The reduction of NMR relaxation rates employing low viscosity fluids

Gaemers, S.

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Chapter 3

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

3.1 Introduction

Given the importance of ruthenium in various fields of chemistry, e.g. catalytic reactions\(^1\) and photochemistry,\(^2\) it is surprising that relatively little \(^{99}\text{Ru}\)-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 \(^{99}\text{Ru}\)-NMR spectroscopy in solution.\(^5\)

Both ruthenium isotopes (\(^{99}\text{Ru}, I= 3/2; {^{101}\text{Ru}, I= 5/2}\)) are quadrupole nuclei, the latter of which has a large quadrupole moment (\(^{99}\text{Ru}, Q= 0.076 \times 10^{-24} \text{ cm}^2; {^{101}\text{Ru}, Q= 0.44 \times 10^{-24} \text{ cm}^2}\)). Therefore the \(^{99}\text{Ru}\) nucleus is favoured for NMR spectroscopy, despite the lower natural abundance (\(^{99}\text{Ru}, 12.7\%; {^{101}\text{Ru}, 17.1}\%\)).\(^5a\) Another problem encountered in \(^{99}\text{Ru}\)-NMR is the low resonance frequency (13.82 MHz at 7.05 T), resulting in acoustic ringing causing distorted baselines.\(^6\) Virtually nothing is known about the dependence of the \(\delta(^{99}\text{Ru})\) on structure and temperature.
In some cases, 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 would like to 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 to analyse 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, $^{13}$C-NMR, UV/Vis, IR, resonance Raman spectroscopy and electrochemical data in ruthenium chemistry.

3.2 Results

A $^{99}$Ru-NMR study of two classes of ruthenium compounds, shown in Figure 3.1a and b, has been conducted.

![Figure 3.1a. Generic structures of the octahedral ruthenium (II) compounds and ligands. X, Y = SnMe3, SnPh3, PbPh3, GePh3, Me, Et, neo-Pe, i-Pr, Mn(CO)5 or RuCp(CO)2, Cl, Br, I.](image)

The collected data have been compiled in Tables 3.1a and b. 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 ppm to 1041 ppm, whereas the coordination complexes 26-29 are observed at much higher ppm values, between 4606 ppm and 4987 ppm.
Table 3.1.a. $^{99}$Ru chemical shifts, line widths and UV/Vis absorption maxima of compounds 1-25(a)

<table>
<thead>
<tr>
<th>Nr.</th>
<th>X</th>
<th>Y</th>
<th>$\delta(^{99}$Ru)(b)</th>
<th>$\Delta\nu_1/2$(c)</th>
<th>$(\Delta\nu)^{-1}$(d)</th>
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<tbody>
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<td>1</td>
<td>Ph$_3$Sn</td>
<td>Ph$_3$Sn</td>
<td>-116±1</td>
<td>96±2</td>
<td>515</td>
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<tr>
<td>2</td>
<td>Ph$_3$Pb</td>
<td>Ph$_3$Pb</td>
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<td>1.5 ±0.1 kHz</td>
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<td>Ph$_3$Ge</td>
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<td>25±2</td>
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<tr>
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<td>Et</td>
<td>I</td>
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<td>60±2</td>
<td>453</td>
</tr>
<tr>
<td>14</td>
<td>neo-Pent</td>
<td>I</td>
<td>625±1</td>
<td>67±2</td>
<td>455</td>
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<td>Cl</td>
<td>Cl</td>
<td>1993±1</td>
<td>695±10</td>
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<td>2.8 ±0.1 kHz</td>
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<td>Ph$_3$Sn</td>
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<td>Me</td>
<td>I</td>
<td>771±1</td>
<td>30±2</td>
<td>405</td>
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<td>22</td>
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<td>I</td>
<td>1041±2</td>
<td>700±10</td>
<td>413</td>
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<tr>
<td>23</td>
<td>Ru$_3$(CO)$_2$</td>
<td></td>
<td>-1286±1</td>
<td>75±2</td>
<td>413</td>
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<tr>
<td>24</td>
<td>[RuCp(CO)$_2$]$_2$</td>
<td></td>
<td>-1338±2</td>
<td>860±10</td>
<td>413</td>
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<tr>
<td>25</td>
<td>K$_4$Ru(CN)$_6$</td>
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<td>= 0</td>
<td>0.5</td>
<td>55</td>
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(a) All $^{99}$Ru NMR spectra have been recorded in THF at T=313 K unless stated otherwise. The ligands are specified in Figure 3.1a. (b) In ppm relative to $K_4Ru(CN)_6$. (c) In Hz. (d) In nm. (e) $^{1}J(^{117/119}$Sn, $^{99}$Ru)=335±5 Hz. (f) $^{1}J(^{207}$Pb, $^{99}$Ru)= 435±5 Hz. (g) $^{1}J(^{117/119}$Sn, $^{99}$Ru)=256±5 Hz. (h) NN=4,4'-dimethyl-2,2'-dipyridyl. (i) NN= bis(p-anisylimino) acetonapthene$^{27}$. (j) NN= (CH$_3$CN)$_2$. (k) Saturated solution in D$_2$O at 293 K.
**Figure 3.1b.** Structures of the octahedral polypyrpyridyl ruthenium (II) compounds.

**Table 3.1.b.** $^{99}$Ru chemical shifts, line widths and UV/Vis absorption maxima of compounds 26-29$^a$

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Compound</th>
<th>$\delta(^{99}$Ru)$^{(b)}$</th>
<th>$\Delta_{1/2}^{(c)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26$^d$</td>
<td>Ru(bpy)$_3$Cl$_2$</td>
<td>4562</td>
<td>86±2</td>
</tr>
<tr>
<td>27a$^c$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(ppt)</a></td>
<td>4987</td>
<td>530±5</td>
</tr>
<tr>
<td>27b$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(ppt)</a></td>
<td>4958</td>
<td>500±5</td>
</tr>
<tr>
<td>27c$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(ppt)</a></td>
<td>4606</td>
<td>950±10</td>
</tr>
<tr>
<td>27d$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(ppt)</a></td>
<td>4734</td>
<td>650±5</td>
</tr>
<tr>
<td>28a$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(pztr)</a></td>
<td>4678</td>
<td>310±5</td>
</tr>
<tr>
<td>28b$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(pztr)</a></td>
<td>4817</td>
<td>215±5</td>
</tr>
<tr>
<td>29a$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(pytr)</a></td>
<td>4700</td>
<td>340±5</td>
</tr>
<tr>
<td>29b$^e$</td>
<td><a href="PF$_6$">Ru(bpy)$_2$(pytr)</a></td>
<td>4853</td>
<td>290±5</td>
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</table>

(a) All $^{99}$Ru NMR spectra have been recorded in CH$_3$CN at $T=313$ K unless stated otherwise. The ligands are specified in Figure 3.1.b. (b) In ppm relative to $K_4$Ru(CN)$_6$. (c) In Hz. (d) In D$_2$O at 313 K. (e) The polydentate nitrogen ligands have been abbreviated: 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.
For a saturated solution of Ru(Cl)(Me)(CO)₂(i-Pr-DAB) (10) in THF, a linear dependence of $\delta^{99}\text{Ru}$ on the temperature between 303 K and 333 K was observed (four points) which amounts to +1.1 ppm/K. A saturated solution of [Ru(bpy)₃]Cl₂ (26) in D₂O, exhibited a linear dependence of $\delta^{99}\text{Ru}$ on the temperature between 293 K and 353 K (four points) of +1.6 ppm/K. At elevated temperatures the line widths of $^{99}\text{Ru}$ 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 $^{99}\text{Ru}$ chemical shift on the concentration for 10 in THF at 313 K from 9.6 mM to 76.2 mM (four points), nor for 26 in D₂O at 293 K from 10.9 mM to 45.0 mM (five points). As we measured our compounds at concentrations varying from 10 mM to 100 mM and carefully thermostated the samples, we estimate our chemical shifts to be accurate to within ±2 ppm. The error is due mainly to small uncertainties 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 Hz to 900 Hz. The complexes 1-6 have line widths from 96 Hz to 162 Hz, the one exception being 2. Compounds 8, 9 and 16 have line widths of 660 Hz, 800 Hz and 695 Hz respectively. Compounds 7, 18, 19 exhibit even broader resonance lines (1.2 ± 0.1 kHz - 2.8 ± 0.1 kHz). The sharpest resonance lines are found for the complexes 10-15 exhibiting line widths between 25 Hz and 83 Hz. For complex 19 we were able only to observe the resonance of the central ruthenium atom at -185 ppm, the $^{99}\text{Ru}$ resonance of the RuCp(CO)₂ moiety is too broad to be observed.

Rotational correlation times ($\tau_c$) were obtained for five representative complexes 1, 7, 8, 10, 17. The acquired T₁, NOE values and calculated T₁DD and $\tau_c$ for the imine (iPr-N=€(H)-€(H)=N-iPr) $^{13}\text{C}$ have been compiled in Table 3.2.

Interestingly, for three complexes, scalar coupling of the spin 1/2 nuclei $^{117/119}\text{Sn}$ or $^{207}\text{Pb}$ to the $^{99}\text{Ru}$ nucleus could be observed in the $^{99}\text{Ru}$-NMR spectra: $^1J(117/119\text{Sn}, \ 99\text{Ru}) = 335 ± 5$ Hz, 1; $^1J(117/119\text{Sn}, \ 99\text{Ru}) = 256 ± 5$ Hz, 6 and $^1J(207\text{Pb}, \ 99\text{Ru}) = 435 ± 5$ Hz, 4.
Table 3.2. Relaxation times $T_1(^{13}\text{C})$, $T_{1\text{DD}}(^{13}\text{C})$, NOE factors and correlation times $\tau_c$ of selected complexes.$^{(a)}$

<table>
<thead>
<tr>
<th>Nr.</th>
<th>X</th>
<th>Y</th>
<th>$\Delta v_{1/2}^{(b)}$</th>
<th>$T_1(^{13}\text{C})^{(c)}$</th>
<th>NOE</th>
<th>$T_{1\text{DD}}(^{13}\text{C})^{(d)}$</th>
<th>$\tau_c^{(e)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph$_3$Sn</td>
<td>Ph$_3$Sn</td>
<td>96±2</td>
<td>0.92</td>
<td>2.69</td>
<td>1.89</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>Ph$_3$Sn</td>
<td>Me</td>
<td>1.7±0.1 kHz</td>
<td>1.29</td>
<td>2.83</td>
<td>1.41</td>
<td>33</td>
</tr>
<tr>
<td>8</td>
<td>Ph$_3$Sn</td>
<td>Cl</td>
<td>660±5</td>
<td>1.33</td>
<td>2.82</td>
<td>1.46</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>Me</td>
<td>Cl</td>
<td>40±2</td>
<td>3.32</td>
<td>2.20</td>
<td>5.53</td>
<td>8.4</td>
</tr>
<tr>
<td>17</td>
<td>I</td>
<td>I</td>
<td>1435±10</td>
<td>2.10</td>
<td>2.58</td>
<td>2.66</td>
<td>18</td>
</tr>
</tbody>
</table>

(a) Determined for the imine carbon in THF-d$_8$ at 313K. (b) In Hz. (c) In s. (d) In s. (e) In 10$^{-12}$ s.

Protonation of the triazole moiety$^7$ of compound 29a by the addition of 8 equivalents of a strong acid (HBF$_4$) to an acetonitrile solution of 29a results in a chemical shift change of the $^{99}\text{Ru}$ of +126 ppm and a broadening of the line from 310 Hz to 620 Hz.

For compounds 27-29 (Figure 3.1b), all ruthenium resonances could be readily identified and assigned. The resonances of the compounds 28a,b have been assigned based on comparison with an authentic, pure sample of 28b. Those of the compounds 29a,b by comparison with an authentic, pure sample of 29a. For the mixtures of compounds 28a,b, a $\Delta \delta^{(99}\text{Ru})$ of 140 ppm between isomers was observed. For the similar compounds 27a,d and 29a,b, a comparable $\Delta \delta^{(99}\text{Ru})$ of 253 and 153 ppm was observed between their respective isomers, which differ in whether N-1 or N-4 is coordinated to ruthenium. 27b,c, a $\Delta \delta^{(99}\text{Ru})$ of 8 ppm was observed. By comparison to the authentic pure samples mentioned above, the $^{99}\text{Ru}$ signals at higher frequency were assigned to the isomers with the triazole coordinating via N-4 (Figure 3.1b). The trend in the $^{99}\text{Ru}$ 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 towards lower $\delta^{(99}\text{Ru})$. 

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3.3 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.

3.3.1 Complexes of type Ru(X)(Y)(CO)$_2$(α-diimine)

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 equation III-1.$^8$ This equation describes the shielding in a d$^6$-octahedral complex, summing over the d-electron excitations.

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

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

Since $\delta^{(99)}$Ru will be governed by the paramagnetic contribution, the crystal field splitting $\Delta E$ and the inverse cube of the radius of the valence shell d-orbitals $<r^{-3}>_d$ are important parameters. As the d-electron configuration and the symmetry of the complexes does not or only slightly vary for the complexes studied, the factor $<0|L^2|0>$ (imbalance of charge) remains essentially constant. For a detailed discussion of the influence of the various parameters on the transition metal chemical shift see the review by J. Mason.$^9$ The $^{99}$Ru chemical shift is very sensitive to subtle changes in the chemical structure of complexes, a chemical shift range of 10000 ppm has been reported.$^{5c}$

The general trends observed for $\delta^{(99)}$Ru are in agreement with the relative position 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 $\delta^{(99)}$Ru. The substituents in the compounds 1-25 are placed higher in the spectrochemical series and hence have lower $\delta^{(99)}$Ru.

Dependence on temperature. The dependence of $\delta^{(99)}$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 $(\Delta E)^{-1}$, 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 observed for e.g. $\delta^{187}$Os, +0.7 ppm/K$^{3f}$ and $\delta^{103}$Rh, +0.5 - 1 ppm/K.$^{10}$

Dependence on $<r^{-3}>_d$. Lower $\delta^{99}$Ru values are expected for larger internuclear distances Ru-X because of a smaller $<r^{-3}>_d$ term in equation III-1. In this respect, the complexes 10, 11 and 12 exhibit a normal halogen dependence of the shielding according to the nephelauxetic series Cl < Br < I (solid lines in Figure 3.2a).$^9$ 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 of compounds 12-15 decreases 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 $<r^{-3}>_d$ 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 $<r^{-3}>_d$ 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. As the same trend is observed for the $\delta^{99}$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 equation III-1 the $\delta^{99}$Ru is for a substantial part determined by the inverse of the average excitation energy $(\Delta E)^{-1}$. The $\delta^{99}$Ru as well as $\Delta E$ are related to the electronic ground and first excited states of the compounds studied.$^{34}$ Hence, it is interesting to see whether a correlation exists between $\delta^{99}$Ru and $(\Delta E)^{-1}$. In Figure 3.2a 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 $\sigma$ donating group 14 elements bound directly to the ruthenium center: M-Ru-M $^\prime$ (compounds 1-7, 18, 20. Where M and M $^\prime$ denote substituents of 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 3.2a). These complexes have $99$Ru chemical shifts between 200 and -300 ppm and a $(\Delta E)^{-1}$ 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 3.2a. These
compounds have chemical shifts from 1100 to 550 ppm, and a $(\Delta E)^{-1}$ ranging from 400 to 475 nm (B in Figure 3.2a). According to the Ramsey equation the trend should be reverse, a decreasing $(\Delta E)^{-1}$ should result in a lower chemical shift.

![Figure 3.2a. Plot of the $\delta^{(99}Ru$ in ppm vs $(\Delta E)^{-1}$ in nm 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 = CI, Br, I.](image)

The difference in $^{99}$Ru chemical shift between the complexes M-Ru-M' (1-7) and M-Ru-X (8-15), can be explained from the difference in character of the HOMO in these two types of complexes, which has implications for the $<r^3>_d$ as well as the $(\Delta E)^{-1}$ term in the Ramsey equation. As has been determined from DFT calculations and resonance Raman spectroscopy, the HOMO in the complexes M-Ru-M' has $\sigma$(M-Ru-M') character, whereas the HOMO in the complexes M-Ru-X has mixed $d\pi$(Ru)/$p\pi$(X) character. The HOMO of the M-Ru-M' (1-7) complexes has $\sigma$(M-Ru-M') character because the $\sigma$ orbital lies higher in energy than the $d\pi$(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 ($\pi^*$) and does not change in the series 1-19. This results in a smaller HOMO/LUMO energy gap, hence a larger $(\Delta E)^{-1}$ is observed for the complexes.
M-Ru-M' 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, 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 further 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 nucleus, hence lower chemical shift values. Therefore, for the whole series of compounds 1-25, the correlation with the energy of the lowest transition does not follow equation III-1. The difference in \( \Delta E \) 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 3.2a, but the \( \langle r^3 \rangle_d \) term is apparently the decisive term for the \(^{99}\)Ru chemical shift in these types of complexes.

**Figure 3.2b.** Plot of the \( \delta(^{99}\text{Ru}) \) in ppm vs \( (\Delta E)^{-1} \) in nm for compounds 1-7, 18 and 20.

A trend between \( (\Delta E)^{-1} \) and the \( \delta(^{99}\text{Ru}) \) is observed in the homologous series of the complexes of type M-Ru-M' (1-7), as shown in Figure 3.2b. Even complexes 18
and 20 fit the observed trend. The correlation of $\Delta (^{99}\text{Ru})$ with $(\Delta E)^{-1}$ is not very good which suggests that $\langle r^{-3} \rangle_d$ plays a significant role (vide supra).

B. Line widths. The broad resonance lines in $^{99}\text{Ru}$-NMR are the result of the very efficient quadrupolar relaxation mechanism. In equation III-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:

$$\Delta v_{1/2} = \frac{1}{\pi T_1} = \frac{1}{\pi T_2} = \frac{3\pi}{10} \left( \frac{2I+3}{I(I^2-1)} \right) \left( 1 + \frac{\eta_5}{3} \right) (\chi)^2 \tau_c$$

where $I$ denotes the nuclear spin, $\eta_5$ is the asymmetry parameter of the complex, $\chi$ is the nuclear quadrupole coupling constant and $\tau_c$ 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 equation III-3:

$$\tau_c = \frac{A\eta_v}{kT}$$

where $\eta_v$ 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)$_2$O'-Pr-DAB) (10) and RuCl$_2$(bpy)$_3$ (26) with increase of temperature is in agreement with equation III-2 and III-3: the rotational correlation time decreases since $T$ increases and the viscosity decreases.

Electric Field Gradient. The variations of the $^{99}\text{Ru}$ line widths for the compounds 1-29 are the result of the variations in symmetry and $\tau_c$ (see below) as a consequence of the various substituents in the compounds. More asymmetric compounds might induce a larger electric field gradient (EFG) at the $^{99}\text{Ru}$ nucleus, resulting in larger nuclear quadrupole coupling constants ($\chi$) and broader NMR resonances. 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 assume that the EFG in the equatorial plane is not very large since two $\pi$-bonding ligands, an $\alpha$-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 3.1a), which are the same or very similar (1, 5, 6), resulting in a low EFG. Changing one of these groups to a chloride or a methyl results in a dramatic increase of the line width (7, 8, 9). The reason for the large line width observed for 2 is not understood. The introduction of a transition metal at one of the axial positions results in a large 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. 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 are subject 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 size, variations in rotational correlation times are to be expected. The rotational correlation time $\tau_c$ can be determined from the $^{13}$C relaxation time $T_{1DD}(^{13}$C) due to C-H dipolar interactions:\(^{15}\)

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

Where $K= 2.147\cdot10^{10}$ s$^{-2}$ if the C-H bond lengths ($r_{CH}$) are assumed to be constant (1.09 Å). The $T_{1DD}(^{13}$C) can be obtained from the $T_1(^{13}$C) and the NOE value, equation III-5:

$$NOE = 1 + \frac{2T_1(^{13}$C)}{T_{1DD}(^{13}$C)}$$
We observe large differences between the rotational correlation times of complexes 1, 7, 8, 10, 17 (Table 3.2). 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 going 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 symmetry of complexes 1 and 17 are similar, hence the line width of 17 would be expected to be lower than that of complex 1 based on the rotational correlation time. The larger line width of complex 17 compared to 1 must therefore be caused by the EFG which is higher in complex 17.

The small difference in chemical shift between 8 and 10 indicates similar electronic properties of the axial ligands, the difference in line width can therefore be attributed mainly to the difference in $\tau_c$. Although the $\tau_c$ of complexes 7 and 8 are comparable, the line width of 7 is three times that of 8, this is attributed mainly to 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. For comparison, the rotational correlation times of zirconocene dichloride complexes with a molecular weight comparable to compound 10, varies between $3.5 \times 10^{-12}$ and $19.7 \times 10^{-12}$ s. The ruthenium compounds of higher molecular weight have relatively long rotational correlation times.

C. 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 magnitude of the scalar coupling in compounds 1 and 6 is attributed to the Ru-Sn bond length, being shorter for 1, in agreement with larger s-character hence larger coupling constant. The $^{99}$Ru spectrum of complex 1 is shown in Figure 3.3 and displays a typical $^{99}$Ru signal with $^{117/119}$Sn satellites.
To date, only three other scalar couplings to $^{99}$Ru were known: $^1J(^{99}$Ru-$^{13}$C) = 44.8 Hz, in $K_4$Ru(CN)$_6$; $^1J(^{99}$Ru-$^{17}$O) = 23.4 Hz in RuO$_4$; $^1J(^{99}$Ru-$^{117/119}$Sn) = 846 Hz in (NEt$_4$)$_4$[Ru(SnCl$_3$)$_5$Cl].

3.3.2. Mixtures of tris-polypyridyl ruthenium(II) complexes

We studied mixtures of the complexes 27-29 shown in Figure 3.1b. These compounds were chosen to determine whether the different coordination modes 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, either because of 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 non zero scalar couplings of the $^{15}$N to $^1$H. The coupling constant 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 \(5^e, f, h\) but mixtures of coordination isomers of compounds like 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 3.4, which shows two well separated $^{99}$Ru signals.

Comparison of the spectrum of the mixture 28a,b with the spectrum of pure 28b and 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 29a,b it appears that the $^{99}$Ru nuclei of the pyridine coordinated compounds (29a,b) resonate at lower frequency than that 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, 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.

![Figure 3.4. The $^{99}$Ru-NMR spectrum of a mixture of compounds 28a,b. [Ru]= [Ru(bpy)$_2$](PF$_6$).](image)
It can be seen that for the triazole coordination the stronger σ-donor (N-1/N-2 coordination) leads to a lower ruthenium chemical shift. This parallels the redox potentials determined previously: \(22^a,b\) \(28a\) has a redox potential 100 mV lower and \(29a\) a redox potential 70 mV lower compared to the N-4 coordinated species (\(28b\), \(29b\)), both have higher ruthenium chemical shifts than the N-2 coordinated species.

The addition of 8 equivalents of HBF₄ to an acetonitrile solution of \(29a\) results in a \(^{99}\text{Ru}\) chemical shift change of +126 ppm and a line broadening of the \(^{99}\text{Ru}\) resonance from 310 Hz 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 coulomb interaction most likely leads to a larger Ru-N internuclear distance, leading to a larger \(<r^3>_d\) which is reflected by the higher \(^{99}\text{Ru}\) chemical shift. This is in good agreement with the Ru-C internuclear distance (described above) and results of \(^{103}\text{Rh-NMR}\) 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.

### 3.4 Conclusions

\(^{99}\text{Ru-NMR}\) spectroscopy is a powerful tool for the analysis of ruthenium(II) organometallic complexes in addition to well established techniques. The \(^{99}\text{Ru}\) chemical shifts and line widths depend strongly on electronic and steric properties of the complexes. The chemical shifts can be 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 \(\delta^{(99}\text{Ru}) vs (\Delta E)^{-1}\) plot. The \(^{99}\text{Ru}\) 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 \(^{99}\text{Ru-NMR}\) spectroscopy. For the complexes containing polydentate nitrogen ligands it is found that complexes with higher redox potentials have higher \(^{99}\text{Ru}\) chemical shifts, possibly allowing the prediction of electrochemical properties of this type of complexes based on \(^{99}\text{Ru-NMR}\) spectroscopy.
3.5 Experimental

Synthesis. The organometallic complexes 1-21 in table 3.1 were synthesised according to or in analogy with published methods: 1-9, 20; 10-15, 21; 17, 18, 19, 22; 17, 18, 19, 22, 20, 21. The compounds: Ru$_3$(CO)$_{12}$ (23, ABCR), [RuCp(CO)$_2$]$_2$ (24, Strem) and K$_4$Ru(CN)$_6$ (25, Alpha) were obtained commercially and used without further purification. Electronic absorption spectra of the compounds 1-25 were recorded at room temperature on a Varian Cary 4E spectrometer. The coordination complexes 27-29 were synthesised according to published methods.\textsuperscript{22, 7b}

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{\textsuperscript{1}H}; 9 MHz-29 MHz). The probe was modified by replacing the dewar by a lead hull to minimise probe-ringing.\textsuperscript{6} This modification does not result in a decrease of the homogeneity over the samples ($^{99}$Ru line width of K$_4$Ru(CN)$_6$, 0.5 Hz at half height). All chemical shifts are reported relative to a saturated solution of K$_4$Ru(CN)$_6$ in D$_2$O\textsuperscript{23} at room temperature as proposed in reference 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$_2$O at 293 K 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 \( \tau_c \) 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, the field drift of the magnet was found to be negligible. The concentration of the solutions varied from 0.01 M-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 hours (overnight acquisition). Digital filtering prevented signals to fold back.
Distorted baselines as a result from acoustic ringing were effectively corrected by employing a combination of an anti-ring sequence and backward linear prediction prior to Fourier transformation, a technique which is analogous to forward linear prediction. Thus, the first 10 to 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-d8 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. Each 1D spectrum resulted from 512 scans, the delay between scans during which a series of 30 ms spaced 135° pulses was applied was 3s. The $^{13}$C T$_1$ values were determined using $^1$H detected one dimensional experiments and relaxation delays of 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5, 3.0 s and 512 scans per relaxation delay.

### 3.6 References


(c) Christine M. O’Connor, Ph D thesis, Dublin City University 1999.
(23) The concentration of IM as mentioned in reference 5b could not be achieved at room temperature.


