3. Direct Observation of ^{103}Rh-Chemical Shifts in Mono- and Dinuclear Olefin Complexes[1])

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Summary

The ^{103}Rh-resonance has been investigated at 2.8 MHz in mono- and dinuclear olefin complexes by steady-state NMR.-pulse techniques. For dirhodium complexes with scalar Rh,Rh-coupling, a selective rf-irradiation was applied to improve sensitivity. Within the same measuring time the signal/noise ratio is improved by the factor $(T_2/T_2^*)^{1/2}$ by this steady-state method in comparison with the usual free-induction technique. (T_1/T_2)-ratios, as obtained from the dependence of signal intensity on the pulse-flip angle are discussed in terms of relaxation mechanisms and chemical exchange phenomena. From (T_1/T_2)- and (T_1+T_2)-experiments, individual T_1 and T_2 values have been determined for $C_5H_5RhC_8H_{12}$ and Rh(acac)$_3$.

The ^{103}Rh-chemical shifts of 39 olefin complexes are reported. Shielding depends upon the (formal) oxidation state of Rh whereby resonances of pure olefin complexes appear at the low-frequency end of the δ-scale, which extends over 10000 ppm. For cyclic 1,3-diene ligands Rh-shielding *increases* with *decreasing* ring size and *decreases* with further conjugation of the diene systems.

In the dirhodium complexes, Rh,Rh spin-coupling constants are < 10 Hz. Rh,C-coupling constants in (diene)RhCp-complexes increase, for the terminal diene C-atom, with increasing ring size of the 1,3-diene, ^1J(Rh,C) = 11.7 to 17.4 Hz.

1. Introduction. – In continuation of our studies on the structure of transition metal(olefin) complexes in solution [2], we have now focussed our interest on the direct observation of the metal centers by NMR.methods. ^{57}Fe-chemical shift determinations in ironcarbonyl(olefin) complexes have already demonstrated [3] that shielding constants of a transition metal are very sensitive to apparently small variations in the structure of a π-bonded 1,3-diene ligand and, hence, they may be a useful probe for metal-to-olefin bonding in general. In view of the presumed importance of this factor for a deeper understanding of homogeneous catalysis we have extended our studies to other group VIII transition metals.

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[1]) Transition Metal NMR. Spectroscopy, Part III; Part II see [1].

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Amongst the group VIII metals the ^{103}Rh-isotope is a particularly promising candidate because of its relatively favorable magnetic properties (100% abundance, spin 1/2, receptivity: 18% of the ^{13}C-nucleus) and the very rich organometallic chemistry of rhodium. Only the small magnetic moment of this nucleus, leading to a very low *Larmor*-frequency and long relaxation times, has prevented extensive direct NMR.studies in the past. More recently, it was shown independently by two research groups that ^{103}Rh-signals can be detected in organometallic structures in solution using conventional pulse techniques at 4.2 T (5.6 MHz) [4] or, preferably a steady-state technique at 2.1 T (2.8 MHz) [5]. Previous, indirect ^{103}Rh-chemical-shift determinations [6] were based on heteronuclear double-resonance experiments, depending in most cases on spin coupling of ^{103}Rh- to ^{1}H-, ^{19}F- or ^{31}P-nuclei.

In this communication we report further results on ^{103}Rh-chemical-shift measurements in low-valent mononuclear and homo- and hetero-dinuclear olefin complexes and studies on relaxation times and Rh,Rh- and Rh,C-spin coupling.

2. Spectroscopic method. – All ^{103}Rh-NMR.measurements were performed using a steady-state technique to avoid any disadvantages due to the relatively long ^{103}Rh-relaxation times [7]. Equal, periodic and coherent rf-pulses or pulse-groups are applied with a repetition rate 1/T the pulse spacing being chosen as $T \ll T_2$ and T_1, the ^{103}Rh-relaxation times of the sample. In this steady-state, built up as a result of the applied pulses, the thermal equilibrium is never reached in the ^{103}Rh-spin system, *i.e.*, no waiting time for this equilibrium is necessary or, in other words, at any time between the rf-pulses or pulse groups an NMR.signal can be received. In order to achieve the highest sensitivity possible, the pulse-spacing T was chosen $T \ll T_2^*$ (the time constant describing the decay of the transverse magnetization due to the inhomogeneity of B_0) (*cf.* p. 381 in [8]). The shape of the absorption line achieved by this technique is given by

$$I(\nu) \sim \sin\{2\pi T(\nu_L - \nu)\}/2\pi T(\nu_L - \nu)$$

with the *Larmor*-frequency ν_L. The NMR.line is broadened to a half-width $\Delta\nu_{1/2} = 0.6$ T and is independent of the inhomogeneity of the field B_0 as well as of the natural linewidth $1/(\pi T_2)$. In this case any loss of NMR.-signal due to the inhomogeneity of B_0 can be avoided, without a use of paramagnetic additives with their well known disadvantages.

When the signal/noise ratio, which can be achieved in a given measuring time using this technique, is compared with that obtained by the usual observation of the free induction decay (FID) in the same measuring time, the steady-state technique is superior to the FID-technique by the factor $(T_2/T_2^*)^{1/2}$ [9].

To investigate the dinuclear Rh-complexes with scalar Rh,Rh-coupling, a selective rf-irradiation had to be used besides the usual wide-band irradiation. *Fourier*-transformation of equal, periodic and coherent rf-pulses (carrier frequency ν_E) as indicated in *Figure 1a* yields a spectrum

$$A(\nu_E \pm n/T) \sim \sin\{n\pi\tau/T\}/\{n\pi\tau/T\} \qquad n = 0, 1, 2, \ldots$$

In the range $n \ll T/(\pi\tau)$ all applied spectral lines have nearly the same intensity. This is the working range of such a wide-band spectrum: $\nu_E \pm 1/(\pi\tau)$. By splitting the single pulse into two halves separated by the time $\Delta\tau$ as indicated in *Figure 1b*, the following *Fourier*-spectrum is applied:

$$A(\nu_E \pm n/T) \sim \sin\{n\pi\tau/2T\} \cdot \cos\{n\pi \cdot \Delta\tau/T\}/\{n\pi\tau/2T\} \qquad n = 0, 1, \ldots$$

For $n \approx T/(2\Delta\tau)$ or $\nu \approx \nu_E \pm \Delta\nu$ with $\Delta\nu = n/T = 1/(2\Delta\tau)$, the applied spectrum vanishes, whereas in the range $n \ll T/(2\pi\Delta\tau)$ or $\nu = \nu_E \pm 1/(2\pi\Delta\tau)$, the amplitude of this selective spectrum is nearly the same as that of the wide band spectrum, *i.e.*, a spin with the *Larmor*-frequency $\nu_L \approx \nu_E$ is flipped by the same angle $\theta = \gamma B_1 \tau$, by a single pulse *(Fig. 1a)* as well as by a selective doublet *(Fig. 1b)*. A spin with the *Larmor*-frequency $\nu_L = \nu_E \pm \Delta\nu$ is not affected by the selective doublet.

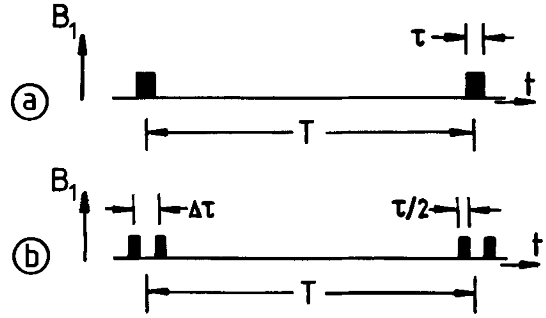


Fig. 1. *Periodic rf-pulse sequence with carrier frequency* ν_E. a) For wide-band irradiation; nearly equally intensive spectral lines are applied in the frequency range $\nu_E \pm 1/(\pi \cdot \tau)$, this is the working range for one NMR. experiment; b) for selective irradiation; the working range extends over the frequency interval $\nu_E \pm 1/(2\pi \cdot \Delta\tau)$. For $\nu_E \pm (k/2 \cdot \Delta\tau)$ (k = odd integer number) the intensity of the applied spectral lines vanishes.

For a measurement of the total ^{103}Rh-spectrum of dinuclear Rh-complexes with scalar Rh,Rh-coupling, wide-band irradiation must be used; to minimize the double-resonance effects, the pulse-repetition rate was raised to 166 Hz, in order to fulfill as well as possible the condition $|J| \ll 1/T$. Three spectra of this kind are shown in *Figure 2*.

In searching for the unknown ^{103}Rh-NMR. signals in the wide-spread frequency range 2.830–2.870 MHz, the *Quadriga*-technique [8] was used. The flip angle of the rf-pulses was chosen ≈60°, this being the optimum value for the ratio of relaxation times $T_1/T_2 = 2$. The precise determination of the ^{103}Rh-resonance frequencies was always carried out using a pulse-repetition rate of 83 Hz. Complexes with two nonisochronous Rh-nuclei were investigated with selective irradiation. The distance $\Delta\tau$ was chosen in such a way that only the line near ν_E was affected by the rf-spectrum in order to avoid homonuclear double-resonance. All other compounds were investigated with wide-band irradiation. Under these conditions, all spectra consisted of a single NMR.-line, and an accurate determination of the resonance frequency was achieved in a single steady-state free-precession experiment with a carrier irradiation frequency ν_E fulfilling the condition $\nu_L - \nu_E = 1/2T = 41.5$ Hz. Depending on the

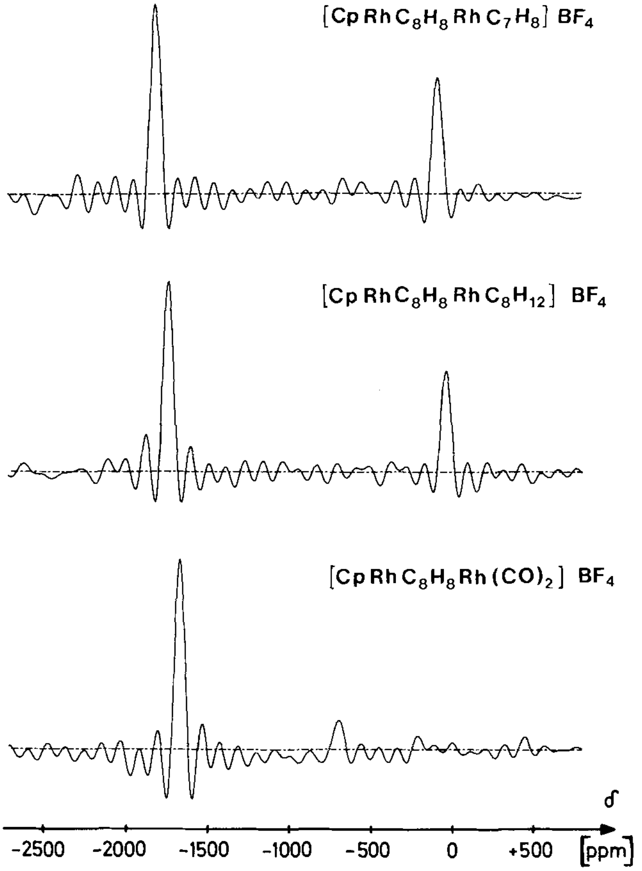


Fig. 2. *^{103}Rh-spectra of three dinuclear Rh-complexes with indirect Rh,Rh spin-coupling, recorded with the* Quadriga-Fourier-*transform technique.* To minimize double-resonance effects, a pulse repetition rate $1/T = 166$ Hz $\gg |J|$ *was chosen. Measuring times were in the range of 4 × 1 h to 4 × 4 h depending on the concentration of the sample. Shielding increases from right to left.*

concentration of the samples (0.03–0.18M) and on the T_1/T_2 ratio, measuring times from 30 minutes up to 1 day were necessary to achieve a signal/noise ratio of at least 10.

It is, therefore, not advisable to refer the ^{103}Rh-resonance frequencies to that of a ^{103}Rh-standard. The ^{73}Ge-NMR. frequency of $GeCl_4$ (≈ 3.139 MHz), which is independent of temperature and which is referred to the *Larmor*-frequency of ^{2}H in D_2O with high accuracy [10], was used as a primary standard. The spectrometer can be tuned to the ^{73}Ge-resonance frequency within less than 5 minutes. To determine the ratios of the *Larmor*-frequencies $\nu(Rh)/\nu(Ge)$, the sample replacement technique was used, and for each Rh-sample at least 10 frequency ratios were determined.

In these ^{103}Rh-experiments, the flip angle θ was varied systematically under control of the *PDP 11/04* computer, *i. e.*, the signal intensity $M(\theta)$ was determined as a function of the flip angle θ. The (T_1/T_2)-ratio can be calculated from this function with the aid of a *Gaussian* least-squares-fitting routine [11]. The measurements performed for an exact determination of the ^{103}Rh-resonance frequency were simultaneously used for the (T_1/T_2)-experiment. These results $M(\theta)$, together with the optimum fit curves, are plotted in *Figure 3* for some selected samples.

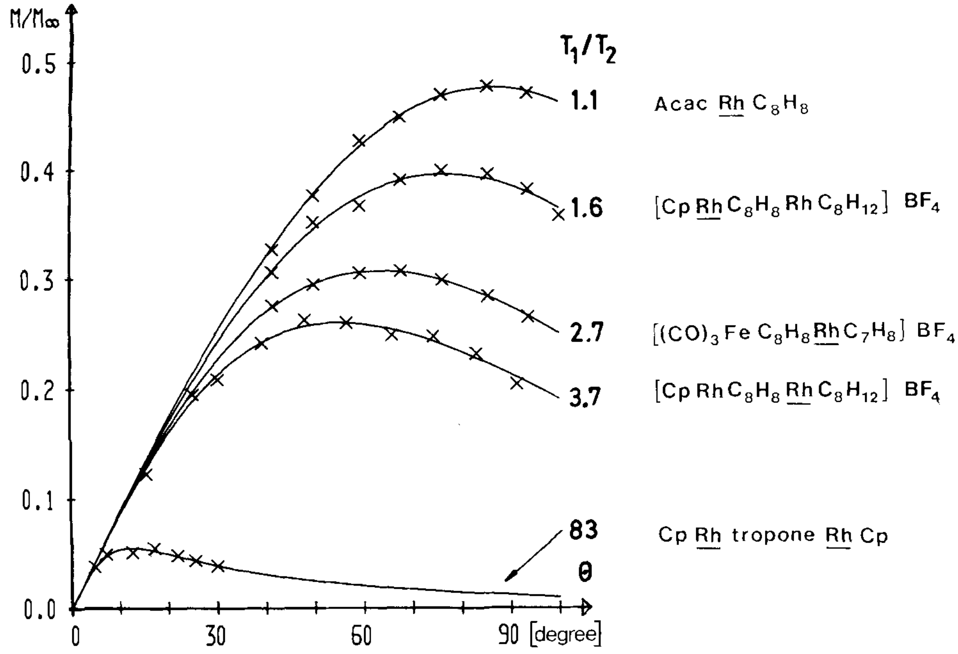


Fig. 3. *Results of the* (T_1/T_2)*-experiment.* ^{103}Rh-NMR. signal intensities M/M_∞ measured as a function of the flip angle θ are plotted together with the Gaussian least squares fit curves. A detailed description of the technique is given in [11].

In order to obtain the absolute values of the relaxation times, the $(T_1 + T_2)$-experiment [11] was performed for two samples with the highest concentrations. The block-averaging technique necessary for this experiment was achieved in the memory of the *PDP 11/04* computer, all functions of the time–averaging computer being controlled by the *PDP 11/04* and its clock. The build-up of the steady-state was determined in 10 intervals of 8 s duration, and during each interval the NMR.-signal of 10^9 pulse cycles was accumulated. The experiment was repeated 256 times to achieve a sufficient signal/noise ratio, and the signals of the 10 acquisiton intervals were block-averaged. The initial unmagnetized state of the sample was established before each experiment by periodic irradiation of 180°-pulses during a time interval $\approx 4\ T_1$. In *Figure 4* (see p. 31) the buildup curves of two Rh-samples are plotted and for comparison, a similar result of the ^{109}Ag-resonance is added.

3. Results and Discussion. – 3.1 *Chemical Shifts.* The main object of the present study was the investigation of the chemical-shift range of low-valent Rh, complexed by olefinic ligands only. Thus, the first group of compounds comprises mononuclear 18e-complexes of the type CpRh(diene). In particular, open-chain and cyclic

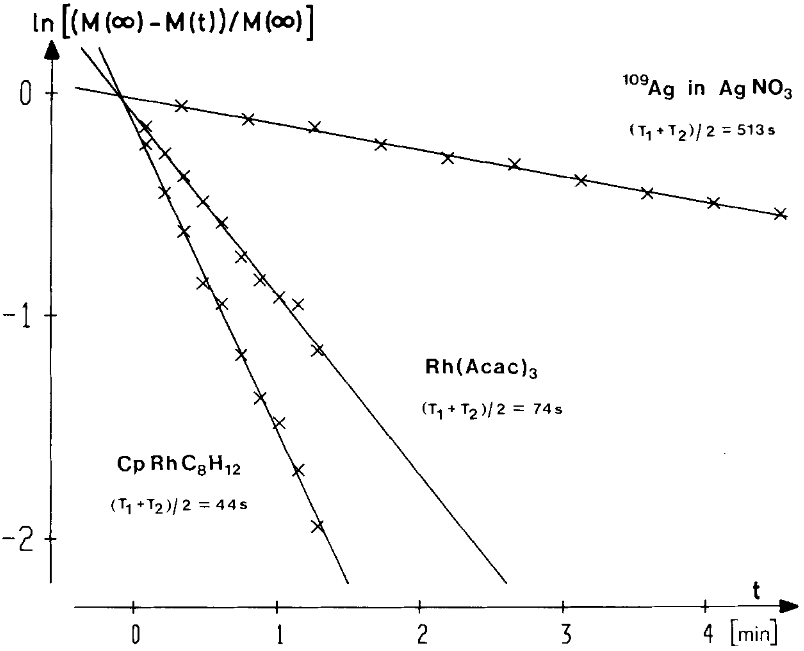


Fig. 4. *Results of the (T_1+T_2)-experiment.* Starting from the unmagnetized state of the sample, the exponential build-up of the magnetization with the time constant $(T_1+T_2)/2$ was investigated using a computer-driven block-averaging technique, as described in detail in [11]. $CpRhC_8H_{12}$: 0.181 M in benzene, $Rh(acac)_3$: 0.19 M in $CHCl_3$, $AgNO_3$: 1 molal in H_2O.

1,3-, 1,4- and 1,5-diene complexes were investigated. In addition, dinuclear 34e-complexes of the general structure CpRh(olefin)RhCp, 34e-complexes of the type $[CpRhC_8H_8Rh(diene)]BF_4$, and some hetero-dinuclear complexes $[(CO)_3FeC_8H_8Rh(diene)]BF_4$ and $(CO)_3FeC_7H_7Rh(diene)$ were studied. The chemical shifts of these compounds are collected in *Tables 1, 2* and *3,* respectively. The chemical shift data of the mononuclear 18e-complexes, when expressed relative to the arbitrary absolute reference $\nu_{Rh}(Ref)/\nu_H(TMS) = 0.0316$, are observed in the range of –300 to –2100 ppm. The Rh-nucleus is thus more highly shielded than in the majority of complexes investigated so far (*cf.* [6]). Chemical shifts in this range were only reported for some compounds containing phosphine or hydride ligands. As in the cases of ^{57}Fe-[3] and ^{59}Co-shielding [12], the (formally) zero-valent Rh-olefin complexes lie at the *low*-frequency end of the chemical-shift scale which extends from +8400 to –2100 ppm. Furthermore, shielding decreases with increasing ring size of the 1,3-diene system, *i.e.*, the resonance of the cyclobutadiene complex **1** exhibits the highest shielding (–2057 ppm), in striking agreement with the highly shielded ^{57}Fe-resonance in $(C_4H_4)Fe(CO)_3$ [3]. The trend in ^{103}Rh-shielding by olefinic ligands is illustrated in *Figure 5,* which also shows the exceptional δ-value of the cyclopentadiene complex **9**, an observation which is made in the Fe- and Co-series as well.

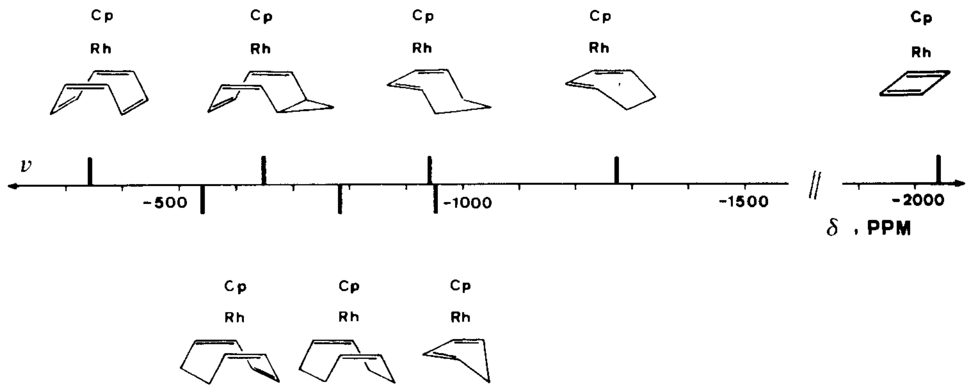


Fig. 5. *^{103}Rh Chemical shift range (δ [ppm]) of CpRh(diene) complexes.*

In contrast to the high shielding of the Rh-nucleus in the 18e-olefin-complexes a significant deshielding effect of +2080 to +2135 ppm is observed for the mononuclear 16e-complexes of the type (acac)Rh(diene) (**22–25**) which may be formally considered as Rh$^{\text{I}}$-complexes. Their resonance lies in the range of +1180 to +1760 ppm *(Table 2).* Further substitution of the olefinic ligands by acetylacetonate ligands leads to the extremely deshielded Rh$^{\text{III}}$-resonance in Rh(acac)$_3$ (+8358 ppm [5]). Thus, the gross correlation of transition-metal chemical shifts with the formal oxidation state of the metal is again confirmed in the present series of Rh-complexes. The same is observed in the dinuclear complexes discussed below.

Within the group of pure olefin-complexes two noticeable effects should be mentioned. First, shielding of the zero-valent Rh-atom decreases with increasing ring size or C,C,C-bond angle of the 1,3-diene-ligand, *e. g.*, cyclobutadiene (–2057.0), 1,3-cyclohexadiene (–1272.2), 1,3-cycloheptadiene (–939.8), 1,2-bis(methylidene)cyclobutane (–705.7 ppm). This effect seems to illustrate the importance of pπ,dπ-overlap between ligand and metal orbitals for the shielding constant of the metal. The same trends were already reported for the ^{57}Fe-resonance in (diene)Fe(CO)$_3$ complexes [3] and recently observed in the ^{59}Co-resonance of isoelectronic CpCo(diene) complexes [12]. A noteworthy exception are the cyclopentadiene complexes which, in the two isoelectronic complexes CpM(C$_5$H$_6$) (M = Rh, Co), have a resonance position very close to the 1,3-cycloheptadiene complexes.

Second, p,d-orbital overlap is also expected to be less efficient in the 1,4- and (1,5-diene)Rh complexes, and indeed considerable deshielding is observed in the chemical shifts of CpRh(norbornadiene) (**14**) (–786.4), CpRh(1,5-cyclooctadiene) (**13**) (–787.2), and CpRh(1,5-hexadiene) (**15**) (–779.6 ppm). Shielding of the Rh-nucleus further decreases upon conjugation of the complexed 1,5-diene system with other double bonds, *i.e.*, in the η-1,2-5,6-cycloocta-1,3,5-triene complex **20** (–538.3), the η-1,2-5,6-cycloocta-1,3,5-trien-7-one complex **19** (–580.4), and the η-1,2-5,6-cyclooctatetraene complex **21** (–347.6 ppm).

Table 1. *^{103}Rh chemical shifts of mononuclear Rh^0-olefin complexes*

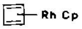
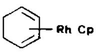
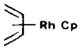
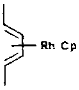
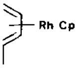
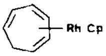
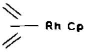
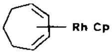
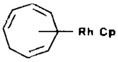
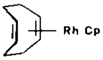
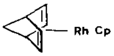
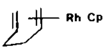
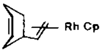
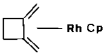
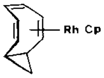
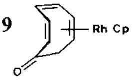
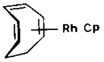
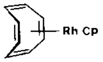
Compound		Ref.[a]	Solvent/conc.	ν(Rh)/ν(Ge)[b]	δ(Rh) [ppm][c]	T_1/T_2
1		[33]	Pentane 32 mM	0.903 990 4(6)	−2057.0 ± 0.8	1.4
2	[Cp Rh Cp][Cl]	[36]	Propylenecarbonate 70 mM	0.904 188 1(7)	−1838.7 ± 0.9	–
3	(CO)$_2$ Rh Cp	[37]	Benzene 43 mM	0.904 656 7(12)	−1321.5 ± 1.4	2.0
			Hexane 45 mM	0.904 660 9(2)	−1316.8 ± 0.5	1.3
4		[38]	THF 100 mM	0.904 701 3(8)	−1272.2 ± 1.0	–
5		[39]	Hexane 80 mM	0.904 716 1(3)	−1255.9 ± 0.6	1.7
6		[39]	Hexane 84 mM	0.904 838 8(3)	−1120.4 ± 0.6	1.8
7		[39]	Benzene 60 mM	0.904 944 5(15)	−1003.7 ± 1.7	1.6
8		d)	Pentane 27 mM	0.904 954 6(14)	− 992.6 ± 1.7	1.4
9		[40]	Benzene 60 mM	0.904 986 3(7)	− 957.6 ± 0.9	–
10		[41]	Acetone 40 mM	0.904 997 3(10)	− 945.4 ± 1.2	–
11		d)	THF 70 mM	0.905 002 4(19)	− 939.8 ± 2.2	82
			Acetone 70 mM	0.905 003 9(16)	− 938.2 ± 1.8	84
12		d)	Pentane 84 mM	0.905 058 4(3)	− 878.0 ± 0.6	1.4
13		[35]	THF 160 mM	0.905 140 6(2)	− 787.2 ± 0.6	–
			Benzene 181 mM	0.905 142 6(2)	− 785.0 ± 0.5	2.2
14		[18]	THF 60 mM	0.905 141 4(5)	− 786.4 ± 0.8	–
15		d)	Hexane 45 mM	0.905 147 5(3)	− 779.6 ± 0.6	1.7

Table 1 (continued)

Compound		Ref.[a])	Solvent/conc.	ν(Rh)/ν(Ge)[b])	δ(Rh) [ppm][c])	T_1/T_2
16		d)	Pentane 38 mM	0.905 202 9(6)	– 718.5 ± 0.8	1.7
17		d)	Hexane 40 mM	0.905 214 5(6)	– 705.7 ± 0.8	1.6
18		d)	Benzene 40 mM	0.905 261 6(10)	– 653.7 ± 1.2	–
19		d)	CH_2Cl_2 30 mM	0.905 328 0(9)	– 580.4 ± 1.1	1.4
20		[42]	Benzene 58 mM	0.905 366 1(5)	– 538.3 ± 0.7	1.7
21		[43]	Acetone 40 mM	0.905 538 9(10)	– 347.6 ± 1.2	–

[a]) References refer to the synthesis of the complexes.

[b]) At 300 K. Frequency ratio relative to the ^{73}Ge-resonance in $GeCl_4$. The reported uncertainties in brackets correspond to the three-fold standard deviation.

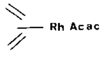
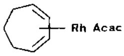
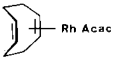
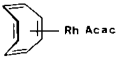
[c]) Relative to the arbitrary standard $\nu_{Rh}(Ref)/\nu_H(TMS) = 0.0316$ [6] and calculated as follows:

$$\delta(\mathrm{Rh}) = \frac{\{\nu_{Rh}/\nu_{Ge} \cdot \nu_{Ge}/\nu_H(\mathrm{TMS})\} - \nu_{Rh}(\mathrm{Ref})/\nu_H(\mathrm{TMS})}{\nu_{Rh}(\mathrm{Ref})/\nu_H(\mathrm{TMS})}$$

with $\nu_{Ge}/\nu_H(TMS) = 0.034\,884\,219(16)$ from [10] and $\delta_H(H_2O) = 4.8$ ppm.

[d]) For preparation see *Exper. Part.*

Table 2. *^{103}Rh chemical shifts of Rh^I-olefin complexes*

Compound		Ref.[a])	Solvent/conc.	ν(Rh)/ν(Ge)[b])	δ(Rh) [ppm][c])	T_1/T_2
22		[44]	CH_2Cl_2 39 mM	0.906 926 4(6)	+ 1184.1 ± 0.8	1.6
23		d)	CH_2Cl_2 53 mM	0.906 936 2(30)	+ 1195.0 ± 3.3	≈ 100
24		[35]	CH_2Cl_2 145 mM	0.907 026 1(2)	+ 1294.2 ± 0.5	1.9
25		[14]	CH_2Cl_2 35 mM	0.907 448 0(12)	+ 1759.9 ± 1.4	1.1
26	Acac Rh C_8H_8 Rh Acac	[14]	CH_2Cl_2 45 mM	0.907 448 2(4)	+ 1760.2 ± 0.6	1.4

[a])–[d]) Footnotes see *Table 1.*

Table 3. *^{103}Rh chemical shifts of dinuclear olefin complexes*

Compound	*Ref.*[a]	Solvent/conc.	$\nu(Rh)/\nu(Ge)$[b]	$\delta(Rh)$[ppm][c]	T_1/T_2
27 $[CpRhC_8H_8RhC_8H_{12}]BF_4$[d]	[13]	Propylenecarbonate 40 mM	0.904 281 0(12) 0.905 816 5(19)	−1736.2±1.4 − 41.1±2.1	1.6 3.8
28 $[CpRhC_8H_8RhC_7H_8]BF_4$[d]	[13]	CH_2Cl_2 76 mM	0.904 221 3(3) 0.905 779 0(6)	−1802.1±0.6 − 82.5±0.8	1–2 >3
29 $[CpRhC_8H_8Rh(CO)_2]BF_4$	[13]	CH_2Cl_2 130 mM	0.904 351 3(3) 0.905 210 2(9)	−1658.6±0.6 − 710.4±1.1	1–2 ≈100
30 $[(CO)_3FeC_8H_8RhC_8H_{12}]BF_4$	[13]	Propylenecarbonate 40 mM	0.905 972 7(11)	+ 131.3±1.3	–
31 $[(CO)_3FeC_8H_8RhC_7H_8]BF_4$	[13]	CH_2Cl_2 79 mM	0.905 792 6(5)	− 67.5±0.7	2.7
32 $[(CO)_3FeC_8H_8Rh(CO)_2]BF_4$	[13]	Acetone 81 mM	[e]	–	>100
33 $(CO)_3FeC_7H_7RhC_8H_{12}$	[17]	Benzene 32 mM	0.905 733 4(6)	− 132.8±0.8	3.4
34 $(CO)_3FeC_7H_7RhC_7H_8$	[17]	Benzene 145 mM	0.905 775 4(3)	− 86.5±0.6	2.0
35 $(CO)_3FeC_7H_7Rh(CO)_2$	[16]	Acetone 77mM	0.905 184 7(8)	− 738.6±1.0	2.8
36 $[CpRhC_7H_7RhCp]Cl$	[17]	Methanol 32 mM	0.904 590 3(2)	−1394.8±0.5	1.5
37 $CpRhC_7H_8RhCp$	[18]	THF 45 mM	0.904 819 2(5) 0.905 241 2(5)	−1142.1±0.7 − 676.2±0.7	2.4 3.6
38 $CpRhC_7H_6ORhCp$[f]	[17]	CH_2Cl_2 70 mM	0.904 873 0(13)	−1082.7±1.5	83
39 $CpRhC_8H_8O_2RhCp$[f]	[17]	CH_2Cl_2 127 mM	0.904 913 5(7)	−1038.0±0.9	64

[a]–[c] Footnotes see *Table 1.*

[d] C_8H_{12} = 1,5-cyclooctadiene; C_7H_8 = norbornadiene.

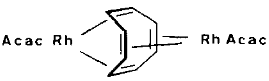
[e] A Rh-NMR.-signal was not observed.

[f] C_7H_6O = Tropone; $C_8H_8O_2$ = Tropolone methylether.

The synthesis, structure and dynamic behavior of dimetallic cationic complexes of the type $[L_lM(C_8H_8)RhL_2]BF_4$ have been described in a previous communication [13]. Formally, these structures contain one metal centre (M) with a closed shell 18e-configuration and an electron deficient 16e-Rh^+ centre, if the cyclooctatetraene is symmetrically bound to the two metal centres. The question arises, therefore, to what extent an electron exchange occurs, either *via* a metal, metal-bond or by an unsymmetrical π-electron donation from the cyclooctatetraene bridging-ligand. It was hoped that the ^{103}Rh-spectra, in particular those of the dirhodium species, might contribute an answer to this question.

The shielding value of the two structurally equivalent Rh-atoms in (acac) RhC_8H_8Rh(acac) (**26**, *Scheme 1*) (+1760.2 ppm) is very close to the resonance of (acac)RhC_8H_8 (**25**) (+1759.9 ppm) *(Table 2)* indicating the analogous η-1,2-5,6-bonding mode in these 32e- and 16e-complexes, respectively. The result is in agreement with the structure containing a tub-shaped cyclooctatetraene-ligand η-1,2-5,6-complexed by two (acac)Rh-moieties [14].

Scheme 1



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The close correspondence between the ^{103}Rh-shielding values of the mono- and the dinuclear complex indicates the effective electronic isolation ot the two 1,5-diene systems. There is no detectable spin, spin-interaction between the two equivalent Rh-nuclei in **26** *(cf. Sect. 3.3).*

On the other hand, the Rh-spectra of the cationic dinuclear complexes **27**, **28** and **29** exhibit two distinctly different signals and the spectra are illustrated in *Figure 2.* The chemical shifts and the relative intensities of the two Rh-signals allow an assignment of the strong and highly shielded resonance to the CpRh-moiety, whereas the signal with variable intensity and chemical shift must be attributed to the RhC_7H_8-, RhC_8H_{12}- and $Rh(CO)_2$-groups, respectively. The large chemical shift difference clearly demonstrates the different oxidation states of the Rh-atoms, the formally zero-valent Rh(1) being even more shielded than in the mononuclear CpRh(diene)-complexes of *Table 1.* The Rh(2)-signal is strongly deshielded and reflects the different electron-donating properties of the cyclooctadiene and norbornadiene ligands on the one hand, and of the carbonyl ligands on the other. Thus, the positive charge of the cationic complexes can be assigned to the Rh(2)-atom. The resonances of both Rh-atoms, however, are shielded when compared with Rh^0- and Rh^I-shifts of mononuclear species, respectively *(cf. Tables 1* and *2),* apparently as a result of Rh,Rh-bonding. The above signal assignment is supported by the observed (T_1/T_2)-ratios being close to 1.2 for Rh(1) but higher and of variable magnitude for Rh(2) *(Table 3).* These effects on the relaxation times are due to structural dynamics of the olefin complexes and will be further discussed in *Sect. 3.2.*

The dinuclear complexes with non-equivalent Rh-nuclei raise the question of Rh,Rh-spin coupling, since the two metal atoms can be expected to be in spatial proximity (*cf.* the crystal structure *(Fig. 6)* of $[(CO)_3FeC_8H_8RhC_7H_8]BF_4$ (**31**), r(Rh-Fe) = 291 pm [15]. In fact, a lowering of the pulse repetition rate 1/T from 83 Hz to 10 Hz in measuring the spectrum of $[CpRhC_8H_8RhC_8H_{12}]BF_4$ (**27**) shows that the Rh-signals can no longer be observed under broad-band excitation (double resonance). However, the two resonances can be obtained with this low pulse-repetition rate using *selective* excitation of each line, whereby a destruction of the steady-state by double-resonance is avoided *(cf. Sect. 3.3.1).* A doublet splitting, however, is still not observable. Even lower pulse-repetition rates 1/T lead to further intensity losses in steady-state experiments, a consequence of field inhomogeneity and diffusion effects, and no line-splitting due to Rh,Rh-spin coupling was observable. It may be concluded *(Sect. 3.3)* that $J(Rh,Rh) < 10$ Hz. A similar value can be extracted from the analysis of the ^{13}C-NMR.spectra of dirhodium complexes *(Sect. 3.3.2).*

The isoelectronic heteronuclear complexes $[(CO)_3FeC_8H_8RhC_8H_{12}]BF_4$ (**30**) and $[(CO)_3FeC_8H_8RhC_7H_8]BF_4$ (**31**) yield Rh-resonance lines in the same δ-region as the Rh^+(2)-atom in the dirhodium complexes **27** and **28**, again supporting the above assignment of the two Rh-resonances. In the $Fe(CO)_3$-series, the $Rh(CO)_2$-resonance must be even weaker than in complex **29** and was not observable due to a larger (T_1/T_2)-ratio. The crystal structure of $[(CO)_3FeC_8H_8RhC_7H_8]BF_4$ illustrated in *Figure 6* indicates an unsymmetrical (3 + 5)e-bonding mode of the C_8H_8-moiety and the presence of a Rh,Fe-bond, both stabilizing the 34e-structure of the complex. Similar structural features may be expected for the isoelectronic dirhodium complexes **27**, **28** and **29**. The X-ray structures will be reported in a later communication.

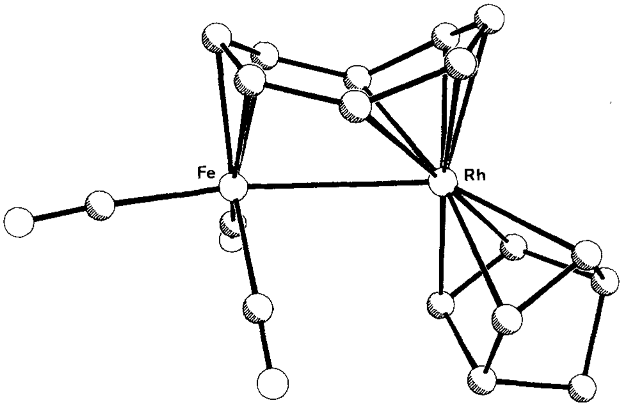
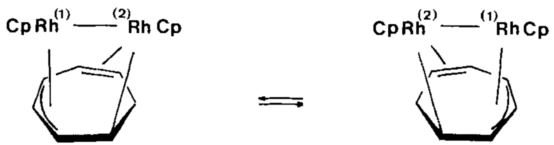


Fig. 6. *Molecular structure of the* $[(CO)_3FeC_8H_8RhC_7H_8]^+$ *cation as obtained by X-ray analysis of the tetrafluoroborate* **31** (r(Fe–Rh) = 291 pm, [15])

The neutral hetero-dimetallic Rh-complexes with a C_7H_7-unit as bridging ligand (**33**, **34** and **35**) can be considered as containing a Rh^IL-moiety complexing a C_7H_7-ligand in an η^4-mode [16]. In fact, the ^{103}Rh-resonances exhibit chemical shifts which lie relatively close to the Rh^I(2)-resonances in the respective dirhodium complexes **30**, **31** and **32**. These 34e-complexes may thus be looked at as structural analogues of the dirhodium(cyclooctatetraene)-compounds [13]. On the other hand, more highly shielded Rh-lines are observed for the dinuclear 34e-complex **36** in which a tropylium ion acts as the bridging ligand for two magnetically equivalent Rh^0-atoms. The δ-value (–1394.8 ppm) is found in the resonance range typical for CpRh-units in dimetallic complexes. The same applies for the 34e-complexes containing a tropone bridging ligand (**38** and **39**), whereby the O-atoms apparently cause a deshielding effect of 300–350 ppm as compared to complex **36**. Bonding of the tropone and tropolone bridging ligands to the two CpRh-units is of a fluxional nature since the Rh,C-splittings in the ^{13}C-spectra are temperature-dependent *(cf. Sect. 3.3.2)*. The structure of these complexes will be treated in more detail in a subsequent communication [17].

The structure of the dimetallic cycloheptatriene complex $CpRhC_7H_8RhCp$ (**37**) was described earlier based upon the temperature-dependence of the ^1H-and ^{13}C-NMR. spectra [18]. The important feature of this structure *(Scheme 2)* is the (temperature-independent) NMR.-spectroscopic non-equivalence of the two CpRh-moieties, which is also observed in the ^{103}Rh-spectrum showing two resonance lines at –1142.1 and –676.2 ppm (Fig. 7).

Scheme 2



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3.2 *Relaxation effects and chemical exchange.* For the following two Rh complexes, the ($T_1 + T_2$)-experiment (see. *Fig. 4*), as well as the (T_1/T_2)-experiment, were performed, *i.e.*, the spin-lattice relaxation time T_1 and the transverse relaxation time T_2 were determined in the field $B_0 = 2.114$ T. To infer the mechanisms for this relaxation, it is worthwhile to compare the present results with the relaxation times of the nucleus ^{109}Ag, which also has the spin $I = 1/2$ and the magnetic moment $\mu = -0.1299615 \cdot \mu_N$ [19] (this is about 1.5 times the magnetic moment of the nucleus ^{103}Rh). For the Ag^+-ion in 1 molal $AgNO_3$-solution in H_2O and in D_2O, the longitudinal relaxation times $T_1 = 962$ s and $T_1 = 1115$ s, respectively, were determined [20]. This example clearly shows that even for the Ag^+-ion the longitudinal relaxation is only to a small part due to magnetic dipole interaction of the ^{109}Ag-nuclei with the protons or deuterons of the solvent, as the magnetic moments of ^{1}H and ^{2}H differ by a factor 3.3. Even more so, magnetic dipole interaction cannot be the dominant relaxation mechanism of the ^{103}Rh-nuclei in the complexes under investigation here, as the longitudinal relaxation rate of ^{103}Rh is higher by more than one order of magnitude than in the case of ^{109}Ag.

Table 4. *Spin-lattice* (T_1) *and spin-spin relaxation times* (T_2) *of* ^{103}*Rh* (300 K, $B_0 = 2.114$ T)

	T_1 [s]	T_2 [s]
$CpRhC_8H_{12}$ (**13**) (benzene, 0.18M)	60 ± 4	27 ± 1
$Rh(acac)_3$ ($CHCl_3$, 0.19M)	82 ± 3	67 ± 2

None of the Rh-complexes investigated is spherically symmetric, *i.e.*, the ^{103}Rh-nucleus is anisotropically shielded. Based on the very different ^{103}Rh-chemical shifts, as pointed out in *Tables 1–3*, a considerable anisotropy of the ^{103}Rh-chemical shift in each complex may be expected. Therefore, relaxation through anisotropic chemical shift combined with molecular reorientation must be assumed to be the predominant relaxation mechanism. As the longitudinal relaxation rate $1/T_1$, as well as the transverse rate $1/T_2$, caused by this mechanism, are $\sim B_0^2$ [21], a variation of the static field B_0 would be an excellent experimental test for this assumption; unfortunately it was not possible to perform this test as the spectrometer used does not allow a field variation. But there is another hint for the relaxation by fluctuating anisotropic chemical shift, since outside the field B_0 a complete demagnetization of the $Rh(acac)_3$ sample was not achieved even after waiting times of more than 30 min (this is about 22 times the relaxation time T_1 as measured in the field $B_0 = 2.114$ T).

Relaxation through anisotropic chemical shift combined with molecular reorientation yields a (T_1/T_2)-ratio of 7/6 in the extreme narrowing case [21]. Although this condition was clearly fulfilled for all samples under investigation, because of the low viscosity of all solvents used, ratios of the relaxation times T_1/T_2 as large as 100 were determined. The NMR. signal of some Rh-complexes was not even detectable, as their (T_1/T_2)-ratio is probably higher than 1000. There are two reasons for a ratio $T_1/T_2 \gg 1$, *i.e.*, for an essentially higher-transverse-relaxation rate $1/T_2$ than the spin-lattice-relaxation rate $1/T_1$, *a)* a chemical exchange in the molecule under investigation, or *b)* a scalar coupling ot the ^{103}Rh-nucleus to another slowly relaxing nucleus, *e.g.*, ^{19}F or ^{31}P.

a) The contribution $1/T_2 - 1/T_2^0$ to the transverse-relaxation rate by a rapid chemical exchange ($\bar{\tau}\Delta\omega \ll 1$) in the molecule under investigation between two sites A and B was pointed out by *Meiboom* [22] and by *Allerhand & Gutowsky* [23] in the following formula:

$$1/T_2 - 1/T_2^0 = P_A \cdot P_B \cdot \Delta\omega^2 \cdot \bar{\tau} = P_A \cdot P_B \cdot 4\pi^2 \cdot \nu_L^2 \cdot \delta_{AB}^2 \cdot \bar{\tau}$$

Here T_2^0 is the transverse-relaxation time which would occur without any chemical exchange. If T_1 is not influenced by chemical exchange, and in the extreme narrowing case, $T_2^0 = T_1$ may be assumed. For very rapid chemical exchange (lifetime of at least one site $\leqslant$ *Larmor*-period), T_1 is also influenced by the exchange and it is certainly $T_1 \leqslant T_2^0 < \infty$.

P_A and P_B are the relative concentrations of sites A and B, respectively, $\Delta\omega = 2\pi \cdot \nu_L \cdot \delta_{AB}$ is the difference of the two ^{103}Rh angular *Larmor*-frequencies of site A and B and $\bar{\tau}$ is calculated from the mean lifetimes τ_A and τ_B of site A and B, respectively:

$$\bar{\tau}^{-1} = \tau_A^{-1} + \tau_B^{-1}$$

It is clearly pointed out that this contribution $1/T_2 - 1/T_2^0$ of the chemial exchange to the transverse-relaxation rate does not only depend on the lifetimes τ_A and τ_B but also on the differential chemical shift δ_{AB} of the ^{103}Rh-resonance in the environments A and B, which is unknown in most cases of rapid chemical exchange. One has to take into account, however, that a very rapid chemical exchange (lifetime of at least one site must be small compared with the *Larmor*-period of ^{103}Rh, *i.e.*, $\bar{\tau} \cdot \nu_L \ll 1$) contributes as well to the spin-lattice-relaxation rate $1/T_1$ as to the transverse one $1/T_2$ and, therefore, does not change significantly the ratio T_1/T_2. From this a lower limit for the lifetimes τ_A and τ_B of the sites A and B may be derived: $\bar{\tau} \gtrsim 10^{-7}$ s for all Rh-complexes with the ratio $T_1/T_2 \gg 1$.

Assuming equal populations for both sites A and B ($P_A = P_B = 1/2$), and for

$$\delta = 100 \text{ ppm and } \bar{\tau} = 10^{-6} \text{ s}$$

or

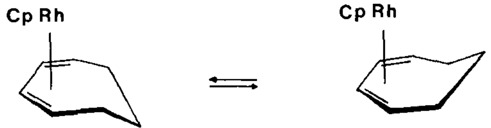
$$\delta = 10 \text{ ppm and } \bar{\tau} = 10^{-4} \text{ s}$$

the *Gutowsky*-formula yields a contribution $1/T_2 - 1/T_2^0 \approx 1$ s^{-1}. This leads to a ratio

$T_1/T_2 \approx 50$–100 assuming spin-lattice relaxation times T_1 as measured for $Rh(acac)_3$ or $CpRhC_8H_{12}$.

(T_1/T_2)-Ratios considerably higher than unity, as given in *Tables 1–3* for some Rh-complexes, indicate a chemical exchange with lifetimes comparable with, or longer than, the *Larmor*-period of the ^{103}Rh-nucleus: $\bar{\tau} > 10^{-7}$ s. Lifetimes $\bar{\tau} > 10^{-3}$ s (within the fast exchange limit) will lead, even for small chemical shifts ($\delta_{AB} \sim 10$ ppm), to such high ratios T_1/T_2 that a detection of the ^{103}Rh-NMR. signal is prevented. The (T_1/T_2)-ratios are thus suitable for the detection of fast exchange processes at ambient temperature. For example, CpRh(1,3-cycloheptadiene) (**11**) and (acac)Rh(1,3-cycloheptadiene) (**23**) exhibit (T_1/T_2)-ratios of 82 and 100, respectively. Here, the dynamic process is undoubtedly the inversion of two half-chair ring conformations leading to diastereoisomeric complexes with different ^{103}Rh-chemical shifts.

Scheme 3



11

The ^{13}C-NMR. spectra of **11** (+30° to –90°) confirm the dynamic process and the predominance of one diastereoisomer (coalescence range at $\approx -70°$, 25.2 MHz).

In the dimetallic series the effects of chemical exchange are evident for $[CpRhC_8H_8Rh(CO)_2]BF_4$ (**29**) in which the Rh^0- and Rh^I-nuclei yield very different (T_1/T_2)-ratios. This difference is much smaller but still significant in $[CpRhC_8H_8RhC_8H_{12}]BF_4$ (**27**) and $[CpRhC_8H_8RhC_7H_8]BF_4$ (**28**). In these cases the dynamic process must be associated with the bridging C_8H_8-ring, since the fluxionality of the 1,5-cyclooctadiene and norbornadiene ligands [13] does not involve a Rh-chemical-shift change.

b) Scalar coupling (coupling constant *J*) of the slowly relaxing ^{103}Rh-nucleus to any other nucleus A will affect the transverse relaxation, since the *Larmor*-frequency of the ^{103}Rh-nucleus depends on the state of spin A, just in the same manner as on the environment in the case of a chemical exchange. If the nucleus A has the spin $I > 1/2$ and a sufficiently high quadrupole moment in a spherically non-symmetric environment, the lifetime of A in a given state ($\approx T_1(A)$) is short enough to establish the case of rapid exchange ($2\pi \cdot |J| \cdot T_1(A) \ll 1$) and the multiplet in the ^{103}Rh-spectrum collapses.

A coupled nucleus A with spin $I = 1/2$ (*e.g.*, ^{19}F or ^{31}P) is in general slowly relaxing and its influence on the ^{103}Rh-spectrum corresponds to a slow exchange ($2\pi \cdot |J| \cdot T_1(A) \gg 1$), *i.e.*, the ^{103}Rh-multiplet may be resolved or the lines are broadened. *McConnell* [24] has pointed out, using modified *Bloch*-equations, that the transverse-relaxation rate of ^{103}Rh in this case is raised by the scalar coupling:

$$1/T_2 = 1/T_2^0 + 1/T_1(A) \approx 1/T_1(A)$$

$1/T_2^0$ is the ^{103}Rh-transverse-relaxation rate without scalar coupling, which may be neglected in most cases. In other words, the transverse-relaxation time T_2 of the ^{103}Rh-nucleus is the same as the spin-lattice-relaxation time $T_1(A)$ of the coupled nucleus A, and this result is independent of the coupling constant J as long as the condition $2\pi \cdot |J| \cdot T_1(A) \gg 1$ for slow exchange holds.

As the spin-lattice relaxation of ^{103}Rh is not affected by this coupling, the ratio T_1/T_2 is raised considerably and the sensitivity of the ^{103}Rh-resonance is lowered by the factor $(T_2/T_1)^{1/2}$. In many cases, such a scalar coupling of the extremely slowly relaxing ^{103}Rh to a nucleus with $I = 1/2$ (*e.g.* ^{19}F or ^{31}P) prevents the detection of the ^{103}Rh-signal, an effect which is well known from faster relaxing spin 1/2 nuclei coupled to a quadrupole nucleus. As an example in the present series of Rh-complexes, scalar coupling of the metal nucleus to ^{31}P in triphenylphosphite ligands, *e.g.*, in $CpRh[P(OC_6H_5)_3]_2$, has prevented a measurement of the Rh-NMR. signal.

On the other hand, it must be emphasized that such a scalar coupling of the ^{103}Rh to a nucleus with spin $I = 1/2$ opens the way to record the ^{103}Rh-spectrum by heteronuclear double-resonance.

3.3 Coupling Constants. – 3.3.1 Scalar Rh,Rh-coupling. Among the dinuclear complexes *(Table 3)*, the dirhodium species possibly show an indirect Rh,Rh spin-coupling, *i.e.*, both ^{103}Rh-NMR. lines with different chemical shifts may be split into doublets. To detect this doublet structure, the resolution had to be raised as much as possible, *i.e.*, the pulse-repetition rate 1/T was lowered down to 10 Hz which is combined, however, with a considerable loss of signal intensity (*cf.* p. 382 of [8]). In a homogeneous field B_0, this pulse repetition rate 1/T = 10 Hz yields an NMR. line-width of 6 Hz, which corresponds to our instrumental ^{103}Rh line-width of about 7 Hz due to the inhomogeneity of B_0, *i.e.*, the pulse-repetition rate 1/T = 10 Hz yields nearly the maximum possible resolution. To avoid a homonuclear double-resonance experiment, selective irradiation was chosen. In the four compounds of *Table 3*, containing two nonisochronous Rh-nuclei, the stronger ^{103}Rh-line was investigated in this way. Neither a doublet structure nor a line broadening due to Rh,Rh-coupling was observed in the spectrum of any of our complexes. This result yields an upper limit of $|J| < 10$ Hz for the coupling constants of all complexes investigated.

On the other hand, the existence of a scalar Rh,Rh-coupling is clearly proven for complexes **27** and **37**, the spectra of which are plotted in *Figures 2* and *7:* Application of a wide-band rf-spectrum *(Fig. 1a)* to the complex, *i.e.*, recording of the total ^{103}Rh-spectrum reduced considerably the intensity of both ^{103}Rh-lines in comparison with the selective irradiation of only one ^{103}Rh-line of the spectrum. This effect is shown in *Figure 7* for the $CpRhC_7H_8RhCp$ complex (**37**); with a pulse-repetition rate 1/T = 83 Hz, non-selective irradiation reduces the signal intensity by a factor ≈ 3. This signal reduction due to a homonuclear double-resonance experiment increases with decreasing pulse-repetition rate, *i.e.*, the effect of signal reduction by double-resonance is the smaller, the better the condition $|J| \ll (1/T)$ is fulfilled.

The striking effect of the scalar Rh,Rh-coupling on the signal intensity, in spite of the small coupling constant, is based on the extremely slow relaxation of the ^{103}Rh-nucleus; from this a lower limit for the coupling constant may be deduced: $|J| > (1/T_2)$. These results, *i.e.*, $1/T_2 < J(\mathrm{Rh,Rh}) < 10$ [Hz], are in good agreement with the conclusions drawn from the analysis of the ^{13}C-spectra.

3.3.2 Scalar ^{103}Rh,^{13}C-coupling. A valuable source of structural information for rigid and fluxional metal complexes are the scalar coupling constants between the transition metal and the ligand C-atoms. They lead, in the case of rhodium(olefin)

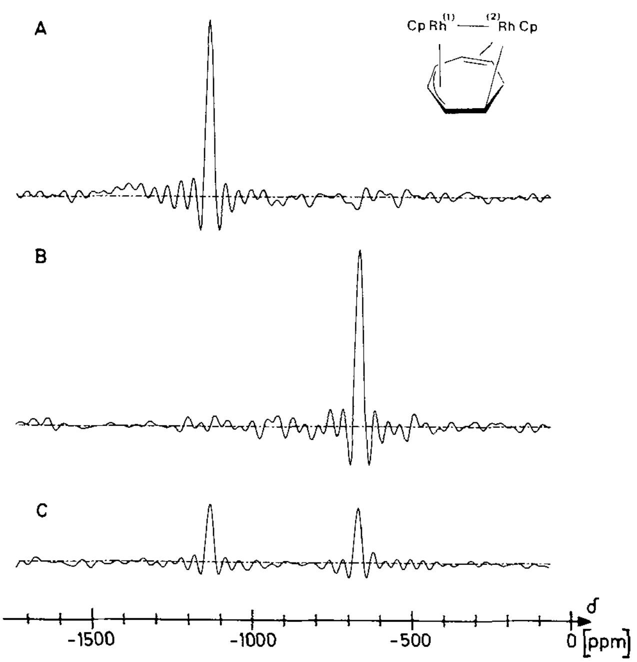


Fig. 7. *^{103}Rh-spectra of the dirhodium complex CpRhC_7H_8RhCp* (**37**) *with selective irradiation* (A and B) and *with wide-band irradiation* (C), *recorded with the aid of the* Quadriga-*technique*. Shielding increases from right to left. All spectra were obtained with a pulse-repetition rate 1/T = 83 Hz. The pulse spacing for selective irradiation was $\Delta\tau = 376 \mu s$ corresponding to the difference $\Delta\nu = 1325$ Hz of the *Larmor*-frequencies of both lines. The carrier frequency ν_E was chosen in spectrum A, near the *Larmor*-frequency of the low-frequency line and, in spectrum B, near the *Larmor*-frequency of the high-frequency line. In spectrum C, recorded in the same measuring time using wide-band irradiation, the signal intensity is reduced by a factor ≈ 3, due to the homonuclear double-resonance experiment performed in the coupled spin-system.

complexes and depending upon the type of Rh,C-bond, to splittings in the proton-noise-decoupled ^{13}C-resonance lines with typical coupling constants of up to 20 Hz.

In dirhodium complexes an olefinic C-atom may be coupled to one or both Rh-nuclei. Thus, in [CpRhC_8H_8RhC_8H_{12}]BF_4 (**27**) the cyclooctatetraene resonance is split into four lines which can be considered as the *X*-part of an *AMX* spin-system, since the relative chemical shift of the two Rh-nuclei is very large (≈ 10 KHz). The two separations in the *X*-resonance (3.9 and 2.1 Hz) are averaged *J*(Rh,C) values because at 30° the eight cyclooctatetraene C-resonances are observed in the fast-exchange limit [13]. In complex **28** the observed values are 3.9 and 2.0 Hz, in complex **29** 3.6 and 2.1 Hz. An assignment to the two non-equivalent Rh-atoms can be made by comparison with the isoelectronic hetero-dimetallic complexes of the type [$(CO)_3$FeC_8H_8RhL]BF_4 (**30**, **31**, **32**) which only contain the Rh^1-atom and give a doublet splitting of 2.1–2.2 Hz for the cyclooctatetraene resonance. If the Rh,C spin-system is of the type *ABX* or *AA'X* the *X*-resonance may contain information about the value of ^1J(Rh,Rh) which is difficult to obtain from the Rh-resonance in steady-state experiments *(cf. Sect. 3.3.1)*. On the other hand, the ^{13}C-signals of all the ligand

C-atoms of CpRh(tropone)RhCp (**38**) are split into triplets at room temperature (30°) whereas at –110° a doublet-splitting results. Hereby, the symmetry of the complex is retained (one Cp-signal). It may, therefore, be concluded that $J(\mathrm{Rh,Rh}) = J_{AA'} \leq 1/2(J_{AX}-J_{AX'})$ [25]. The three olefinic C-atoms of the tropone ring show coupling constants between 8 and 12 Hz. Hence, with $J_{AX} = 12$, and $J_{AX'} = 0$ Hz, an upper limit of 6 Hz is obtained for $^1J(\mathrm{Rh,Rh})$, in agreement with the estimated value resulting from line-width considerations on the ^{103}Rh-resonance of [(CpRhC$_8$H$_8$RhC$_8$H$_{12}$)]BF$_4$ (**27**). Rh,Rh coupling-constants of this magnitude were also observed in trinuclear Rh-complexes, *e.g.*, in $[\mathrm{Rh_3H_3}(\eta^5\text{–}\mathrm{C_5H_5})_3\mathrm{O}]\mathrm{PF_6}\cdot\mathrm{H_2O}$, for which a value of 10.3 Hz was obtained from a simulation of the ^{1}H-spectrum of the hydride nuclei [26].

The dimetallic cycloheptatriene complex CpRhC$_7$H$_8$RhCp (**37**) also shows a temperature-dependence of Rh,C spin-coupling [18]. In this case, however, the low-temperature structure exhibits η^3-allyl-, η^2-ene- and η^1-σ-bonding to the Rh-atoms whereas at room temperature fluxional averaging of the bonding modes occurs. It can be seen from the published J(Rh,C) data of **37** and related complexes that a Rh-C(sp^3)-σ-bond exhibits coupling constants (10–20 Hz) considerably larger than for π-bonded olefinic C-atoms.

Rh,C spin-coupling shows an interesting structural dependence in the mononuclear CpRh(diene)-complexes. For the terminal C-Atom C(1) J(Rh,C) values of 11.7 Hz (cyclobutadiene), 11.9 Hz (cyclopentadiene), 15.4 Hz (cyclohexadiene), and 17.4 Hz (cycloheptadiene) are observed. Relatively large values are also found in the 1,2-bis(methylidene)cyclobutane complex **17** (15.9 Hz) and the η-1,2-6,7-coordinated cycloocta-1,3,6-triene complex **12** (17.1 Hz). This increase can be attributed to an increasing *s*-contribution in the orbital responsible for coordination to the metal. Such a rehybridization effect at the terminal diene C-atom has previously been recognized in group VIII transition metal(olefin) complexes on the basis of H,H-, C,H- and C,C-coupling constants [2]. A detailed study of the effects on J(Rh,C) and a correlation with X-ray data is in progress.

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4. Experimental part. – The ^{103}Rh-measurements were performed with a pulse spectrometer especially developed for investigations of weak NMR. signals in the frequency range 1–4.5 MHz [7]. The static field $B_0 = 2.114$ T (corresponding to 90-MHz-proton *Larmor*-frequency) was obtained by a *Bruker B-E 45* electromagnet and externally locked on a proton signal by the *Bruker* NMR. stabilizer *B-SN 15*. The spatial homogeneity of $|\Delta B_0|/B_0 \leq 10^{-6}$ in the range of the relatively large sample (20 mm inner diameter, 40 mm filling height) was achieved by 12 gradient electric shims. The temperature of the samples was stabilized to (300 ± 1) K by a thermostat.

The NMR.-signal between the rf-pulses was accumulated in a time-averaging computer (Signal analyzer *5480 A* of *Hewlett-Packard*) to improve the signal/noise ratio. The data (1000 channels of 24 bits) were transferred *via* coaxial line at a rate of 10^5 baud to a *PDP 11/04* computer, which also controlled the experimental procedure, *i.e.*., measuring time, data transfer, length and frequency of the applied rf-pulses. The evaluation of the experimental data by *Fourier*-transformation and by *Gaussian* least-squares-fitting routines was performed by a *PDP 11/23* computer with floating-point arithmetic.

The ^{13}C-NMR. spectra were measured on *Varian XL-100-12* and *XL-200 FT* spectrometers at 25.2 and 50.3 MHz, respectively. Chemical shifts of the new complexes described below are given in δ/ppm relative to tetramethylsilane (TMS) as internal reference. ^{103}Rh,^{13}C-coupling constants [Hz] are given in brackets and were obtained from the proton-noise-decoupled spectra (digital resolution and reproducibility of *J*(Rh,C) ± 0,3 Hz).

All CpRh-complexes were prepared from $[(C_2H_4)_2RhCl]_2$ by displacement of C_2H_4 and subsequent treatment of the $[(diene)RhCl]_2$-complexes with CpTl by the general methods given below.

$[(C_2H_4)_2RhCl]_2$ [27], CpTl [28], 1,2-bis(methylidene)cyclobutane [29], cycloocta-1,3,6-triene [30], cycloocta-1,3,5-triene-7-one [31], and bicyclo [6.1.0] nonatriene [32] were synthesized following the respective literature procedure. All operations were carried out under N_2-atmosphere using dry and oxygen-free solvents.

General preparation of $[(diene)RhCl]_2$-complexes. An excess of the appropriate diene (1–5 mmol) was added to a suspension of $[(C_2H_4)_2RhCl]_2$ (0.5–1 mmol) in diethyl ether (10 ml) and stirred until no more ethylene evolved. The precipitates formed were filtered off and washed with pentane.

General preparation of (diene)RhCp-complexes. These complexes were prepared by treating a suspension of the appropriate $[(diene)RhCl]_2$ complex in diethyl ether or acetone with an equimolar amount of CpTl. The mixture was stirred for 3–12 h, the TlCl formed filtered off, the solvent evaporated and the residue chromatographed with pentane on *Alox III*, to give yellow-orange solids which could be crystallized from pentane.

Several complexes used in this work have already been structurally characterized (see references in *Tables 1, 2* and *3*). For the new compounds ^{13}C-NMR.-spectroscopic data are reported below after the respective syntheses.

(Cyclobutadiene) (cyclopentadienyl)rhodium (**1**). The unsatisfactory yield of the synthetic method of *Gardner & Rausch* [33] lead us to the substitution of $[(CO)_2RhCl]_2$ by $[(C_2H_4)_2RhCl]_2$. α-Pyrone (2.5 ml, 2.3 mmol) in benzene was irradiated for 24 h with a 125 W high-pressure Hg-lamp leading to the formation of α-photo-pyrone. $[(C_2H_4)_2RhCl]_2$ (0.3 g, 0.9 mmol) was added and the suspension was stirred under further irradiation for 12 h. The solution was worked up as described above. Yield of white complex **1**: 0.08 g (26%).

(η-1-4-Cyclohepta-1,3,5-triene) (cyclopentadienyl)rhodium (**8**). The method described above lead, as reported by *Lewis et al.* [18], to the dinuclear complex $CpRhC_7H_8RhCp$ as the major product. As a second product a mononuclear complex C_7H_8RhCp was isolated which we could characterize by ^{13}C-NMR. as complex (**8**). Yield: 18%. – ^{13}C-NMR.: 83.8 (5.1) Cp; 84.5 (6.3), 78.8 (6.5), 51.5 (18.2) and 47.1 (16.6) coord. olefinic C; 128.9 (9.2) and 125.6 (2.1) uncoord. olefinic C; 32.1 (1.5) aliphatic C.

(1,3-Cycloheptadiene) (cyclopentadienyl)rhodium (**11**). Yield: 72%; ^{13}C-NMR.: 84.0 (4.8) Cp; 78.3 (6.1) and 49.7 (17.4) coord. olefinic C; 30.0 (1.5) and 26.3 (0.5) aliphatic C.

(η-1,2–6,7-Cycloocta-1,3,6-triene) (cyclopentadienyl)rhodium (**12**). Yield: 75%. – ^{13}C-NMR.: 85.4 (4.2) Cp; 48.4 (16.9), 46.4 (17.1), 19.0 (5.6) and 18.7 (5.4) coord. olefinic C; 131.0 (3.4) and 128.2 (1.8) uncoord. olefinic C; 27.9 (1.2) and 22.7 (2.7) aliphatic C.

(1,5-Hexadiene) (cyclopentadienyl)rhodium (**15**). The corresponding $[(diene)]RhCl]_2$-complex [35] and, subsequently, complex **15** were prepared by the above described methods. Yield: 81%. – ^{13}C-NMR.: 86.7 (3.8) Cp; 62.7 (13.1) and 37.7 (14.0) coord. olefinic C; 33.9 (0.7) aliphatic C.

(4-Vinyl-1-cyclohexene) (cyclopentadienyl)rhodium (**16**). Yield: 69%. – ^{13}C-NMR.: 86.9 (3.7) Cp; 68.6 (11.7), 56.9 (12.8), 46.6 (15.4) and 38.1 (13.9) coord. olefinic C; 42.3 (0.8), 33.4 (0.8), 24.1 (≈0) and 21.4 (1.3) aliphatic C.

1,2-Bis(methylidene)cyclobutane) (cyclopentadienyl)rhodium (**17**). Yield: 72%. – ^{13}C-NMR.: 83.5 (5.0) Cp; 107.2 (7.3) and 27.1 (15.9) coord. olefinic C; 34.2 (1.1) aliphatic C.

(η-2,3-6,7-Bicyclo[6.1.0]nona-2,4,6-triene)(cyclopentadienyl)rhodium (**18**). The corresponding [(diene) $RhCl]_2$-complex [34] and, subsequently, complex **18** were prepared by the methods described above. Yield: 86%. – ^{13}C-NMR.: 86.5 (3.8) Cp; 65.7 (13.0) and 65.2 (14.8) coord. olefinic C; 134.5 (0.7) uncoord. olefinic C; 20.5 (1.3) and 10.1 (1.5) aliphatic C.

(η-1,2-5,6-Cycloocta-1,3,5-trien-7-one) (cyclopentadienyl)rhodium (**19**). Yield: 77%. – ^{13}C-NMR.: 87.2 (4.1) Cp; 69.0 (13.8), 67.2 (13.2), 63.8 (15.3) and 41.9 (10.9) coord. olefinic C; 135.3 (0.8) and 133.7 (0.5) uncoord. olefinic C; 202.4 (1.0) and 36.8 (1.0) aliphatic C.

(1,3-Cycloheptadiene) (acac)rhodium (**23**). The synthesis followed the method of *Bennet & Saxby* [14] by treating 0.3 g of the $[(diene)RhCl]_2$-complex (prepared by the above described method) with an excess of 2,4-pentanedione (2 ml) in dry petroleum ether (b.p. 60–80°) (15 ml) and anh. K_2CO_3. The solution was stirred for 2 h, then filtered and the solvent evaporated. Recrystallization was possible from pentane. Yield: 76%. – ^{13}C-NMR.: 186.6, 99.8 and 27.3, acac; 78.1 (8) and 67.7 (15) coord. olefinic C; 32.5 and 23.0 aliphatic C.

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