106. Dimetallic Complexes with Bridging Seven-membered Cycloolefins. Synthesis, Multinuclear NMR.-Spectroscopic Properties and Structure[1])

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Summary

The synthesis of dimetallic olefin complexes of the type $L^1M^1C_7H_7M^2L^2$ (M^1 = Fe, Co, Rh; M^2 = Rh, Ir, Pd; L^1 = CO, C_5H_5; L^2 = diene, allyl, $P(OR)_3$) is described. The fluxional structures were investigated by ^{13}C-, ^{57}Fe- and ^{103}Rh-NMR.-spectroscopy, and a *cisoid* dimetallic coordination, including a (metal, metal)-bond, can be deduced for the C_7H_7-ring. ^{57}Fe- and ^{103}Rh-chemical shifts give indications for the charge distribution in the 34e-complexes. The homo-dimetallic complex (Cp)Rh(tropone)Rh(Cp) (**13**, Cp = cyclopentadienyl) and the corresponding 2-methoxytropone complex **14** were synthesized in addition to the above mentioned complexes. A fluxional bis(1-3-η-allyl)-coordination of the two Rh-atoms was derived from the temperature-dependent ^{13}C-NMR.-spectra. A spin simulation of the (Cp)-multiplets of **12** and **13** yields information about (Rh, Rh)-spin-coupling which amounts to ≈ 5 Hz at 30°.

1. Introduction. – The use of seven-membered cycloolefins, such as cyclohepta-triene as ligands in organometallic chemistry is well established [3]. Only seldom, however, complexes are formed in which two transition metals are attached to the same cycloolefin. Examples of cycloheptatrienyl complexes containing two different metal atoms are even rarer.
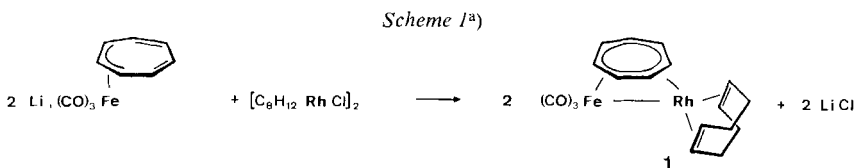
Our recent work on heterodimetallic compounds with bridging cyclooctatetraene has revealed a quite general synthetic route to such complexes [1] [4]. It was shown that cycloolefin complexes, *i.e.* $(C_8H_8)Fe(CO)_3$ or $(C_8H_8)Co(Cp)$ (Cp = cyclopenta-dienyl) with two uncoordinated double bonds, readily react with unsaturated organometallic groups to yield dimetallic complexes in which both metals are linked by a (metal, metal)-bond and a common fluxional cyclooctatetraene ligand. A closed-shell configuration for both metal centres is formally achieved either *via* a donor (metal, metal)-bond or an unsymmetrical bonding mode of the bridging cyclooctatetraene. Structural arguments were obtained by spectroscopic as well as X-ray data [2] [4]. Curiously, the ^{103}Rh-NMR. data of complexes containing two

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different Rh-nuclei showed only a small change in the chemical shifts for the two metal centers when compared with their monomeric precursors, indicating that in the dimetallic compounds the metals largely retain their previous oxidation states [2]. A structurally related system was prepared by *Bennett et al.* [5] who reported that treatment of $[(1-3-\eta-C_7H_7)Fe(CO)_3]Li$ with $[(CO)_2RhCl]_2$ yields a dimetallic complex $(CO)_3Fe(C_7H_7)Rh(CO)_2$, albeit in low yields, with a bridging fluxional cycloheptatrienyl ring. The anionic complex $[(1-3-\eta-C_7H_7)Fe(CO)_3]^-$ again serves as electron-rich $(18+4)$e-precursor reacting with *in situ*-generated $[(CO)_2Rh]^+$, a 12 e-species. The X-ray structure shows an unsymmetrical bonding mode of the bridging C_7H_7-ring, the $Fe(CO)_3$-unit coordinating to three C-atoms and the $Rh(CO)_2$-moiety, having one electron less, to four C-atoms of the common C_7H_7-ligand.

We were interested to extend this work by using a variety of unsaturated organometallic groups as well as other electron-rich olefin complexes and to further probe the spectroscopic and chemical properties of heterodimetallic systems with fluxional bridging ligands. An additional aim was the synthesis of various homonuclear dimetallic Rh-compounds with carbocyclic bridging ligands. That way we hoped to gain better insight into the mechanisms of organometallic rearrangements as well as the nature of such (metal, metal)-bonds, in particular by the use of ^{103}Rh- [2] and ^{57}Fe- [6] NMR. spectroscopy.

2. Results and Discussion. – 2.1. *Heteronuclear complexes.* Treatment of violet-red solutions of $[(C_7H_7)Fe(CO)_3]Li$ in THF with $[(C_8H_{12})RhCl]_2$ $(C_8H_{12} = 1,5$-cyclo-octadiene) lead, after workup, to golden-brown platelets of complex **1** in up to 50% yield. Elemental analyses confirmed the expected composition $(CO)_3Fe(C_7H_7)$-$Rh(C_8H_{12})$ *(Scheme 1).*

<div align="center">

Scheme 1[a]

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2 Li, $(CO)_3$ Fe   + $[C_8H_{12}$ Rh Cl$]_2$ $\longrightarrow$ 2 $(CO)_3$ Fe —— Rh   + 2 LiCl

<div align="center">1</div>

[a]   The drawing of the bridging ring in this and subsequent *Schemes* does not imply a planar structure of the C_7H_7-unit *(cf. Scheme 2).*

In a side reaction, the previously described complex $[(C_7H_7)Fe(CO)_3]_2$ [5] was formed by oxidative coupling.

At room temperature, the noise-decoupled ^{13}C-NMR. spectrum of **1** *(Table 1)* shows a doublet (due to $(^{103}$Rh, ^{13}C)-coupling) at 64.5 ppm for the cycloheptatrienyl ring, two doublets at 83.8 and 31.7 ppm for the cyclooctadiene ligand as well as a singlet at 216.8 ppm which we assign to the three carbonyl groups. The observation of only one signal for the C_7H_7-group in the ^{13}C-NMR.-spectrum is clearly irreconcilable with a rigid bonding of the bridging ligand, but can be explained in terms of a rapid rotation of the cycloheptatrienyl moiety above the two attached metal centers, thereby resulting in a single, time-averaged environment for all seven C-atoms of the ring. The slow-exchange limiting spectrum of the cyclo-heptatrienyl ring could not even be reached at $-125°$. This is in agreement with

previous observations by *Bennett et al.* on $(CO)_3Fe(1-3-\eta: 4-7-\eta-C_7H_7)Rh(CO)_2$ [5]. It is a general phenomenon that *cisoid* dimetallic derivatives of conjugated cyclic polyolefins have activation barriers for internal reorientation which are much smaller than for the related *transoid* complexes. For instance, the limiting spectrum of *trans*-[$(C_5H_5)(CO)_2Mo(C_7H_7)Fe(CO)_3$] was already reached at $-71°$ [7].

Similar differences in fluxional behaviour have been observed in organometallic derivatives of cyclooctatetraene. For instance, *trans*-[$(CO)_3Fe(C_8H_8)Fe(CO)_3$] shows no fluxionality [8], the ^{13}C-NMR. spectrum of *cis*-[$(CO)_2Fe(\mu-CO)(C_8H_8)Fe(CO)_2$], however, exhibits a single peak for the C_8H_8-unit, even at $-100°$ [9]. Additional examples of this phenomenon were given in our own previous work [1] [4], in which all *cisoid* dimetallic complexes with bridging cyclooctatetraene showed fluxional behaviour down to $-120°$, the lowest temperature we could reach for solubility reasons, whereas the *transoid* compounds proved non-fluxional even at room temperature.

The observation of only two signals for the cyclooctadiene ligand in the ^{13}C-NMR. spectrum of **1**, again not in agreement with a rigid bonding mode, can also be explained by rapid rotational movement of this ligand, as observed in similar compounds [1]. Indeed, at $-50°$ the two doublets began to broaden and at $-75°$ four new signals reemerged, two doublets for the coordinated olefinic C-atoms and two singlets (within the limited digital resolution) for two different types of aliphatic C-atoms of the C_8H_{12}-ligand. We assume that cyclooctadiene adopts the sideway orientation shown in *Scheme 1*, the mode of complexation for a chelating diolefin observed in the X-ray structure of the related complex [$(CO)_3Fe(C_8H_8)$-$Rh(C_7H_8)$]BF_4 (C_7H_8 = norbornadiene) [2] [10]. This arrangement will render non-equivalent the two C-atoms of each double bond as well as the two pairs of 'upper' and 'lower' aliphatic C-atoms.

Reaction of [$(C_7H_7)Fe(CO)_3$]Li with [$(C_7H_8)RhCl$]$_2$ likewise produced deep-red needles of a complex $(CO)_3Fe(C_7H_7)Rh(C_7H_8)$ (**2**) in almost 90% yield. No side-products were observed in this reaction, making **2** the most convenient compound for further chemical studies. Complex **2** shows similar fluxionality in the cyclo-heptatrienyl and the norbornadiene ligands, the slow-exchange limit not being reached for both systems at $-80°$.

A third organometallic group that we used was the 1,3-cyclohexadiene complex [$(C_6H_8)RhCl$]$_2$ which gave orange platelets of $(CO)_3Fe(C_7H_7)Rh(C_6H_8)$ (**3**) in 20% yield. The ^{13}C-NMR. spectrum *(Table 1)* shows a symmetrically bound cyclo-hexadiene, which most likely is not involved in any fluxional process. An analogous complex to **1** is the iridium-iron compound $(CO)_3Fe(C_7H_7)Ir(C_8H_{12})$ (**4**) prepared as above from [$(C_7H_7)Fe(CO)_3$]Li and [$(C_8H_{12})IrCl$]$_2$. At room temperature, this compound exhibits four broad ^{13}C-signals for the 1,5-cyclooctadiene unit suggesting that the recorded spectrum is close to the coalescence point. At $-10°$ all lines become sharp, two singlets at 68.1 and 66.7 ppm for the coordinated olefinic C-atoms and two singlets at 34.5 and 32.3 ppm in the aliphatic region. The coalescence point was reached on heating to $50°$, but the fast exchange limit could not be measured due to decomposition of the complex above $70°$.

It seems unlikely that complexes **1–4** will have a different bonding mode in the solid state from that observed for $(CO)_3Fe(1-3-\eta: 4-7-\eta-C_7H_7)Rh(CO)_2$ [5], as this

Scheme 2

2
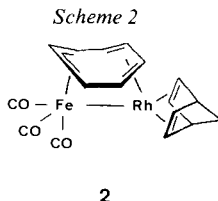
coordination of the bridging ring will give both metals a closed-shell configuration. As an example, the structure of **2** is illustrated in *Scheme 2*. With respect to the electron distribution, chemical-shift data for the metal centers (Rh and Fe) are of particular interest, and these will be discussed further below.

Cationic Rh(I)-olefin complexes are generally susceptible to nucleophilic attack and displacement reactions by *Lewis* bases such as tertiary phosphines. We could not observe any reaction of complexes **1-4** with various aryl- or alkylphosphines, not even on moderate heating. On switching to phosphites, however, a quite rapid displacement of the terminal diolefins is observed in **1-3**, **4** being again inert to ligand exchange. We isolated deep-red crystals of $(CO)_3Fe(C_7H_7)Rh[P(OCH_3)_3]_2$ (**5**) and $(CO)_3Fe(C_7H_7)Rh[P(OC_6H_5)_3]_2$ (**6**) in excellent yields. In the ^{13}C-NMR. spectra these complexes show multiplets for the cycloheptatrienyl ligand due to coupling with the Rh- and the two P-nuclei.

Scheme 3

2

5 R = CH₃
6 R = C₆H₅
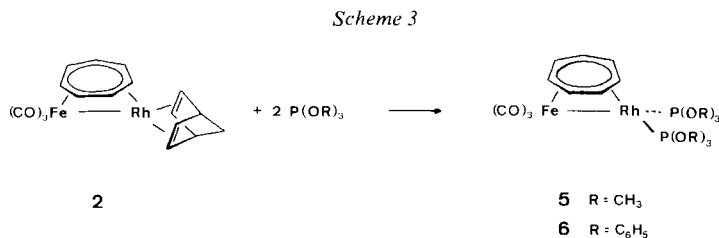
The dienes can also be displaced by carbon monoxide at atmospheric pressure giving good yields of the previously described $(CO)_3Fe(C_7H_7)Rh(CO)_2$ [5]. The Rh-center in these dimetallic complexes, therefore, appears to be a more suitable coordination site for ligands which are good π-acceptors (*i.e.* olefins, phosphites, carbon monoxide) rather than for σ-donors, such as phosphines.

In extension of this work, we looked for other organometallic groups that might react with the anionic (18 + 4)e-species $[(C_7H_7)Fe(CO)_3]^-$. Likely candidates were dimeric Pd-compounds [(allyl)PdCl]₂ and [(2-methylallyl)PdCl]₂ that show many similarities in reactivity compared to $[(C_8H_{12})RhCl]_2$ and $[(C_7H_8)RhCl]_2$ [11]. On reaction with $(C_8H_8)Co(Cp)$ these compounds had produced dimetallic species with a rigid *transoid*-arrangement of the two metals, a 'pseudo-tripledecker' structure [1]. This type of bonding with four largely unconjugated double bonds seems, however, peculiar to cyclooctatetraene, and less likely to occur with the preferentially conjugated cycloheptatrienyl ligand. The ^{13}C-NMR. spectra of the dimetallic Fe,Pd-compounds **7** and **8**, prepared in a completely analogous manner as

Scheme 4
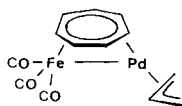
7

described above, suggested indeed the usual *cisoid*-bonding mode with a fluxional cycloheptatrienyl ligand and a symmetrically bound allyl group.

The complexes $(CO)_3Fe(C_7H_7)Pd(C_3H_5)$ (**7**) and $(CO)_3Fe(C_7H_7)Pd(C_4H_7)$ (**8**) react rapidly with *Lewis* bases such as triphenylphosphine, the only isolated product in both cases being the well-known $Pd(PPh_3)_4$. So far, we have not been able to elucidate the mechanism of this reaction or to trace the cycloheptatrienyl-iron unit.

A last example for a heterodimetallic complex with a bridging cycloheptatrienyl ring was provided by the reaction of $(1\text{-}3\text{-}\eta\text{-}C_7H_7)Co(CO)_3$ [12], the isoelectronic Co-analogue of $[(1\text{-}3\text{-}\eta\text{-}C_7H_7)Fe(CO)_3]Li$, with $[(C_7H_8)Rh]BF_4$. Complex **9** has the expected analytical composition $[(CO)_3Co(C_7H_7)Rh(C_7H_8)]BF_4$ and exhibits a ^{13}C-NMR. spectrum very similar to its analogue $(CO)_3Fe(C_7H_7)Rh(C_7H_8)$ (**2**) *(Table 1)*.

Table 1. ^{13}C-NMR. data of hetero-dinuclear olefin complexes[a])

Complex	Temp. [°]	$(CO)_3$	C_7H_7	Olefinic-C	Aliphatic-C
1 $(CO)_3Fe(C_7H_7)Rh(C_8H_{12})$	+30	216.8	64.5 (*d*, 2.5)	83.8 (*d*, 9.6)	31.7 (*d*, 0.5)
	−70	217.1	64.3 (*s*)[b])	83.7 (*d*, 10)	32.8 (*s*)[c])
				83.2 (*d*, 10)	30.3 (*s*)[c])
2 $(CO)_3Fe(C_7H_7)Rh(C_7H_8)$	+30	217.1	64.7 (*d*, 2.6)	50.3 (*d*, 7.5)	57.8 (*d*, 5.3, CH)
					47.1 (*d*, 2.1, CH$_2$)
3 $(CO)_3Fe(C_7H_7)Rh(C_6H_8)$	+30	214.2	61.8 (*d*, 2.9)	78.6 (*d*, 7.9)	20.8 (*d*, 0.3)
				65.3 (*d*, 12.3)	
4 $(CO)_3Fe(C_7H_7)Ir(C_8H_{12})$	−10	214.4	61.1	68.1, 66.7	34.5, 32.3
5 $(CO)_3Fe(C_7H_7)Rh[P(OCH_3)_3]_2$	+30	–[e])	63.4 (*m*)[d])		51.4 (*t*, 1.6)
6 $(CO)_3Fe(C_7H_7)Rh[P(OC_6H_5)_3]_2$	+30	–[e])	64.4 (*m*)[d])	151.8 (*t*, 4.9)	
				129.3 (*s*)	
				123.9 (*s*)	
				120.9 (*t*, 2.4)	
7 $(CO)_3Fe(C_7H_7)Pd(CH_2)_2CH$	+30	–[e])	84.3	113.1 (CH)	
				69.6 (CH$_2$)	
8 $(CO)_3Fe(C_7H_7)Pd(CH_3(CH_2)_2C)$	+30	–[e])	84.5	128.7 (C)	22.9 (CH$_3$)
				69.4 (CH$_2$)	
9 $(CO)_3Co(C_7H_7)Rh(C_7H_8)$	+30	–[e])	75.3 (*d*, 2.9)	67.0 (*d*, 6.2)	62.1 (*d*, 4.7, CH)
					48.8 (*d*, 2.0, CH$_2$)

[a]) ^{13}C-chemical shifts (ppm), obtained from proton-noise-decoupled spectra in D_6-acetone, internal reference TMS; letters and numbers in brackets refer to signal multiplicities and (Rh,C)-coupling constants (Hz), or averaged values.
[b]) Exchange-broadened.
[c]) Due to limited resolution.
[d]) Multiplicities in **5** and **6** are due to (Rh,C)- and (P,C)-spin-coupling.
[e]) (CO)-resonance not obtained.

The formation of these dimetallic complexes **1–8** from two charged precursors $[(C_7H_7)Fe(CO)_3]^-$ and $[LM]^+$ raises the question of electron distribution in the neutral products. Due to the unfavorable electronic state of the C_7H_7-anion as an antiaromatic system, one may attribute the negative charge in the $[(C_7H_7)Fe(CO)_3]Li$-complex to the Fe-atom rather than to the seven-membered ring. This is also indicated by the very low ^{57}Fe-resonance frequency corresponding to a high shielding of the Fe-atom, *i.e.* -172 ppm in $[(CO)_3Fe(C_7H_7)]Li$ compared with $+300$ ppm for $(C_8H_8)(CO)_3Fe$ and $+170$ ppm for $(C_7H_8)(CO)_3Fe$ [6]. Based upon a large number of ^{57}Fe-shielding data for olefin complexes this shielding effect must be attributed to a negative charge density.

In the 34 e-dimetallic complexes described above, there are two limiting cases for the charge distribution: *a)* the negative charge can be shifted towards the Rh-atom to compensate its positive charge. This would result in (formally) two 17e-moieties, (allyl)Fe(CO)$_3$ and (diene)Rh(diene), connected by a (metal, metal)-bond, or *b)* the negative charge remains on the Fe-atom so that the dimetallic complex would be composed of the negative 18 e-part $[(allyl)Fe(CO)_3]^-$ and the positive 16 e-part $[(diene)Rh(diene)]^+$, also connected by a (metal, metal)-single bond. In case of the cyclooctatetraene complexes, the metal chemical shifts have proved to be a useful probe for electron distribution and oxidation state. It was shown that the complexes are $(18+16)e$ rather than $(17+17)e$-species and that the ^{103}Rh-NMR. resonances lie in the range of the dimetallic Rh(I)-complexes ($+131.3$ ppm for $[(CO)_3Fe(C_8H_8)Rh(C_8H_{12})]BF_4$ and -67.5 ppm for $[(CO)_3Fe(C_8H_8)Rh(C_7H_8)]BF_4$) [2]. The analogous cycloheptatrienyl complexes give ^{103}Rh-chemical shifts in the same range, namely at -132.8 ppm for $(CO)_3Fe(C_7H_7)Rh(C_8H_{12})$ (**1**) and at -86.5 ppm for $(CO)_3Fe(C_7H_7)Rh(C_7H_8)$ (**2**). For complex **2** it was also possible to measure the ^{57}Fe-NMR. spectrum. This resonance lies in the region of high-shielding $(-223.5$ ppm) and, if a (Fe, Rh)-coordination shift is taken into account, near the resonance of the mononuclear (cycloheptatrienyl)Fe(CO)$_3$-anion $(-172$ ppm). All these results are very good indications for case *b (Scheme 5)* with the negative charge concentrated on the Fe-atom and the positive charge on the Rh-atom leading to an electron distribution similar to the dinuclear cyclooctatetraene complexes, *i.e.* $(18+16)e$.

Scheme 5
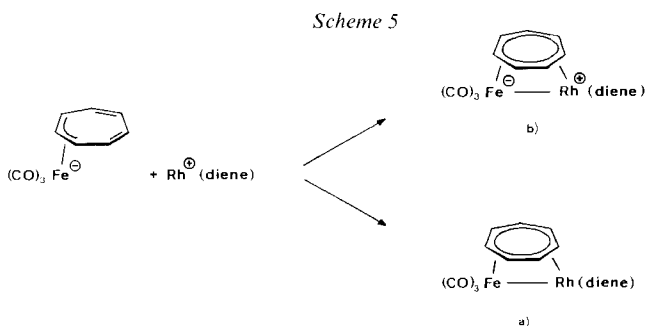
2.2. Homonuclear Complexes. For a study of charge distribution and (metal, metal)-bonding in this type of complexes it should be advantageous to

substitute the Fe-atom by a second Rh-atom since the 100%-isotope ^{103}Rh is more easily detected by NMR. than ^{57}Fe with its very low natural isotope abundance of 2.2%. The dirhodium complexes should also allow to investigate (Rh, Rh)-spin-coupling, as previously shown in the case of the dinuclear cyclooctatetraene complexes [2]. However, we did not succeed to prepare the mononuclear reactant $(C_7H_7)Rh(CO)_3$ which might have lead to the homo-dinuclear analogue of the cationic complex **9**. On the other hand, neutral dirhodium complexes of type $(Cp)Rh(C_7H_7)Rh(diene)$, the analogues of complexes **1-3**, were not obtained because of the low yield in the synthesis of $(C_7H_8)Rh(Cp)$, (C_7H_8 = cyclohepta-triene), and the instability of its anion.

The only homonuclear dimetallic Rh-complexes with a bridging cyclohepta-triene ring are those described by *Evans et al.* [13], *i.e.* $(Cp)Rh(C_7H_8)Rh(Cp)$ **(10)** with one Rh-atom coordinated in an $(1-3-\eta$-allyl)- and the other Rh-atom in a π,σ-bonding mode, and the protonated form of this complex, $[(Cp)Rh(\mu-H)(C_7H_8)-Rh(Cp)]X$ **(11)** with both Rh-atoms coordinated to the seven-membered ring in the

Scheme 6

10   11
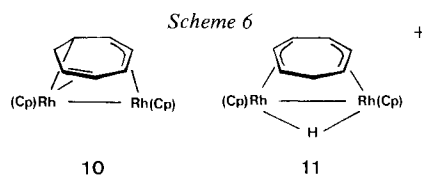
$(1-3-\eta$-allyl)-mode *(Scheme 6)*. Abstraction of a hydride ion from the complex **10** by $[(C_6H_5)_3C]BF_4$ to yield a tropylium complex did not prove possible. However, we were surprised that this reaction took place when stirring the red solution of **10** in pure CH_2Cl_2 for 48 h at room temperature leading, in almost quantitative yield, to a violet crystalline product characterized as $[(Cp)Rh(C_7H_7)Rh(Cp)]Cl$ **(12)**. The ^{13}C-NMR. spectrum obtained at room temperature shows a sharp triplet at 63.3 ppm

Table 2. ^{13}C-NMR. data of homo-dinuclear olefin complexes[a])

Complex	Temp.	Solvent	(Cp)-ligand	Bridging ligand
12 [(Cp)Rh(C$_7$H$_7$)Rh(Cp)]Cl	+ 30	CD$_3$OD	87.5 (*sext*)	63.3 (*t*, 4.0)
13 (Cp)Rh(C$_7$H$_6$O)Rh(Cp)[b])	+ 30	CDCl$_3$	84.5 (*qi*)	167.9 (*s*), CO
				61.2 (*t*, 4.7); 55.2 (*t*, 5.7); 52.0 (*t*, 4.0)
	− 70	CD$_3$OD	86.6 (*d*, 5.1)	61.2 (*s*)[c]); 55.2 (*s*)[c])
	−110	Freon 21	86.6 (*d*, 5)[c])	67.4 (*d*, 8)[c]); 59.2 (*d*, 12)[c]); 51.2 (*d*, 7)[c])
14 (Cp)Rh(C$_8$H$_8$O$_2$)Rh(Cp)[b])	+ 30	CDCl$_3$	85.6 (*qi*)	157.8 (*t*, 1.5, CO)
				107.5 (*t*, 4.1); 59.0 (*t*, 4.4); 50.8 (*t*, 4.2)
				49.6 (*t*, 4.1); 47.7 (*t*, 6.0); 41.1 (*t*, 5.7)
	−100	Freon 21	88.8 (*d*, 4)	−[c])
			85.6 (*d*, 5)	

[a]) ^{13}C-chemical shifts (ppm) obtained from proton-noise-decoupled spectra, internal reference TMS, letters and numbers in brackets refer to signal multiplicities (*qi* = quintuplet, *sext* = sextuplet) and (Rh,C)-coupling constants (or averaged values).
[b]) C_7H_6O = tropone; $C_8H_8O_2$ = 2-methoxytropone.
[c]) Exchange-broadened, not all C-signals observed.

Scheme 7

A　　　　　　　　　　B　　　　　　　　C
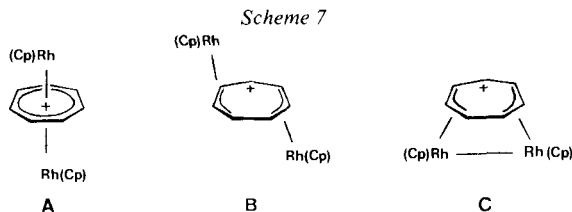
for the C_7H_7-unit and a six-line multiplet at 87.5 ppm for the two cyclopentadienyl rings. The observation of only two signals indicates a symmetrical structure for this compound which is also supported by the observation of only one [103]Rh-chemical shift. The ^{13}C-NMR. spectrum shows no changes upon cooling to $-70°$. Based on these findings either an inherently symmetrical or a dynamic structure can be envisaged. The first case would correspond to a structure in which the (Cp)Rh-units are located on opposite sides of the ring and equally coordinated to all seven C-atoms (i.e. a non-dynamic triple-decker, (A), Scheme 7). Whereas the triplet-splitting of the C_7H_7-^{13}C-resonance is to be expected for this structure, the six-line resonance of the two equivalent (Cp)-units, the typical X-pattern of an ABX spin-system, could only be rationalized if the two Rh-nuclei were spin-coupled via the π-system of the common C_7H_7-ligand. For the dynamic structures, on the other hand, transoid-(B) and cisoid-(C) bis(allyl)-bonding arrangements may be discussed. However, (Rh,Rh)-spin coupling is more easily envisaged in a cisoid-dinuclear structure (C) in which both Rh-atoms are coordinated to the same side of the π-system and connected by a (Rh,Rh)-bond. Support for this structure comes from the magnitude of J(Rh,Rh) (5.2 Hz) which lies in the range of values for analogous complexes with bridging cyclooctatetraene [2]. J(Rh,Rh) was obtained by simulation[2]) of the six-line (Cp)-multiplet of 12 using as input $J(Rh^A,C)=5.5$ Hz (typical value for ((Cp),Rh)-coupling), $J(Rh^B,C)=0$ and a (^{13}C/^{12}C)-isotope shift in the [103]Rh-resonance of 1.3 Hz (at 3.15 MHz corresponding to 25.2 MHz for ^{13}C). The experimental and simulated spectra are illustrated in Figure 1a.

The invariance of the ^{13}C-NMR.-spectrum of 12 to a lowering of temperature $(-70°)$ points towards a fast rotation or valence tautomerism of the coordinated C_7H_7-unit. The charge distribution within the cationic complex is indicated by the shielding value of the [103]Rh-resonance (-1394.8 ppm) [2] which is found in the region of dimetallic Rh(0)-complexes and shows that the positive charge is largely stabilized in the seven-membered tropylium ring. If the charge would be located on one of the Rh-atoms an averaged shift between Rh(I) and Rh(0), i.e. $\approx -(800\pm200)$ ppm were to be expected. The respective structural representations of 12 are given in Scheme 8. The reduction of this complex with sodium borohydride in ethanol regenerates, in quantitative yield, the cycloheptatriene complex 10.

Scheme 8

12
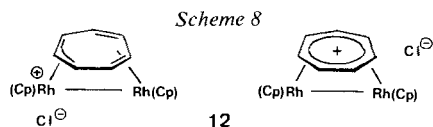
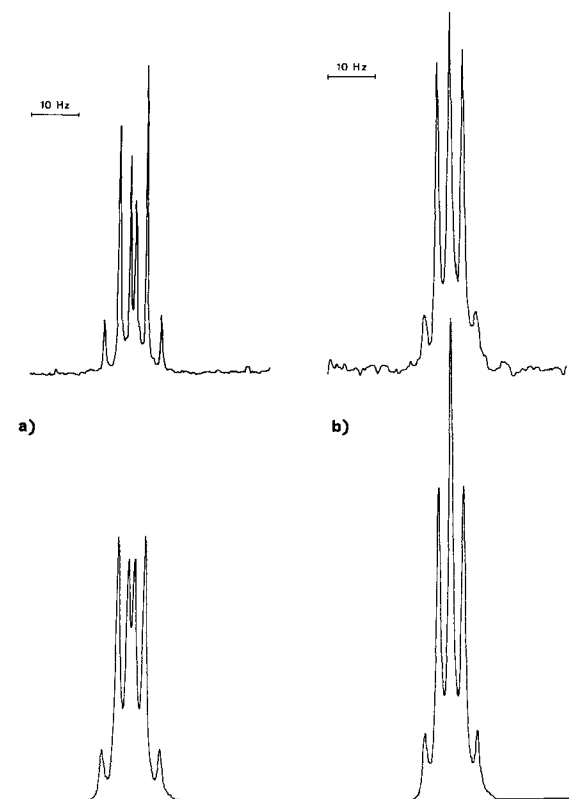[2]) From the spin-simulation only the absolute values of $J(Rh^A,C)$ and $J(Rh,Rh)$ can be determined.

Figure. a) *Experimental* (upper) *and simulated* (lower) *^{13}C-NMR. spectra* (CD$_3$OD; +30°) *of the cyclopentadienyl-C-atoms of* $[(Cp)Rh(C_7H_7)Rh(Cp)]Cl$ **(12)**; b) *corresponding spectra* (CDCl$_3$; +30°) *of* $(Cp)Rh(C_7H_6O)Rh(Cp)$ **(13)** (for parameters see text)

A complex of similar structure as **12** can be expected from the cyclohepta-trienone (tropone) ligand which exhibits a highly polarized carbonyl group and a tropylium-like π-electron system. Indeed, reaction of $[(C_2H_4)_2RhCl]_2$ with tropone in acetone, followed by treatment with cyclopentadienylthallium ((Cp)Tl) yielded deep-violet crystals of a complex characterized by microanalysis as (Cp)Rh (C$_7$H$_6$O)-Rh (Cp) **(13)**. Its room-temperature ^{13}C-NMR. spectrum shows a five-line multiplet at 84.5 ppm for the (Cp)-group and three triplets at 61.2, 55.2 and 52.0 ppm for the coordinated olefinic ring C-atoms. These data indicate an effective symmetry of the dinuclear complex, just as in the case of **12**. The multiplet of the (Cp)-C-atoms exhibits the typical X-pattern of an $AA'X$-system, as shown by spin-simulation using the parameters J (Rh, Rh) = 4.8, J (Rh^A, C) = 5.0 and J (Rh$^{A'}$, C) = 0 Hz *(Figure, b)*. If there were an isotopic shift similar to Δv (A, B) in **12**, its value would have to be smaller than the digital resolution (<0.5 Hz). The triplet structure (3.5–6.0 Hz-splitting) of the olefinic C-atoms can be interpreted as arising from the X-part of ABX-systems, or A_2X-systems which result from dynamic averaging of chemical shifts and coupling constants. The latter proved to be the case since on cooling to −30° the (Cp)-signal vanishes and reappears at −70° as a sharp doublet (86.6 ppm,

Scheme 9
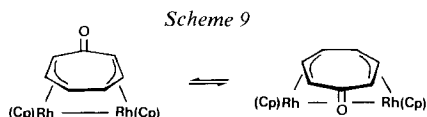
13

$J(Rh,C)=5$ Hz), while the olefinic triplets begin to broaden and reappear in the slow-exchange limit ($-110°$) as doublets at 67.4, 59.2 and 51.2 ppm with $J(Rh,C)$ = 8, 12 and 7 Hz, respectively. These coupling constants are just about twice the averaged splitting values observed in the fast-exchange limit. From the number of resonances it can be concluded that coordination of the Rh-atoms to the three rings remains unchanged. The doublet structure of the olefinic and cyclopentadienyl C-atoms shows that the Rh-nuclei couple only to the directly coordinated C-atoms and that $J(Rh^1,Rh^2) < \Delta v(Rh^1,Rh^2) \pm 1/2 [J(Rh^1,C) - J(Rh^2,C)]$. The smallest $J(Rh^1,C)$ in **13** is observed for the (Cp)-C-atoms (5 Hz). Therefore, if we assume very small values for the isotope shift Δv and (Rh^2,C)-coupling, $|J(Rh^1,Rh^2)|$ becomes smaller than 2.5 Hz at the temperature of the slow-exchange limit ($< -70°$). In good agreement with this result spectral simulation of the (Cp)-doublet sets an upper limit of 1 Hz for $J(Rh,Rh)$. It appears, therefore, that the value of $J(Rh,Rh)$ differs for the slow- and fast-exchange limits.

Based on these NMR.-spectroscopic observations the dynamic structure of the tropone complex **13** can be formulated as in *Scheme 9* with a bis(1-3-η-allyl)-co-ordination of the two (Cp)Rh-units. At room temperature, a fast reorientation of the tropone ring above the (Cp)Rh-moiety would account for the temperature-dependence of the ^{13}C-NMR. spectrum. This *Scheme* is also consistent with the temperature-dependent NMR.-spectroscopic behaviour of the analogous dinuclear complex **14** formed from 2-methoxytropone. At room temperature, the ^{13}C-NMR. spectrum exhibits a single five-line multiplet for the two (Cp)-rings and seven triplets for the C-atoms of the seven-membered ring. At $-100°$, two doublets at 88.8 and 85.6 ppm with $J(Rh,C)=4$ and 5 Hz, respectively, are observed for the cyclopentadienyl rings, whereas the C-atoms of the seven-membered ring have not yet reached the slow-exchange limit (doublet structure) at this temperature.

The ^{103}Rh-NMR. spectra of **13** and **14** are in accord with the dynamic structure of these dirhodium complexes. At 27°, they show a single resonance line at -1082.7 and -1038.0 ppm, respectively [2]. When compared with the tropylium complex **12** (-1394.8 ppm), the considerable deshielding in **13** and **14** has to be attributed to the electron-withdrawing O-substituents. Similar effects have already been observed in (olefin)Fe(CO)$_3$ complexes [6]. The (T_1/T_2)-ratios observed for **13** (83) and **14** (64) clearly indicate that the structures are fluxional and that species with different ^{103}Rh *Larmor*-frequencies are involved in the dynamic process [2]. A possible rationale for this behaviour could be an extension of *Scheme 9* including other types of bis(1-3-η-allyl)-coordination *(Scheme 10)*. In this representation of fluxional bis(1-3-η-allyl)-coordination only five out of the fourteen possible structures (seven pairs of degenerate structures) are illustrated. The scheme shows one of the possible pathways by which structure **I** can be converted into **V**. The pair **I/V** would then correspond to the low-temperature structure of **13**. In the case of the

Scheme 10

| I | II | III | IV | V |

13 R = H
14 R = OCH₃
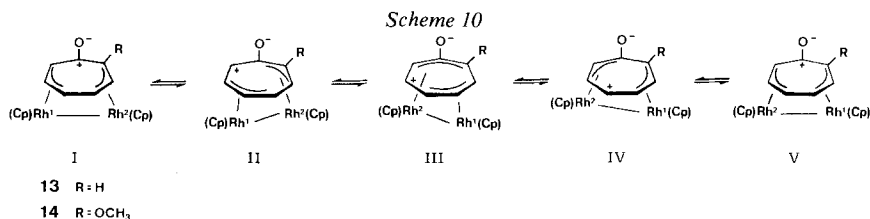
tropylium complex **12** the five structures become equivalent and, hence, the dynamic process does not increase the (T_1/T_2)-value of this complex $(T_1/T_2 = 1.5)$.

Note added in proof. A re-investigation of the ^{103}Rh-NMR. spectrum of **13** (at 12.6 MHz using conventional pulsing conditions) has shown that at 20° two resonances $(\Delta\delta = 123$ ppm) can actually be observed, the low-frequency signal being very broad. The high-frequency line corresponds to the resonance reported earlier [2]. At $-80°$ the spectrum clearly indicates the presence of more than one species.

3. Experimental Part. – *General.* Preparation and handling of all complexes and solvents were carried out under purified N₂-atmosphere using *Schlenk*-type apparatus.

The ^{13}C-NMR. spectra were measured on a *Varian XL-100-12 FT* spectrometer at 25.2 MHz. Chemical shifts *(Table 1)* of the new complexes described below are given in δ [ppm] relative to tetramethylsilane (TMS) as internal reference. (^{103}Rh,^{13}C)-coupling constants were obtained from the proton-noise-decoupled spectra, digital resolution and reproducibility of $J(\text{Rh},\text{C}) \pm 0.3$ Hz. The ^{57}Fe- and ^{103}Rh-NMR.-spectra were recorded under steady-state conditions with a pulse spectrometer described in [2].

[(C₇H₇)Fe(CO)₃]Li [14], (C₇H₇)Co(CO)₃ [12], [(C₈H₁₂)RhCl]₂, [(C₇H₈)RhCl]₂, [(C₆H₈)RhCl]₂ [15], [(C₈H₁₂)IrCl]₂ [16], [(C₃H₅)PdCl]₂ & [(C₄H₇)PdCl]₂ [17], (C₇H₈)(RhC₅H₅)₂ [13], [(C₂H₄)₂RhCl]₂ [18], tropone [19], and 2-methoxytropone [20] were synthesized according to procedures given in the respective references. Abbreviations: r.t. = room temperature.

Preparation of the complexes. – μ-(η-Cycloheptatrienyl)-tricarbonyliron cyclooctadienerhodium (Fe-Rh) (**1**) was obtained by addition of [(C₈H₁₂)RhCl]₂ (492 mg, 1 mmol) to a cold ($-10°$) dark-red solution of [(C₇H₇)Fe(CO)₃]Li (475 mg, 2 mmol) in 20 ml THF. After warming to r.t. and further stirring for 2 h the solvent was removed and the residue was extracted with boiling hexane. The filtered extract was concentrated and placed on a chromatography column packed with *Alox* III. Elution with hexane produced a major orange band which was collected, concentrated and slowly cooled to $-80°$. Golden-brown platelets were obtained by decantation of the supernatant liquid (483 mg, 54.6%). – IR. (hexane): 1943s, 2007vs.

C₁₈H₁₉O₃FeRh (442.08)   Calc. C 48.90   H 4.33   Fe 12.63%   Found C 48.95   H 4.22   Fe 12.79%

μ-(η-Cycloheptatrienyl)-tricarbonyliron norbornadienerhodium (Fe-Rh) (**2**) was obtained in the same way as **1** from [(C₇H₇)Fe(CO)₃]Li and [(C₇H₈)RhCl]₂. It was purified solely by filtration of the hexane solution and recrystallization at $-80°$. Yield: 89%. – IR. (hexane): 1941s, 2006vs.

C₁₇H₁₅O₃FeRh (426.04)   Calc. C 47.92   H 3.55   Fe 13.11%   Found C 47.76   H 3.62   Fe 13.02%

μ-(η-Cycloheptatrienyl)-tricarbonyliron cyclohexadienerhodium (Fe-Rh) (**3**) was synthesized in the same way as **1** from [(C₇H₇)Fe(CO)₃]Li and [(C₆H₈)RhCl]₂, yield: 27%. – IR. (hexane): 1946s, 2010vs.

C₁₆H₁₅O₃FeRh (414.03)   Calc. C 46.41   H 3.65   Fe 13.49%   Found C 46.28   H 3.70   Fe 13.33%

μ-(η-Cycloheptatrienyl)-tricarbonyliron cyclooctadieneeiridium (Fe-Ir) (**4**) was obtained in the same manner as **1** from [(C₇H₇)Fe(CO)₃]Li and [(C₈H₁₂)IrCl]₂, yield: 32%. – IR. (hexane): 1951s, 2016vs. – Further characterization by ^{13}C-NMR. (see *Table 1*).

μ-(η-Cycloheptatrienyl)-tricarbonyliron-bis(trimethylphosphite)rhodium(Fe-Rh) (**5**). A solution of **2** in hexane was treated with an excess of $P(OCH_3)_3$ at r.t. After stirring for 2 h at r.t. the deep-red precipitate was filtered off and recrystallized from toluene/hexane at $-30°$, yield: 92%. – IR. (hexane): 1928s, 1986vs.

$C_{16}H_{25}O_9P_2FeRh$ Calc.   C 33.01   H 4.33   P 10.64   Fe 9.59%
(582.06)   Found ,, 32.80   ,, 4.22   ,, 10.55   ,, 9.73%

μ-(η-Cycloheptatrienyl)-tricarbonyliron-bis(triphenylphosphite)rhodium(Fe-Rh) (**6**) was obtained in the same way as **5** from **2** and $P(OC_6H_5)_3$, yield: 88%. – IR. (hexane): 1924s, 1985vs. – Further characterization by ^{13}C-NMR. (see *Table 1*).

μ-(η-Cycloheptatrienyl)-(1-3-η-allyl)palladiumtricarbonyliron(Pd-Fe) (**7**) was synthesized in the same way as **1** from $[(C_7H_7)Fe(CO)_3]Li$ and $[(C_3H_5)PdCl]$, yield: 35%. – IR. (hexane): 1930s, 1941s, 2004vs. – ^{13}C-NMR.: see *Table 1*.

μ-(η-Cycloheptatrienyl)-tricarbonyliron[1-3-η-(2-methylallyl)]palladium(Fe-Pd) (**8**) was prepared in the same manner as **1** from $[(C_7H_7)Fe(CO)_3]Li$ and $[(C_4H_7)PdCl]_2$, yield: 38%. – IR. (hexane): 1932s, 1943s, 2002vs. – Further characterization by ^{13}C-NMR. (see *Table 1*).

μ-(η-Cycloheptatrienyl)-tricarbonylcobaltnorbornadienerhodium tetrafluoroborate(Co-Rh) (**9**). This complex was obtained from $(C_7H_7)Co(CO)_3$ and $[(C_7H_8)Rh]BF_4$ by the general method outlined in [1], yield: 66%.

$C_{17}H_{15}BF_4O_3CoRh$ Calc.   C 39.57   H 2.93   F 14.73   Rh 19.95%
(515.93)   Found ,, 39.42   ,, 3.06   ,, 14.63   ,, 20.12%

μ-(η-Cycloheptatrienyl)-bis[(η-cyclopentadienyl)rhodium]chloride(Rh-Rh) (**12**). $(C_7H_8)(RhC_5H_5)_2$ (0.42 g, 1.0 mmol) in 20 ml CH_2Cl_2 was stirred at r.t. for 48 h. The colour of the solution gradually changed from red to violet and **12** precipitated. After evaporation of the solvent the residue was placed on a chromatography column packed with *Alox* III. Elution with methanol/ether gave **12** in 91% yield.

$C_{17}H_{17}ClRh_2$ (462.57)   Calc. C 44.14   H 3.70%   Found C 43.87   H 3.91%

μ-(Tropone)-bis[(η-cyclopentadienyl)rhodium](Rh-Rh) (**13**). $[(C_2H_4)_2RhCl]_2$ (0.39 g, 1.0 mmol) in 15 ml acetone was treated with 1 ml of tropone and stirred until no more ethylene evolved. To the reaction mixture 0.55 g (2.0 mmol) of cyclopentadienylthallium ((Cp)Tl) were added and stirring was continued for a further 4 h. Thallium chloride was filtered off and the solvent evaporated. The residue was washed with hexane and recrystallized from acetone, yield: 35%.

$C_{17}H_{16}ORh_2$ (442.12)   Calc. C 46.18   H 3.65%   Found C 46.25   H 3.62%

μ-(2-Methoxytropone)-bis[(η-cyclopentadienyl)rhodium](Rh, Rh) (**14**) was obtained in the same way as **13** using 2-methoxytropone, yield: 74%.

$C_{18}H_{18}O_2Rh_2$ (472.14)   Calc. C 45.79   H 3.84   Rh 43.59%   Found C 45.69   H 3.95   Rh 43.44%

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107. Synthesis and Properties of 1,1-Dihalogenocycloprop[b]anthracenes[1])

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Summary

The synthesis of 1,1-difluoro-1*H*-cycloprop[*b*]anthracene (**3**) is described. The key step of the synthesis is the cycloaddition of 1,2-dichloro-3,3-difluorocyclopropene (**6**) to 2,3-dimethylidene-1,2,3,4-tetrahydronaphthalene (**5**). The ^{13}C-NMR. spectrum of **3** is assigned on the grounds of C,F-coupling constants, selective H-decoupling and the resulting residual C,H-coupling. The 1,1-dichloro derivative **4** was synthesized by the same route, but could not be isolated pure. Experiments for the reduction to 1*H*-cycloprop[*b*]anthracene (**2**) and for the ionization of **3** or **4** to the cation **16** failed.

Introduction. – Since their discovery in 1964 [2] the chemistry of cyclopropabenzenes has been extensively investigated [3]. This research is motivated by the desire to understand limits and consequences of strain and distortion imposed on the benzenoid framework. In addition, since cyclopropabenzenes are usually very unstable compounds, their preparation also represents a considerable synthetic challenge. Recent achievements in the field consist in the synthesis of both isomeric cyclobutacyclopropabenzenes [4] [5]. Extension to the arene homologues led to the discovery of several cyclopropanaphthalenes [6] including the shock-sensitive 1*H*,4*H*-dicyclopropa[*b,g*]naphthalene [7]. Contrary to the general expectation however, the synthesis of the still higher homologues, the cyclopropanthracenes, could not be achieved by straightforward extension of the methodology used for synthesis of cyclopropabenzenes or -naphthalenes.

Both *Garratt* [5] and *Billups* [8] investigated the *Billups* approach, *i.e.* bis-dehydrohalogenation of the dichlorocarbene adduct **1** of 1,4-dihydroanthracene with *t*-BuOK in dimethylsulfoxide, for the preparation of 1*H*-cycloprop[*b*]anthracene (**2**); however, only substituted anthracenes could be obtained. The failure of this procedure is not too surprising. Although it works particularly well for the

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[1])   For a preliminary report, s. [1].