^{99}Ru NMR Spectroscopy of Organometallic and Coordination Complexes of Ruthenium(II)

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The ruthenium(II) organometallic and coordination complexes of type Ru(X)(Y)$(CO)_2$(*i*-Pr-DAB) (*i*-Pr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene; X, Y = Cl, Br, I, Me, Et, *i*-Pr, *neo*-Pe, Ph_3Sn, Me_3Sn, Ph_3Pb, Ph_3Ge, $Mn(CO)_5$, $RuCp(CO)_2$) have been analyzed by means of ^{99}Ru NMR spectroscopy. The ^{99}Ru NMR resonances for these compounds are generally sharp, allowing scalar couplings to group 14 nuclei to be observed. Correlation times τ_c have been determined from NOE factors and ^{13}C T_1 values for selected compounds and were found to parallel the molecular weight of the compounds studied. The M−Ru−M′ and M−Ru−X complexes have ^{99}Ru NMR resonances in distinct chemical shift regions. In the series M−Ru−M′ a correlation between the inverse of the crystal field splitting energy ΔE and $\delta(^{99}\mathrm{Ru})$ exists. These complexes have a HOMO which is delocalized over the M−Ru−M′ σ system and a LUMO which has predominantly π^*-DAB character; therefore, $(\Delta E)^{-1}$ is dominant in the paramagnetic shielding of the ruthenium nucleus. The difference in the observed chemical shift regions of the M−Ru−M′ and M−Ru−X compounds can be attributed to differences in d-orbital radius $\langle r^{-3}\rangle_d$, which is in good agreement with previously performed DFT calculations. For the Ru(I)(R)$(CO)_2$(*i*-Pr-DAB) complexes, $\delta(^{99}\mathrm{Ru})$ follows the same trend as for a series of iron compounds, indicating an increase of the Ru−C bond length in the series Me < Et < *neo*-Pe < *i*-Pr. This finding emphasizes the power of transition-metal NMR spectroscopy in the structural analysis of transition-metal complexes. Furthermore, ^{99}Ru NMR provides a tool to identify and assign isomers in mixtures of Ru−polypyridyl complexes. The ^{99}Ru NMR resonances of coordination isomers of various triazole-containing ruthenium complexes are found at different frequencies, which can be used to unambiguously identify coordination isomers in mixtures by means of ^{99}Ru NMR spectroscopy. The $\delta(^{99}\mathrm{Ru})$ value is found to increase with increasing redox potential of the polypyridyl compounds.

Introduction

Given the importance of ruthenium in various fields of chemistry, e.g. homogeneous catalytic reactions[1] and photochemistry,[2] it is surprising that relatively few ^{99}Ru NMR spectroscopic studies have been conducted. Transition-metal NMR can be used to explore the structure, electronic properties, and catalytic activity of transition-metal complexes.[3] Many coordination and organometallic chemists have been reluctant to use transition-metal NMR, the main reason being that approximately 75% of the transition-metal nuclei have a nuclear quadrupole moment ($I > {}^1/_2$), resulting in (extremely) broad resonance lines in the NMR spectrum.[4] Specifically for ruthenium, a very limited amount of chemical shift data is available in the literature for comparison. Other reasons may be lack of experience concerning NMR spectroscopy of quadrupole nuclei and lack of spectrometer hardware and time. Nevertheless, several classes of compounds have been studied successfully by means of ^{99}Ru NMR spectroscopy in solution.[5]

Both ruthenium isotopes (^{99}Ru, $I = {}^3/_2$; ^{101}Ru, $I = {}^5/_2$) are quadrupole nuclei, the latter of which has a large quadrupole moment (^{99}Ru, $Q = 0.076 \times 10^{-24}$ cm^{-2};

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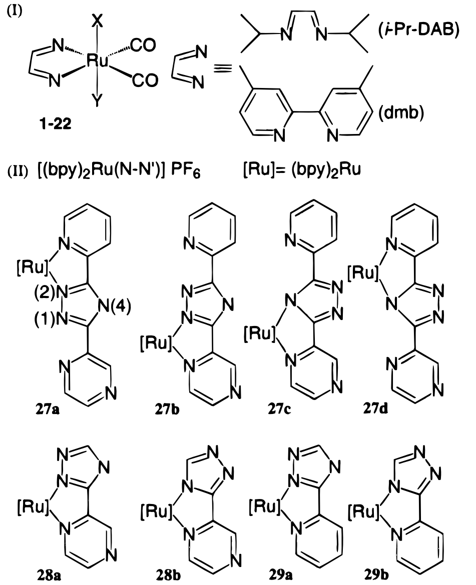

Figure 1. Generic structures of the octahedral ruthenium(II) compounds and ligands. X, Y = $SnMe_3$, $SnPh_3$, $PbPh_3$, $GePh_3$, Me, Et, *neo*-Pe, *i*-Pr, $Mn(CO)_5$ or $RuCp(CO)_2$, Cl, Br, I.

^{101}Ru, $Q = 0.44 \times 10^{-24}$ cm^{-2}). Therefore, the ^{99}Ru nucleus is favored for NMR spectroscopy, despite the lower natural abundance (^{99}Ru, 12.7%; ^{101}Ru, 17.1%).[5a] Another problem encountered in ^{99}Ru NMR is the low resonance frequency (13.82 MHz at 7.05 T), resulting in acoustic ringing that causes distorted baselines.[6] Virtually nothing is known about the dependence of $\delta(^{99}Ru)$ on structure and temperature.

In some cases, a distinction between coordination isomers of ruthenium complexes based on routine ^{1}H and ^{13}C NMR is tedious. In such cases, ^{99}Ru NMR could be very helpful or even decisive. Here we present a ^{99}Ru NMR study of two classes of organometallic complexes, in which we demonstrate the accessibility of NMR data of this nucleus and the analytical power of this technique. We have explored the feasibility of analysis of mixtures of a number of coordination isomers by means of ^{99}Ru NMR spectroscopy. It clearly demonstrates that ^{99}Ru NMR complements routine analytical techniques, e.g. ^{1}H and ^{13}C NMR, UV/vis, IR, resonance Raman spectroscopy, and electrochemical data, in ruthenium chemistry.

Results

Table 1. ^{99}Ru Chemical Shifts, Line Widths and UV/Vis Absorption Maxima of Compounds 1−29[a]

compd	X	Y	$\delta(^{99}Ru)$[b]	$\Delta\nu_{1/2}$[c]	$(\Delta E)^{-1}$[d]
1[e]	Ph_3Sn	Ph_3Sn	−116 ± 1	96 ± 2	515
2	Ph_3Pb	Ph_3Pb	200 ± 5	1.5 ± 0.1 kHz	543
3	Ph_3Sn	Ph_3Ge	−40 ± 1	137 ± 2	519
4[f]	Ph_3Pb	Ph_3Ge	115 ± 1	162 ± 2	538
5	Me_3Sn	Ph_3Sn	−222 ± 1	122 ± 2	515
6[g]	Me_3Sn	Me_3Sn	−316 ± 1	100 ± 5	513
7	Ph_3Sn	Me	100 ± 5	1.7 ± 0.1 kHz	521
8	Ph_3Sn	Cl	669 ± 1	660 ± 5	435
9	Ph_3Pb	Cl	920 ± 5	800 ± 10	444
10	Me	Cl	794 ± 1	40 ± 2	435
11	Me	Br	712 ± 1	25 ± 2	449
12	Me	I	551 ± 1	30 ± 2	463
13	Et	I	618 ± 1	60 ± 2	453
14	*neo*-Pe	I	625 ± 1	67 ± 2	455
15	*i*-Pr	I	721 ± 1	83 ± 2	479
16	Cl	Cl	1993 ± 1	695 ± 10	423
17	I	I	1036 ± 1	1435 ± 10	454
18	Ph_3Sn	$Mn(CO)_5$	103 ± 5	1.2 ± 0.1 kHz	542
19	Ph_3Sn	$RuCp(CO)_2$	−185 ± 5	2.8 ± 0.1 kHz	570
20[h]	Ph_3Sn	Ph_3Sn	100 ± 15	4.4 ± 0.1 kHz	518
21[i]	Me	I	771 ± 1	30 ± 2	405
22[j]	I	I	1041 ± 2	700 ± 10	413
23	$Ru_3(CO)_{12}$		−1286 ± 1	75 ± 2	
24	$[RuCp(CO)_2]_2$		−1338 ± 2	860 ± 10	
25[k]	$K_4Ru(CN)_6$		≡0	0.5	
26[m]	$[Ru(bpy)_3]Cl_2$		4562	86 ± 2	
27a[m]	$[Ru(bpy)_2(ppt)](PF_6)$		4987	530 ± 5	
27b[m]	$[Ru(bpy)_2(ppt)](PF_6)$		4598	500 ± 5	
27c[m]	$[Ru(bpy)_2(ppt)](PF_6)$		4606	950 ± 10	
27d[m]	$[Ru(bpy)_2(ppt)](PF_6)$		4734	650 ± 5	
28a[m]	$[Ru(bpy)_2(pztr)](PF_6)$		4678	310 ± 5	
28b[m]	$[Ru(bpy)_2(pztr)](PF_6)$		4817	215 ± 5	
29a[m]	$[Ru(bpy)_2(pytr)](PF_6)$		4700	340 ± 5	
29b[m]	$[Ru(bpy)_2(pytr)](PF_6)$		4853	290 ± 5	

[a] All ^{99}Ru NMR spectra have been recorded in THF at $T = 313$ K unless stated otherwise. The ligands are specified in Figure 1. [b] In ppm relative to $K_4Ru(CN)_6$. [c] In Hz unless marked otherwise. [d] In nm. [e] $^1J(^{117/119}Sn, ^{99}Ru) = 335 \pm 5$ Hz. [f] $^1J(^{207}Pb, ^{99}Ru) = 435 \pm 5$ Hz. [g] $^1J(^{117/119}Sn, ^{99}Ru) = 256 \pm 5$ Hz. [h] NN = 4,4′-dimethyl-2,2′-dipyridyl. [i] NN = bis(*p*-anisylimino)acetonaphthene: van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88. [j] NN = $(CH_3CN)_2$. [k] Saturated solution in D_2O at 293 K. [l] In D_2O at 313 K. [m] In CH_3CN at 313 K. The polydentate nitrogen ligands have been abbreviated as follows: 3-(pyridin-2-yl)-1,2,4-triazole, Hpytr; 3-(pyrazin-2-yl)-1,2,4-triazole, Hpztr; 3-(pyrazin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole, Hppt.

A ^{99}Ru NMR study of two classes of ruthenium compounds, shown in Figure 1, has been conducted. The collected data have been compiled in Table 1. The compounds **1**−**25** (class **I**) and **26**−**29** (class **II**) are found in distinct chemical shift regions. The organometallic compounds **1**−**25** have chemical shifts ranging from −1338 to 1041 ppm, whereas the coordination complexes **26**−**29** are observed at much higher values, between 4606 and 4987 ppm.

For a saturated solution of $Ru(Cl)(Me)(CO)_2$(*i*-Pr-DAB) (**10**) in THF, a linear dependence of $\delta(^{99}Ru)$ on the temperature between 303 and 333 K was observed (four points) which amounts to +1.1 ppm/K. A saturated solution of $[Ru(bpy)_3]Cl_2$ (**26**) in D_2O exhibited a linear dependence of $\delta(^{99}Ru)$ on the temperature between 293 and 353 K (four points) of +1.6 ppm/K. At elevated temperatures the line widths of ^{99}Ru resonances were found to decrease. The line width of **10** decreased from 39 Hz at 303 K to 32 Hz at 333 K; the line width of **26** was found to decrease from 86 Hz at 293 K to 37 Hz at 353 K.

We did not observe any dependence of the ^{99}Ru chemical shift on the concentration for **10** in THF at 313 K from 9.6 to 76.2 mM (four points) nor for **26** in D_2O at 293 K from 10.9 to 45.0 mM (five points). As we measured our compounds at concentrations varying from 10 to 100 mM and carefully thermostated the samples, we estimate our chemical shifts to be accurate

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Table 2. Relaxation Times T_1(^{13}C), T_{1DD}(^{13}C), NOE Factors, and Correlation Times (τ_c) of Selected Complexes[a]

compd	X	Y	$\Delta\nu_{1/2}$[b]	T_1(^{13}C)[c]	NOE	T_{1DD}-(^{13}C)[d]	τ_c[e]
1	Ph_3Sn	Ph_3Sn	96 ± 2	0.92	2.69	1.89	43
7	Ph_3Sn	Me	1.7 ± 0.1 kHz	1.29	2.83	1.41	33
8	Ph_3Sn	Cl	660 ± 5	1.33	2.82	1.46	32
10	Me	Cl	40 ± 2	3.32	2.20	5.53	8.4
17	I	I	1435 ± 10	2.10	2.58	2.66	18

[a] Determined for the imine carbon in THF-d_8 at 313 K. [b] In Hz. [c] In s. [d] In s. [e] In 10^{-12} s.

to within ±2 ppm. The error is due mainly to small ambiguities in the determination of the peak maximum of broad resonances.

The resonance lines of the compounds **1**−**25** are generally narrow; line widths of the complexes are found to vary from 25 Hz to 4.4 kHz. The complexes **27**−**29** exhibit line widths ranging from 200 to 900 Hz. The complexes **1**−**6** have line widths from 96 to 162 Hz, the one exception being **2**. Compounds **8**, **9**, and **16** have line widths of 660, 800, and 695 Hz, respectively. Compounds **7**, **18**, and **19** exhibit even broader resonance lines ((1.2 ± 0.1)−(2.8 ± 0.1) kHz). The sharpest resonance lines are found for the complexes **10**−**15**, exhibiting line widths between 25 and 83 Hz. For complex **19** we were able only to observe the resonance of the central ruthenium atom at −185 ppm; the ^{99}Ru resonance of the $RuCp(CO)_2$ moiety is too broad to be observed.

Rotational correlation times (τ_c) were obtained for the five representative complexes **1**, **7**, **8**, **10**, and **17**. The acquired T_1(^{13}C) and NOE values and calculated T_{1DD}-(^{13}C) and τ_c values for the imine (iPrN=C(H)C(H)=NiPr) have been compiled in Table 2.

Interestingly, for three complexes, scalar coupling of the spin $^1/_2$ nuclei $^{117/119}$Sn or ^{207}Pb to the ^{99}Ru nucleus could be observed: (^1J($^{117/119}$Sn, ^{99}Ru) = 335 ± 5 Hz, **1**; ^1J($^{117/119}$Sn, ^{99}Ru) = 256 ± 5 Hz, **6**; (^1J(^{207}Pb, ^{99}Ru) = 435 ± 5 Hz, **4**).

Protonation of the triazole moiety[7] of compound **29a** by the addition of 8 equiv of a strong acid (HBF_4) to an acetonitrile solution of **29a** results in a chemical shift change of the ^{99}Ru signal of +126 ppm and a broadening of the line from 310 to 620 Hz.

For compounds **27**−**29** (Figure 1), all ruthenium resonances could be readily identified and assigned. The resonances of the compounds **28a**,**b** have been assigned on the basis of comparison with an authentic, pure sample of **28b** and those of the compounds **29a**,**b** by comparison with an authentic, pure sample of **29a**. For the mixtures of compounds **28a**,**b**, a $\Delta\delta$(^{99}Ru) value of 140 ppm between isomers was observed. For the similar compounds **27a**,**d** and **29a**,**b**, comparable $\Delta\delta$(^{99}Ru) values of 253 and 153 ppm were observed between their respective isomers, which differ in whether N-1 or N-4 is coordinated to ruthenium. For **27b**,**c**, a $\Delta\delta$(^{99}Ru) value of 8 ppm was observed. By comparison to the authentic pure samples mentioned above, the ^{99}Ru signals at higher frequency were assigned to the isomers with the triazole coordinating via N-4 (Figure 1). The trend in the ^{99}Ru line width supports this assignment: coordination of the triazole via N-4 as in **27c**,**d**, **28b**, and **29b** to the ruthenium results in narrower resonance lines than in **27a**,**b**, **28a**, and **29a**. A similar observation can be made for the substitution of a pyridine (**29**) by a pyrazine (**28**), which leads to a decrease of the line width and of a shift toward lower δ(^{99}Ru).

Discussion

Compounds of class **I** have so far not been studied by means of ^{99}Ru NMR, while the ^{99}Ru data of compounds of class **II** constitute an important supplement to the data set of similar compounds studied previously.

1. Complexes of the Type Ru(X)(Y)(CO)$_2$(*i*-Pr-DAB). A. Chemical Shift. As commonly accepted, the chemical shift of transition-metal nuclei is determined by the paramagnetic shielding term according to the Ramsey equation, shown in eq 1:[8]

$$\sigma = \sigma_d - \sigma_p$$

where

$$-\sigma_p = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{e^2}{m^2}\right)(\Delta E)^{-1}\langle r^{-3}\rangle_d\langle 0|L^2|0\rangle \qquad (1)$$

This equation describes the shielding in a d^6-octahedral complex, summing over the d-electron excitations.

Since δ(^{99}Ru) will be governed by the paramagnetic contribution, the crystal field splitting ΔE and the inverse cube of the radius of the valence shell d orbitals $\langle r^{-3}\rangle_d$ are important parameters. As the d-electron configuration and the symmetry of the complexes does not vary or only slightly varies for the complexes studied, the factor $\langle 0|L^2|0\rangle$ (imbalance of charge) remains essentially constant. For a detailed discussion of the influence of the various parameters on the transition-metal chemical shift see ref 9. Due to the large chemical shift range of ^{99}Ru (10 000 ppm[5c]) subtle changes in the chemical structure of complexes result in relatively large chemical shift changes.

The general trends observed for δ(^{99}Ru) are in agreement with the relative positions of the respective ligands in the spectrochemical series. For **26**−**29** all ligands are low in the spectrochemical series; therefore, these compounds occur at high δ(^{99}Ru). The substituents in the compounds **1**−**25** are placed higher in the spectrochemical series and hence have lower δ(^{99}Ru) values.

Dependence on Temperature. The dependence of δ(^{99}Ru) on temperature and concentration was investigated for two compounds. The temperature dependence of the chemical shift is the result of the population of higher vibrational states of the electronic ground state, resulting in a larger $(\Delta E)^{-1}$ and, hence, higher chemical shift values at elevated temperatures. The values found for the temperature dependence (+1.1 ppm/K for **10**; +1.6 ppm/K for **26**) of the chemical shift are slightly higher than those observed for e.g. δ(^{187}Os) (+0.7 ppm/K)[3e] and δ(^{103}Rh) (+0.5−1 ppm/K).[10]

Dependence on $\langle r^{-3}\rangle_d$. Lower δ(^{99}Ru) values are expected for larger internuclear distances Ru−X be-

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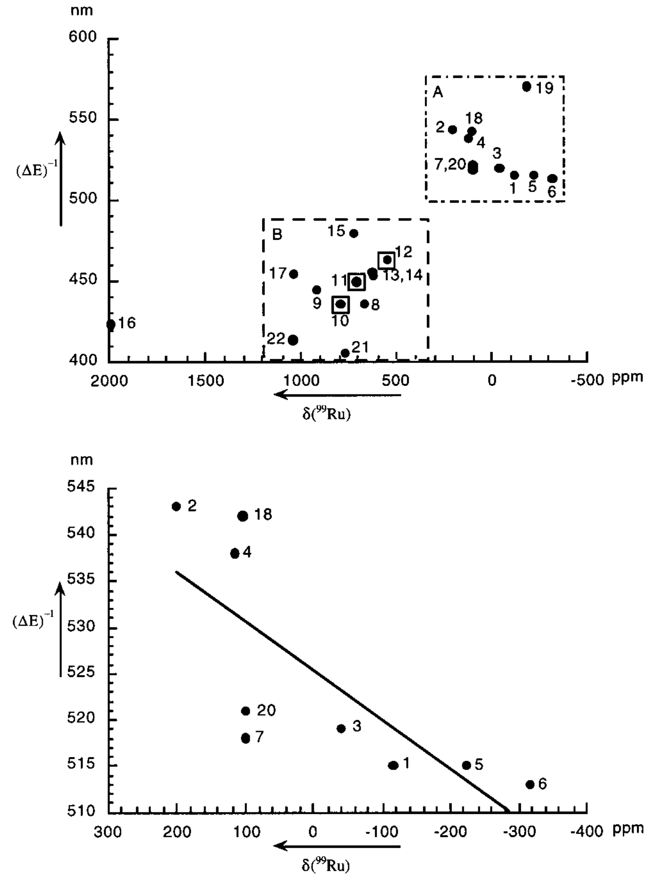

Figure 2. (a) Correlation between $(\Delta E)^{-1}$ in nm and $\delta(^{99}Ru)$ in ppm for compounds **1**−**22**: (—) Me−Ru−X; (-·-, A) M−Ru−M′; (- - -, B) M−Ru−X. M, M′ = SnR_3, PbR_3, GeR_3, $Mn(CO)_5$, or $RuCp(CO)_2$; X = Cl, Br, I. (b) Correlation between $(\Delta E)^{-1}$ in nm and $\delta(^{99}Ru)$ in ppm for compounds **1**−**7**, **18**, and **20**.

cause of a smaller $\langle r^{-3}\rangle_d$ term in eq 1. In this respect, the complexes **10**−**12** exhibit a normal halogen dependence of the shielding according to the nephelauxetic series Cl < Br < I (solid lines in Figure 2a).[9] Indeed, substitution of chloride by bromide results in a more shielded ruthenium nucleus by 82 ppm, and substitution of the bromide by iodide causes a further shielding by 161 ppm.

The $\delta(^{99}Ru)$ values of compounds **12**−**15** decrease in the order Me < Et < *neo*-Pe < *i*-Pr. The same order was found for $\delta(^{57}Fe)$ of the compounds Fe(R)(Cp)(CO)$_2$ (R = Me, Et, *neo*-Pe, *i*-Pr).[11] This can be attributed to the $\langle r^{-3}\rangle_d$ term as well, since it is known that the C−Fe bond length increases in the order Me < *n*-Bu < *i*-Pr (SOS-DFPT calculations[11]). This implies that the orbital overlap is largest for Me; hence, *r* is large and $\langle r^{-3}\rangle_d$ relatively small compared to the other alkyl groups. Recently, similar changes were observed and calculated for $\delta(^{103}Rh)$ with increasing Rh−N and Rh−P distance.[12] As the same trend is observed for $\delta(^{99}Ru)$, the Ru−C bond lengths are expected to increase in the order Me < Et < *neo*-Pe < *i*-Pr.

Dependence on $(\Delta E)^{-1}$. According to eq 1 the $\delta(^{99}Ru)$ value is substantially determined by the inverse of the average excitation energy $(\Delta E)^{-1}$. The $\delta(^{99}Ru)$ as well as ΔE values are related to the electronic ground and first excited states of the compounds studied.[3g] Hence, it is interesting to see whether a correlation exists between $\delta(^{99}Ru)$ and $(\Delta E)^{-1}$. In Figure 2a the ^{99}Ru chemical shift is plotted against the average excitation energy (in nm, which is proportional to $(\Delta E)^{-1}$), as determined from UV/vis spectroscopy in THF for compounds **1**−**22**. In this figure, two distinct regions can be observed. The first region contains the compounds with two σ-donating group 14 elements bound directly to the ruthenium center: M−Ru−M′ (compounds **1**−**7**, **18**, **20**, where M and M′ denote substituents of the type SnR_3, PbR_3, GeR_3, $Mn(CO)_5$, or RuCp(CO)$_2$). Complex **18**, which contains a manganese pentacarbonyl moiety, also falls in this region (A in Figure 2a). These complexes have ^{99}Ru chemical shifts between 200 and −300 ppm and $(\Delta E)^{-1}$ values ranging from 510 to 545 nm. The compounds containing both a group 14 element and a halogen bound to the ruthenium center, M−Ru−X (compounds **8**−**15** and **21**), are found in a different region of Figure 2a. These compounds have chemical shifts from 1100 to 550 ppm and $(\Delta E)^{-1}$ values ranging from 400 to 475 nm (B in Figure 2a). According to the Ramsey equation the trend should be reverse; a decreasing $(\Delta E)^{-1}$ value should result in a lower chemical shift.

The difference in ^{99}Ru chemical shifts between the complexes M−Ru−M′ (**1**−**7**) and M−Ru−X (**8**−**15**) can be explained by invoking the difference in character of the HOMO in these two types of complexes, which has implications for the $\langle r^{-3}\rangle_d$ as well as the $(\Delta E)^{-1}$ term in the Ramsey equation. As has been determined from DFT calculations and resonance Raman spectroscopy,[13] the HOMO in the complexes M−Ru−M′ has σ(M−Ru−M′) character, whereas the HOMO in the complexes M−Ru−X has mixed dπ(Ru)/pπ(X) character. The HOMO of the M−Ru−M′ (**1**−**7**) complexes has σ(M−Ru−M′) character because the σ orbital lies higher in energy than the dπ(Ru) orbitals due to the electron-donating character of the axial ligands. The LUMO of the complexes **1**−**22** is located on the bidentate nitrogen ligand (π*) and does not change in the series **1**−**19**. This results in a smaller HOMO/LUMO energy gap; hence, a larger $(\Delta E)^{-1}$ value is observed for the M−Ru−M′ complexes **1**−**7** compared to the M−Ru−X complexes **8**−**15**. Due to the different character of the HOMO different electronic transitions are observed in the UV/vis spectra; for the M−Ru−X complexes this transition is apparently not as important to the paramagnetic shielding in the Ramsey equation as for the complexes M−Ru−M′ (vide infra).

Furthermore, the highest electron density in the M−Ru−M′ complexes lies farther from the ruthenium center with respect to that of the complexes M−Ru−X. Hence, the radial factor $\langle r^{-3}\rangle_d$ is smaller for complexes of type M−Ru−M′, resulting in a more shielded ^{99}Ru

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nucleus and, hence, lower chemical shift values.[9] Therefore, for the whole series of compounds **1**−**25**, the correlation with the energy of the lowest transition does not follow eq 1. The difference in ΔE related to the character of the HOMO *does* cause the complexes M−Ru−M′ and M−Ru−X to be found in distinctly separate regions of Figure 2a, but the $\langle r^{-3}\rangle_d$ term is apparently the decisive term for the ^{99}Ru chemical shift in these types of complexes.

A trend between $(\Delta E)^{-1}$ and the $\delta(^{99}\text{Ru})$ value is observed in the homologous series of the complexes of type M−Ru−M′ (**1**−**7**), shown in Figure 2b. Even complexes **18** and **20** fit the observed trend. The correlation of $\delta(^{99}\text{Ru})$ with $(\Delta E)^{-1}$ is not very good, since $\langle r^{-3}\rangle_d$ also plays a significant role.

B. Line Widths. The broad resonance lines in ^{99}Ru NMR are the result of the very efficient quadrupolar relaxation mechanism. In eq 2 the formula for the line width at half-height, which is proportional to $1/\pi T_1$, for nuclei with $I > {}^1/_2$, is given[4]

$$\Delta\nu_{1/2} = \frac{1}{\pi T_1} = \frac{1}{\pi T_2} = \frac{3\pi}{10}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\eta_s}{3}\right)\chi^2\tau_c \qquad (2)$$

where I denotes the nuclear spin, η_s is the asymmetry parameter of the complex, χ is the nuclear quadrupole coupling constant, and τ_c is the rotational correlation time of a molecule in solution. The rotational correlation time is dependent on the viscosity and temperature of the solvent according to eq 3

$$\tau_c = \frac{A\eta_v}{kT} \qquad (3)$$

where η_v is the bulk viscosity of the solvent, k is the Boltzmann constant, T is the temperature, and A is a constant determined by the molecular volume of the solute. Hence, the observed decrease of the line widths of Ru(Cl)(Me)(CO)$_2$(*i*-Pr-DAB) (**10**) and [Ru(bpy)$_3$]Cl$_2$ (**26**) with increase of temperature is in agreement with eqs 2 and 3: the rotational correlation time decreases since T increases and the viscosity decreases.

Electric Field Gradient. The variations of the ^{99}Ru line widths for the compounds **1**−**29** are the result of the variations in symmetry and τ_c (see below) as a consequence of the various substituents in the compounds. More asymmetric compounds might induce a larger electric field gradient (EFG)[14] at the ^{99}Ru nucleus, resulting in larger nuclear quadrupole coupling constants (χ) and broader NMR resonances.[4] As compounds **1**−**19** have the same ligands in the equatorial plane (*i*-Pr-DAB and CO), the discussion can in a first approximation be limited to the axial groups. We are assuming that the EFG in the equatorial plane is not very large, since two π-bonding ligands, an α-diimine and CO, are present.

Despite the fact that the variation of the EFG causing the differences in line widths is difficult to quantify, several trends can be observed. The compounds **1**−**6** have narrow resonances in the range of 96−162 Hz (the exception being **2**). These compounds have group 14 elements for X and Y (Figure 1), which are the same or very similar (**1**, **5**, **6**), resulting in a low EFG. Changing one of these groups to a methyl or a chloride results in a dramatic increase of the line width (**7**−**9**). Introduction of two large groups at the axial position results in distortion of the complexes resulting in larger EFG, which might account for the line width of **2**. Similarly, the introduction of a transition metal at one of the axial positions results in a dramatic increase of the line width (**18**, **19**). Furthermore, an increase of the EFG is observed changing *i*-Pr-DAB (**1**) to the aromatic dmb (**20**) dinitrogen ligand.

The compounds **10**−**15** have surprisingly narrow resonances. Although intuitively these compounds appear to be more asymmetric than compounds **1**−**6**, this particular configuration results in a very low EFG at the ruthenium nucleus.[14] The variation of the halide in the compounds **10**−**12** causes only small variations, close to the experimental error, in the line widths. Increasing the Ru−C bond length (see above) from **12** to **15** causes an increase of the line width. Currently several of these complexes have been subjected to detailed DFT calculations in order to quantify the subtle influence of the variation of the ligands in octahedral ruthenium compounds on the EFG.

Rotational Correlation Time. As the complexes **1**−**25** have different molecular weights and sizes, variations in rotational correlation times are to be expected. The rotational correlation time τ_c can be determined from the ^{13}C relaxation time $T_{1DD}(^{13}\text{C})$ due to C−H dipolar interactions[15]

$$\frac{1}{T_{1DD}(^{13}\text{C})} = \frac{\mu_0^2 N[\gamma(^1\text{H})]^2[\gamma(^{13}\text{C})]^2\hbar^2\tau_c}{16\pi^2 r_{CH}^6} = NK\tau_c \qquad (4)$$

where $K = 2.147 \times 10^{10}$ s^{-2} if the C−H bond lengths (r_{CH}) are assumed to be constant (1.09 Å). The $T_{1DD}(^{13}\text{C})$ value can be obtained from the $T_1(^{13}\text{C})$ and NOE values:

$$\text{NOE} = 1 + \frac{2[T_1(^{13}\text{C})]}{T_{1DD}(^{13}\text{C})} \qquad (5)$$

We observe large differences between the rotational correlation times of complexes **1**, **7**, **8**, **10**, and **17** (Table 2). The shortest rotational correlation time observed in this study is found for complex **10**, accounting for the narrow resonance line observed. It can be seen that the line widths of complexes **11**−**15** increase with increasing molecular weight, in particular as one goes from **12** to **15**. The rotational correlation time generally parallels the molecular weight of the complexes. It can be seen that the symmetric complex **1** has a long rotational correlation time, which accounts for the rather large line width observed, especially compared to the less symmetric **10**. The symmetries of complexes **1** and **17** are similar; hence, the line width of **17** would be expected to be lower than that of complex **1** on the basis of the rotational correlation time. The larger line width of complex **17** compared to that of **1** must therefore be caused by the EFG, which is higher in complex **17**.

The small difference in chemical shifts between **8** and **10** indicates similar electronic properties of the axial

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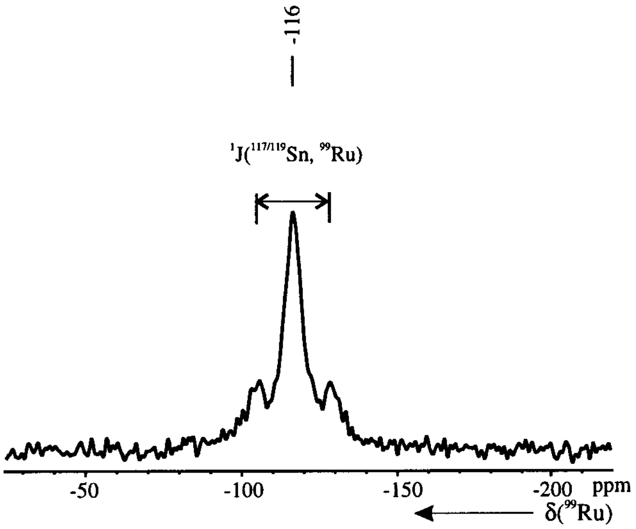

Figure 3. 13.82 MHz ^{99}Ru NMR spectrum of compound **1** with $^{117/119}$Sn satellites.

ligands; the difference in line width can therefore be attributed mainly to the difference in τ_c. Although the τ_c values of complexes **7** and **8** are comparable, the line width of **7** is 3 times that of **8**, which can be attributed mainly to the different EFG's of the complexes. The large influence of the rotational correlation time on the quadrupolar relaxation mechanism is in agreement with that observed for ^{91}Zr line widths.[15b] For comparison, the rotational correlation times of zirconocene dichloride complexes with a molecular weight comparable to that of compound **10** vary between 3.5×10^{-12} and 19.7×10^{-12} s. The ruthenium compounds of higher molecular weight have relatively long rotational correlation times.

Scalar Coupling. The complexes **1**, **4**, and **6** exhibit narrow resonance lines relative to the scalar coupling with the group 14 elements; hence, we could determine the scalar coupling of the spin $^1/_2$ nuclei $^{117/119}$Sn and ^{207}Pb to the ^{99}Ru nucleus for three complexes (**1**, **4**, **6**). The difference in magnitudes of the scalar couplings in compounds **1** and **6** is attributed to the Ru–Sn bond length, being shorter for **1**, in agreement with larger s character and, hence, a larger coupling constant. The ^{99}Ru spectrum of complex **1** is shown in Figure 3 and displays a typical ^{99}Ru signal with $^{117/119}$Sn satellites. To date, only three other scalar couplings to ^{99}Ru are known:[5c] $^1J(^{99}Ru-^{13}C) = 44.8$ Hz in $K_4Ru(CN)_6$, $^1J(^{99}Ru-^{17}O) = 23.4$ Hz in RuO_4, and $^1J(^{99}Ru-^{117/119}Sn) = 846$ Hz in $(NEt_4)_4[Ru(SnCl_3)_5Cl]$.

2. Mixtures of Tris(polypyridyl)ruthenium(II) Complexes. We studied mixtures of the complexes **27**–**29** shown in Figure 1. These compounds were chosen to determine whether the different coordination modes[7] of the polydentate ligands could be observed in the ^{99}Ru NMR. Analysis of these mixtures by ^{1}H and ^{13}C NMR can be troublesome due to overlapping signals. The use of nitrogen NMR (either ^{14}N or ^{15}N) could resolve the matter of the coordination mode of the ligands. However, both of the nitrogen isotopes are difficult to measure, because of either the low natural abundance (^{15}N) or the quadrupole moment of the nucleus (^{14}N). ^{15}N NMR is possible via inverse correlation spectroscopy, employing nonzero scalar couplings of ^{15}N to ^{1}H. The coupling constants of protons to nitrogens in the triazole are extremely small; correlation spectroscopy is therefore difficult. Instead, recourse could be taken to ^{14}N NMR, but the chemical shift range of ^{99}Ru exceeds that of nitrogen by an order of magnitude. As small differences in coordination modes are expected to be reflected more clearly in ^{99}Ru NMR spectra, we chose ^{99}Ru NMR spectroscopy to study the coordination isomers **27**–**29**. Previously, cis/trans isomerism has been successfully studied by means of ^{99}Ru NMR for similar compounds,[5e,f,h] but mixtures of coordination isomers of compounds such as **27**–**29** have to date not been studied by means of ^{99}Ru NMR. A typical spectrum of the mixture **28a**,**b** is presented in Figure 4, which shows two well-separated ^{99}Ru signals.

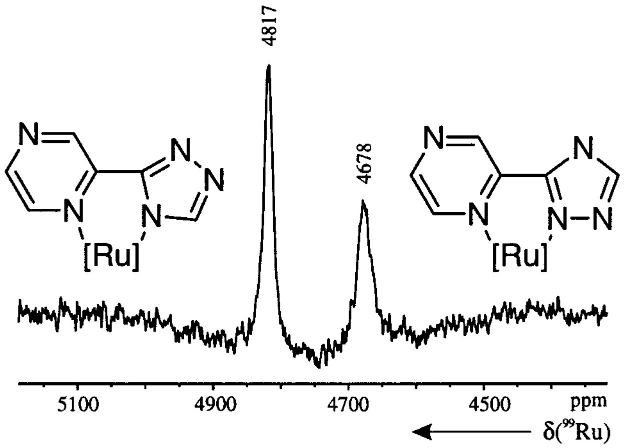

Figure 4. ^{99}Ru NMR spectrum of a mixture of compounds **28a**,**b**. [Ru] = $[Ru(bpy)_2](PF_6)$.

Comparison of the spectrum of the mixture **28a**,**b** with the spectrum of pure **28b** and of **29a**,**b** with the spectrum of pure **29a** leads to identification of the resonances. For the mixtures **27a**,**b**, **27c**,**d**, and **29a**,**b** the resonances of the isomers were well-separated in the ^{99}Ru NMR spectrum and the respective isomers have been assigned by analogy.

From the spectra of **28a**,**b** compared to those of **29a**,**b** it appears that the ^{99}Ru nuclei of the pyridine-coordinated compounds (**29a**,**b**) resonate at lower frequency than those of the pyrazine-coordinated complexes (**28a**,**b**). It is also apparent that the line width of the pyridine-coordinated complexes is slightly larger than that of the pyrazine species, which is caused by the higher electric field gradient at the ruthenium nucleus resulting from the different electronic properties of the pyridine compared to the pyrazine. The assignments above for **28** and **29** lead to the assignment of **27a**,**b**. The pyridine-coordinated complex **27a** has a higher chemical shift value and a wider resonance than the pyrazine complex **27b**. Similarly, complex **27c** has a lower chemical shift value and larger line width than complex **27d**.

It can be seen that the stronger σ-donor (N1/N2 coordination) leads to a lower ruthenium chemical shift. This parallels the redox potentials determined previously:[22a,b] **28a** has a redox potential 100 mV higher and

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29a a redox potential 70 mV higher for the N4 coordinated species; both have higher ruthenium chemical shifts than the N2-coordinated species.

The addition of 8 equiv of HBF_4 to an acetonitrile solution of **29a** results in a ^{99}Ru chemical shift change of +126 ppm and a line broadening of the ^{99}Ru resonance from 310 to 620 Hz. The protonation of the triazole results in a weaker donor nitrogen, the redox potential increases by 300 mV, and the chemical shift increases, in agreement with the trend found for **28a**,**b** and **29a**,**b**. Furthermore, the reduced Coulombic interaction most likely leads to a larger Ru−N internuclear distance, leading to a larger $\langle r^{-3}\rangle_d$, which is reflected by the higher ^{99}Ru chemical shift. This is well in agreement with the Ru−C internuclear distance (described above) and results of ^{103}Rh NMR studies.[12] The line broadening can be attributed to a change of the EFG caused by the change of the electronic properties of the protonated triazole.

Conclusion

^{99}Ru NMR spectroscopy is a powerful tool for the analysis of ruthenium(II) organometallic complexes in addition to well-established techniques. The ^{99}Ru chemical shifts and line widths depend strongly on electronic and steric properties of the complexes. The chemical shifts can be readily interpreted in terms of the paramagnetic shielding from the Ramsey equation. Complexes with a different character of the lowest excited state (M−Ru−M′ and M−Ru−X) can be distinguished in a $\delta(^{99}\mathrm{Ru})$ vs $(\Delta E)^{-1}$ plot. The ^{99}Ru chemical shift can be used to predict the order of increasing bond lengths in a homologous series of ruthenium−alkyl complexes. The variations in line widths indicate large differences in the EFG in the series **1**−**25**; these variations can be explained in a qualitative manner. Various compounds in mixtures of coordination isomers of tris(polypyridyl)ruthenium(II) complexes can be readily identified by ^{99}Ru NMR spectroscopy. For the complexes containing polydentate nitrogen ligands it is found that complexes with higher redox potentials have higher ^{99}Ru chemical shifts, possibly allowing the prediction of trends in the electrochemical properties of these types of complexes based on ^{99}Ru NMR spectroscopy.

Experimental Section

Synthesis. The organometallic complexes **1**−**21** in Table 1 were synthesized according to or in analogy with published methods: **1**−**9**;[16] **10**−**15**, **21**;[17] **17**;[18] **18**−**20**;[19] **22**;[20] **26**.[21] The compounds $Ru_3(CO)_{12}$ (**23**; ABCR), $[RuCp(CO)_2]_2$ (**24**; Strem) and $K_4Ru(CN)_6$ (**25**; Alfa) were obtained commercially and used without further purification. Electronic absorption spectra of THF solutions of the compounds **1**−**25** were recorded at room temperature on a Varian Cary 4E spectrometer. The coordination complexes **27**−**29** were synthesized according to published methods.[7b,22]

NMR Spectroscopy. The ^{99}Ru spectra were recorded on a 300 MHz Bruker DRX-300 spectrometer employing a 10 mm low-frequency broad-band probe (^{103}Rh−^{91}Zr{^{1}H}; 9−29 MHz). The probe was modified by replacing the Dewar with a lead hull to minimize probe ringing.[6] This modification does not result in a decrease of the homogeneity over the samples (^{99}Ru line width of $K_4Ru(CN)_6$, 0.5 Hz at half-height). All chemical shifts are reported relative to a saturated solution of $K_4Ru(CN)_6$ in D_2O[23] at room temperature, as proposed in ref 5b.

The ^{99}Ru NMR spectra of **1**−**24** were recorded in THF solutions at 313 K. Compounds **25** and **26** were measured in D_2O at 293 and 313 K, respectively, and the ^{99}Ru NMR spectra of the tris(polypyridyl) complexes **27**−**29** were recorded in acetonitrile solutions at 313 K. The elevated temperature is employed to reduce the line widths by decreasing τ_c and to increase the solubility of the compounds. We chose 313 K as, at this temperature, we did not expect the compounds under study to either decompose or react with THF or acetonitrile.

The spectra were recorded unlocked, shimming was performed on the proton signals of the THF or the acetonitrile, and the field drift of the magnet was found to be negligible. The concentration of the solutions varied from 0.01 to 0.1 M; in some cases saturated solutions were used, depending on the amount of complex available and the solubility of the complex. A total of 8 K points was sampled over a spectral width of 75 kHz, resulting in acquisition times of 55 ms; a preacquisition delay of 1 ms was used. The number of scans varied from 10^3 to 10^6, depending on the line width of the ^{99}Ru resonance and the concentration of the sample, resulting in total acquisition times varying from several minutes to 16 h (overnight acquisition). Digital filtering prevented signals from folding back.

Distorted baselines as a result from acoustic ringing were effectively corrected by employing a combination of an antiring sequence and backward linear prediction prior to Fourier transformation, a technique which is analogous to forward linear prediction.[24] Thus, the first 10−32 complex points of the FID were truncated and recalculated from the following 256 complex points, using 10 coefficients for the calculations. This resulted in undistorted baselines. Exponential multiplication with a line broadening factor of one-tenth of the natural line width was applied.

^{13}C{^{1}H} heteronuclear NOE values and ^{13}C T_1 values were measured in degassed THF-d_8 solutions on a 5 mm ^{1}H,^{31}P{^{103}Rh−^{31}P} inverse probe including *Z* gradients. ^{13}C{^{1}H} heteronuclear NOE values for the imine carbons were measured using a ^{1}H detected pulse sequence.[25] Each 1D spectrum resulted from 512 scans, the delay between scans during which a series of 30 ms spaced 135° pulses was applied was 3 s. The ^{13}C T_1 values were determined using ^{1}H detected one-dimensional experiments[26] and relaxation delays of 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5, and 3.0 s and 512 scans per relaxation delay.

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