in Table III.

Comparison of ^{99}Ru NMR with Other Transition-Metal NMR

It is interesting to draw some comparisons between our results and those concerning other transition metals, especially when they belong to the same column of the periodic table.

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Table III. $^1J_{\text{Ru-X}}$ Coupling Constants and Measured Isotopic Shifts ($\Delta\delta$)

	X		
	^{13}C	$^{17}\text{O}^b$	$^{117,119}\text{Sn}$
$^1J_{\text{Ru-X}}$, Hz	44.8 ^a	23.4	846 ^c
$\Delta\delta$	+0.37	+0.02	<i>d</i>

^a In $\text{Ru}(\text{CN})_6\text{K}_4$ in D_2O ; obtained from both ^{99}Ru and ^{13}C NMR. ^b In RuO_4 , 1 M in CCl_4 .⁴ ^c In $\text{Ru}(\text{SnCl}_3)_3\text{Cl}^-(\text{NEt}_4^+)_4$ in CH_3CN ; already obtained by Sn NMR⁹ and clearly visible in the ruthenium spectrum as a multiplet structure due to $^{117,119}\text{Sn}$ natural abundance (see, for example, ref 2, pp 6, 9). ^d Lines too broad to be measured accurately.

If osmium NMR is practically nonexistent,^{2,3} on the other hand, a very well-documented paper¹¹ allows a fruitful parallelism between ^{99}Ru and ^{57}Fe results. Two sets of compounds are strictly comparable, namely, the two metallocenes and the hexacyano complexes. Then

$$\delta_{\text{Fe}(\text{CN})_6} - \delta_{\text{FeCp}_2} = -962 \quad \delta_{\text{Ru}(\text{CN})_6} - \delta_{\text{RuCp}_2} = -1270$$

The ratio $\delta_{\text{Ru}}/\delta_{\text{Fe}} = 1.3$ ($\delta_{\text{Pb}}/\delta_{\text{Sn}} = 3.0$,¹² $\delta_{\text{Te}}/\delta_{\text{Se}} = 1.8$,¹³ $\delta_{\text{Hg}}/\delta_{\text{Cd}} = 2.9$ ¹⁴).

It should be interesting to compare $\text{Fe}(\text{CO})_5$ and $\text{Ru}(\text{CO})_6$, but the latter is known as very unstable, although, taking into account the 1.3 factor between the ^{99}Ru and ^{57}Fe scales, one should expect the $\text{Ru}(\text{CO})_6$ resonance around -3280 ppm, in good agreement with the chemical shift of the ruthenium cluster $\text{Ru}_3(\text{CO})_{12}$ ($\delta = -1208$ ppm) if one remembers the deshielding effect of a metal-metal bond (ref 3, p 47). This expected chemical shift value should be one of the lowest resonance frequencies in Ru NMR. It is also worthwhile to compare the ruthenium results with those for cobalt, for which much data are available.^{2a,3} Then

$$\delta_{\text{Co}(\text{bpy})_3^{3+}} - \delta_{\text{Co}(\text{CN})_6^{3+}} = 6620 \quad (^{99}\text{Ru}: 4518)$$

If we do not take into account the charge difference between cobalt and ruthenium in each compound, then $\delta_{\text{Co}}/\delta_{\text{Ru}} = 1.46$. One more point of comparison is found in $\delta_{\text{M}_x(\text{CO})_{12}}$, where M = Ru or Co and x = 3 (Ru) or 4 (Co). Then, the difference in chemical shift between the hexacyano complex and the metal cluster is equal to 1800 ppm for cobalt and 1200 ppm for ruthenium, which gives again $\delta_{\text{Co}}/\delta_{\text{Ru}} = 1.50$.

Of course, more measurements are necessary to set up a more precise comparison. But right now, one could observe that this general Ru NMR study gives a chemical shift value trend that spans the entire range of ruthenium oxidation states. It is worth noting that Ru NMR furnishes at once the main features of the chemical shift scale for this transition metal. Many of the results obtained are missing for other parent elements (e.g., $\text{Fe}_3(\text{CO})_{12}$, high oxidation states for ^{57}Fe).

Ruthenium NMR and Chemical Applications

Ru NMR seems to be one of the methods to study molecular or electronic environment in ruthenium organometallic chemistry; it can also be used as a tool to go deeper in dynamic studies. We present in this section the study of the $\text{Ru}_2(\text{C-O})_6\text{Cl}_4$ dimer and $\text{Ru}(\text{CO})_3\text{Cl}_3\text{-Cs}^+$ in several solvents.

1. $\text{Ru}_2(\text{CO})_6\text{Cl}_4$. Several authors have already studied the solvent behavior of the $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ dimer.^{6,15,16} It was shown that, in a solvent such as acetone, this μ -chloro-bridged dimer

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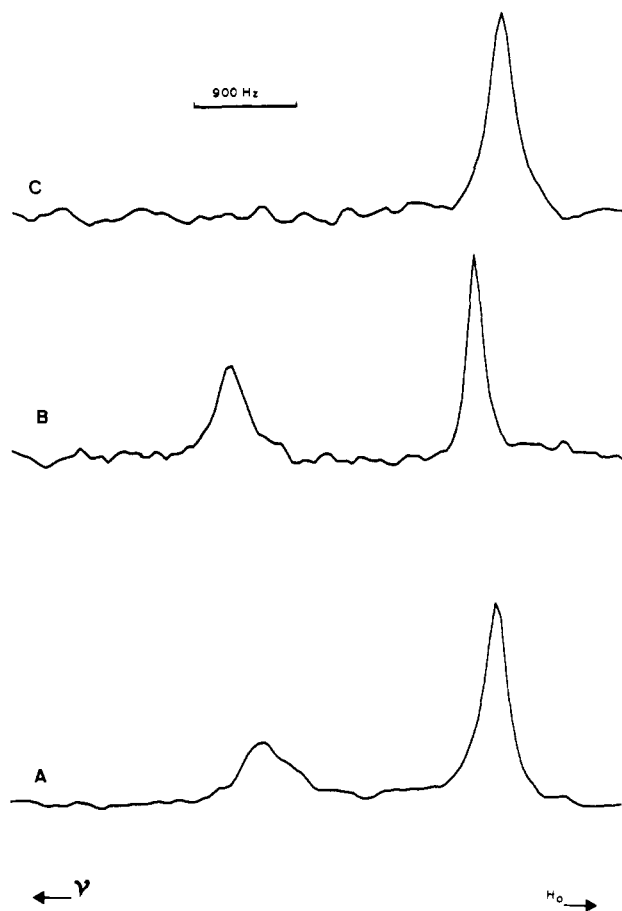


Figure 3. ^{99}Ru spectra of $\text{Ru}(\text{CO})_3\text{Cl}_3\text{Cs}^+$ in D_2O ca. 0.3 M): (A) 296 K; (B) 333 K; (C) 296 K (acidified solution (HCl)).

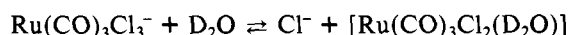
brakes down into two (monomer-solvent) units. In fact, a solution of the dimer in CCl_4 or EtOH failed to give any detectable Ru signal, certainly because of the large electronic field gradient existing around the metal center in the dimeric form. On the contrary, for a solution of the dimer in acetone or pyridine, a line is observed at +1204 or +806 ppm, respectively. Again, when the ethanolic solution of the dimer is acidified with HCl as described in ref 16, a sharp resonance is found at +966 ppm. This latter case corresponds undoubtedly to $\text{Ru}(\text{CO})_3\text{Cl}_3\text{H}^+$ by comparison with $\text{Ru}(\text{CO})_3\text{Cs}^+$, which resonates at +1001 ppm (see Table II). Moreover, due to the sharp line observed, one could infer a *fac* isomer, which should present, theoretically, a null electronic field gradient around the ruthenium atom.¹⁷

The results obtained in acetone and pyridine should correspond to the neutral species $[\text{Ru}(\text{CO})_3\text{Cl}_2\text{-solvent}]$. Benedetti et al.⁶ suggest two possibilities, the first one with the ruthenium atom at the center of a trigonal bipyramid, the second one with the ruthenium atom at the center of an octahedron. The

“solvent dependence” of the chemical shift of this line is characteristic enough to reflect the influence of the solvent coordinating heteroatom X (X = oxygen, nitrogen) (Table II) and rules out together with the sharp lines observed the trigonal bipyramid structure.

2. $\text{Ru}(\text{CO})_3\text{Cl}_3\text{Cs}^+$. The aqueous solutions of $\text{Ru}(\text{CO})_3\text{Cl}_3\text{Cs}^+$ show an interesting behavior that does not seem to have been explored before and that can be enlightened by Ru NMR. Two lines are observed around +1290 and +1100 ppm (Figure 3), which are temperature dependent. The low-field (high-frequency) line is broader and corresponds to a lower symmetry species. Its chemical shift parallels the $[\text{Ru}(\text{CO})_3\text{Cl}_2\text{-acetone}]$ chemical shift, and this species could be viewed as $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{D}_2\text{O})]$. The high-field (low-frequency) line in Figure 3A,B or the only line in Figure 3C has a chemical shift close to that of the *fac*- $[\text{Ru}(\text{CO})_3\text{Cl}_3]\text{H}^+$ compound existing in the acidified solution of the $\text{Ru}_2(\text{CO})_6\text{Cl}_4$ dimer.

One has then



This equilibrium is displaced toward the left side with excess Cl^- and toward the right side with an increase in the temperature. Such a behavior is known for chloro complexes of ruthenium.¹⁸

Conclusion

Our results show unambiguously that ruthenium NMR should bring a new insight in ruthenium chemistry, as a direct probe for structural or electronic changes at the metal center itself. Such a tool will be welcome in organometallic or homogeneous catalysis chemistry. On the other hand, one should keep in mind the quadrupolar nature of both ruthenium isotopes, which will certainly mask a number of lines and render methods such as INEPT^{2b} useless to enhance the sensitivity. Meanwhile, fast-pulsing recording conditions associated with large spectral width and superconducting magnets will allow detection of lines as broad as 1 kHz with a suitably equipped high-resolution high-field spectrometer.

Acknowledgment. We thank Dr. B. R. James (University of British Columbia) for the $\text{Ru}(\text{SnCl}_3)_5\text{Cl}(\text{NET}_4)_4$ sample and Dr. C. Marzin (University of Montpellier) for the tris(1-pyridylpyrazole)ruthenium(II) compound. Dr. Harrison, Union Carbide Corp., is greatly acknowledged for having pointed out to C.B. the imbrication of the ^{99}Ru and K^+ chemical shift ranges. Comments and suggestions from reviewers were helpful in the modification of the original manuscript.

Registry No. ^{99}Ru , 15411-62-8; ^{101}Ru , 14914-61-5; RuCp_2 , 1287-13-4; $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Ru}(\text{CN})_6\text{K}_4$, 15002-31-0; $\text{Ru}_2(\text{CO})_6\text{Cl}_4$, 22594-69-0; $\text{Ru}(\text{CO})_3\text{Cl}_3\text{Cs}^+$, 22594-81-6; $\text{Ru}(\text{SnCl}_3)_5\text{Cl}^-(\text{NET}_4^+)_4$, 78607-98-4; RuO_4 , 20427-56-9; $\text{Ru}(\text{CO})_2\text{Cl}_4^{2-}\text{Cs}^+_2$, 16391-99-4; $\text{Ru}(\text{bpy})_3^{2+}\text{Cl}^-_2$, 14323-06-9; *mer*- $\text{Ru}(\text{PzPy})_3^{2+}(\text{PF}_6^-)_2$, 83928-01-2; *fac*- $\text{Ru}(\text{PzPy})_3^{2+}(\text{PF}_6^-)_2$, 83997-29-9; $[\text{Ru}(\text{NH}_3)_6]^{2+}\text{Cl}^-_2$, 15305-72-3.

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