136. Protonated Diolefin Complexes: Model Systems for C–H Activation *via* Metal Complexation[1])

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On protonation of the diolefin complexes [$M(C_5R_5)$(diene)] (R = H, CH_3; M = Co, Rh, Ir; diene = 2,3-dimethylbutadiene, 1,3-cyclohexadiene) with HBF_4, cationic species are isolated which, at room temperature, show fluxional behaviour on the NMR time scale. Depending on R and M, three different ground states are observed for these cationic complexes in the NMR spectra at low temperatures. While for M = Ir a classical metal-hydride structure M–H is observed, the Co and Rh complexes show ground states with 'agostic' H-bridges M · · H · · C. The protonated species are characterized by ^{1}H-, ^{13}C- and ^{103}Rh-NMR spectra. Total line-shape analysis of the ^{1}H and ^{13}C spectra in the 298–154 K range gave the free enthalpies of activation $\Delta G^{\neq}$ for methyl rotation and 1,4-H shift in the agostic structures **2b**, **2b′**, **2c**, and **2c′**. The Rh complexes show the lowest $\Delta G^{\neq}$ values for the 1,4-H shift, and the strength of the agostic bond appears to decrease in the order $CoC_5H_5 > CoC_5Me_5 > RhC_5H_5 > RhC_5Me_5$. Only for R = H and M = Rh and in the presence of traces of *Lewis* bases (H_2O, pyridine, or acetone), variable amounts of coordinatively saturated allyl complexes competing with the agostic species are observable. More than equimolar amounts of basic solvents lead to irreversible deprotonation and recovery of the starting complexes. Stable allyl-halide complexes are formed on reaction with HCl, while protonation with HBF_4, in the presence of CO, gives high yields of complexes [M(CO)(allyl)(C_5R_5)] [BF_4]. The different ground states observed for the protonated complexes and the dynamic behaviour in solution are compared with other hydride-transfer reactions observed in organometallic chemistry, specifically with the β-hydride elimination and the catalytic hydrogenation of olefins.

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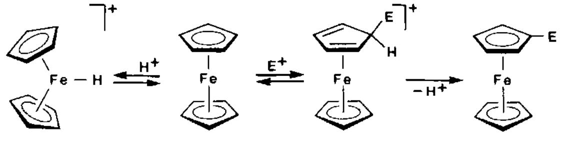
1. Introduction. – Electrophilic additions or substitutions on metal-coordinated olefins and aromatic compounds are among the more important synthetic methods for the functionalization of organic groups in organometallic complexes. This is exemplified by the rich organic chemistry of ferrocene and its derivatives. Under *Friedel-Crafts* conditions, facile electrophilic substitutions at one or both rings are observed with a variety of substrates [3]. These proceed most likely through electrophilic *attack at one of the π-cyclopentadienyl rings* (C_5H_5) leading to a coordinatively unsaturated 16-electron intermediate, followed by fast removal of a proton *(Scheme 1)*. Protonation with very strong acids may on the other hand proceed by *addition at the metal* to produce a labile

Scheme 1



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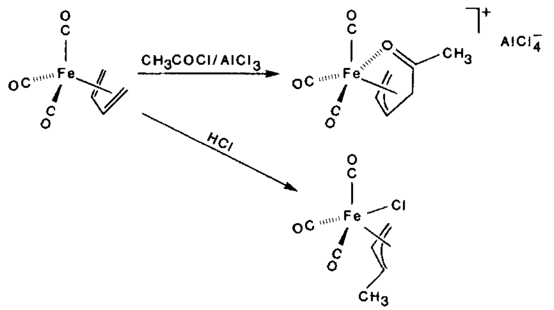
[1]) Reactions with Metal-Coordinated Olefins, Part VI. Part V: [1]; Transition-Metal NMR Spectroscopy, Part X. Part IX: [2].

18-electron $[FeH(C_5H_5)_2]^+$ species, detectable by ^1H-NMR spectroscopy [4]. There is, however, also evidence for a reversible ring protonation, as slow deuterium incorporation is observed when using deuterated acids. A M–D species as intermediate in this process has been ruled out from spectroscopic and kinetic measurements on ruthenocene [5].

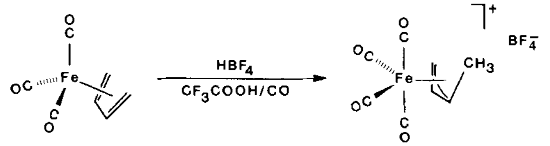
Likewise, the protonation and acetylation reactions of tricarbonyl(η^4-diene)iron complexes have been studied extensively. *Friedel-Crafts* acetylation leads to the initial formation of $[Fe(allyl)(CO)_3]^+$ species, where a closed-shell electronic configuration for the Fe-atom is obtained by an intramolecular σ-donation of a lone-pair of electrons from the acyl-*O*-atom [6]. Protonation with HCl or HBr, where the halide ion is a strongly coordinating anion, yields coordinatively saturated π-allyltricarbonyliron halides [7] *(Scheme 2)*.

Scheme 2



In acids with weakly cordinating anions, the situation is somewhat more complex. On treatment with HBF_4 in Ac_2O, small amounts of $[Fe(allyl)(CO)_4]^+$ cations can be isolated, with the extra CO group apparently arising from partial decomposition of an unsaturated tricarbonyl intermediate [8]. In the presence of excess CO and a special solvent mixture, this reaction proves to be a very efficient method for the synthesis of cationic allyl complexes [9] [10] *(Scheme 3)*.

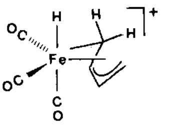
Scheme 3



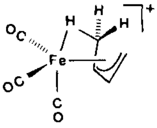
This reaction is, however, restricted to acyclic diolefin complexes; with tricarbonyl(cyclohexadiene)iron, stable allyl complexes are not formed, although in deuterated acids rapid exchange of the *'endo'*-protons of the CH_2 groups is observed [9]. This is also found for acyclic dienes, where complete exchange of the terminal protons for deuterium occurs before formation of the allyltetracarbonyliron cations. A notable difference is observed in the configuration of the allyl ligand formed on protonation, as reaction with HBF_4 invariably leads to allyl complexes with *'anti'*-CH_3 substituents, while in the presence of halides the *'syn'*-isomers are formed.

The nature of the initial products formed in solution by protonation of various [Fe(CO)$_3$(η^4-diene)] complexes in highly acidic media (HSO$_3$F-SO$_2$) was revealed by detailed NMR studies at low temperatures [11] [12]. For these species, which were not isolable in substance, two alternative structures were proposed, based on ^{1}H- and ^{13}C-NMR shift arguments as well as C,H-coupling constants [13].

Structure **I** represents a σ,π-coordinated allyl complex with a metal-hydride group, while structure **II** involves an H-atom bridging between Fe- and C-atom. The latter structure was thought to be more lileky, as ^{1}H chemical shifts as well as J(C,H) values were in better agreement with structure **II**.



I

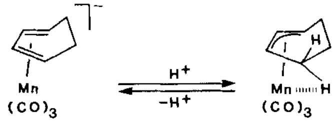


II

The first structural evidence for the type of bonding represented by **II** was found in complexes where CO groups have been substituted by P(OCH$_3$)$_3$ ligands. Protonation of (η^4-diene)tris(phosphite)iron complexes smoothly proceeded yielding isolable (η^3-alkenyl)tris(phosphite)iron cations with Fe··H··C bonds [14]. A neutron diffraction study of [Fe(P(OMe)$_3$)$_3$(η^3-C$_8$H$_{13}$)]BF$_4$ definitely showed the position of the bridging H-atom [15].

The complexes discussed above exhibit a unique mode of interaction between an unsaturated metal center and the C–H bond of an adjacent CH$_3$ group. Other examples recently described in the literature include a detailed ^{1}H-NMR and kinetic study of tricarbonyl(η^3-cyclohexenyl)manganese and derivatives thereof, in which again the metal centre attains an 18-electron configuration *via* coordination of an *endo*-C–H bond adjacent to the π-allyl unit [16] [17] *(Scheme 4)*.

Scheme 4

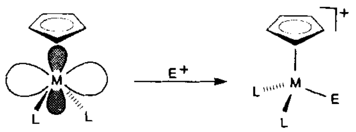


The C–H bond in the cases discussed above serves as a nonclassical donor ligand through sharing of its σ electrons with the metal and formation of a two-electron, three-centre M··H··C bonding arrangement, in principle similar to B··H··B bonding in electron-deficient boranes and carboranes. The term 'agostic' has been proposed for this type of bonding [18]. It can be argued that interactions M··H··C may be involved in intermediates of many fundamental organometallic reaction mechanisms in which C–H bonds are formed or cleaved, especially in homogenous catalysis. In fact, a four-centre transition state involving such a bond had been postulated for homogenous hydrogenation [19]. Complexes, in which M··H··C bonding persists in the *ground-state* structure, may, therefore, act as important model systems to study reaction mechanisms involving the making or cleaving of C—H bonds, *e.g.* C—H activation, hydrogenation, isomerisation, or β-elimination [20]. In these reactions, M··H··C bonding has been postulated to occur in intermediates or transition states, but never been detected directly.

We, therefore, searched for other organometallic systems, in which the occurrence of M··H··C bonding and its intermediacy in basic organometallic reaction mechanisms might be more clearly demonstrated by additional information on the structural and spectroscopic properties of this novel type of three-centre bond.

2. Results and Discussion. – 2.1. *Protonation of Complexes [M(C_5R_5)(dimethylbutadiene)] (M = Co, Rh, Ir; R = H, CH_3).* Several investigations have shown that the electron-rich half-sandwich complexes of the type [$ML_2(C_5R_5)$] (M = Co, Rh, Ir; L = CO, PR_3, $P(OR)_3$) can act as nucleophiles and form addition complexes with various *Lewis* acids [21]. These complexes have, therefore, been referred to as 'metal bases'. According to theoretical calculations, these complexes have an occupied molecular orbital of high energy, which is non-bonding with respect to the metal-ligand bonds and acts as 'the spearhead of nucleophilic activity of complexes [$ML_2(C_nR_n)$] [22]' *(Scheme 5)*. The nucleophilic reactivity of the metal centre can be considerably enhanced, when the good electron-acceptor ligand CO, which decreases electron density at the metal, is replaced by a more basic and less electron-accepting phosphine ligand. The electron density of the central metal also increases, when C_5H_5 is replaced by C_5Me_5 [21]. Electrophilic addition in all these complexes is, therefore, predominantly directed at the metal (with carbocations, electrophilic substitution at the C_5H_5 ring is, however, a possible side reaction [21]).

Scheme 5



Very little was known about the nucleophilic reactivity of olefin or diolefin complexes of the general type [M(diene)(C_5R_5)]. On protonation of [$Rh(C_5H_5)(C_2H_4)_2$] with HCl the only isolable product was [$RhCl(C_5H_5)(C_2H_5)(C_2H_4)$] with no evidence for metal protonation [23]. Diolefin complexes of the general type [M(C_5R_5)(diene)] (M = Co, Rh, Ir; R = H, CH_3) are readily accessible and are generally more stable than the corresponding mono-olefin complexes. The following study initially concerned the protonation of the complexes [M(C_5H_5)(2,3-dimethylbuta-1,3-diene)] (**1a–c**) and [M(C_5Me_5)(2,3-dimethylbuta-1,3-diene)] (**1a′–c′**). No systematic study has yet been performed on their behaviour towards electrophiles (for some earlier results on cyclohexadiene complexes, see [24]; see later). An attractive feature of this group of complexes is the fact, that three homologous metals, Co, Rh, and Ir can be compared and, additionally, the electron density at the metal can be influenced by the exchange of the ubiquitous C_5H_5 ligand with the more electron-rich C_5Me_5. This allows more variation than in the other systems studied so far and was expected to give information, how these parameters might influence the course of the reaction.

After reacting the complexes **1a–c** and **1a′–c′** with equimolar amounts of HBF_4 in propionic anhydride, the protonated cationic complexes **2a–c** and **2a′–c′** could be precipitated with Et_2O in almost quantitative yields *(Scheme 6)*.

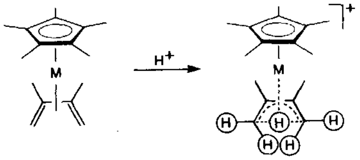
Scheme 6

$$\underset{\mathbf{1}}{[M(C_6H_{10})(C_5R_5)]} + HBF_4 \rightarrow \underset{\mathbf{2}}{[M(C_6H_{11})(C_5R_5)][BF_4]}$$

	M = Ir		M = Co		M = Rh
a	R = H	**b**	R = H	**c**	R = H
a′	R = CH_3	**b′**	R = CH_3	**c′**	R = CH_3

All complexes of type **2** are fluxional at room temperature and show similar averaged ^1H-NMR spectra, which mainly differ in the position of the broad low-frequency resonance attributed to five protons involved in exchange processes *(Scheme 7)*.

Scheme 7



Noticeable differences become apparent in the ^1H-NMR spectra at the slow-exchange limit. The Ir complexes **2a** and **2a′** show below 180 K the spectrum of a classical symmetrical diolefin-hydride complex **A** *(Table 1, Fig. 1)*.

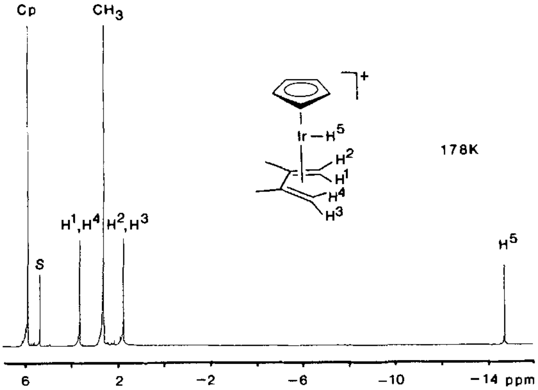


Fig. 1. *^1H-NMR Spectrum* (CD_2Cl_2, 400 MHz) *of* **2a** *at 178 K*

The disappearance of the low-frequency proton signal for the Ir—H group as well as the *'endo'*- and *'exo'*-protons of the terminal CH_2 groups of the diolefin on warming up suggests a dynamic process involving the three centres C(1), C(4), and Ir, which was also confirmed by spin-saturation transfer experiments at 240 K. The most likely intermediates or transition states for this process are the species **B**, **B′**, **C**, and **C′** *(Scheme 8)*.

Scheme 8

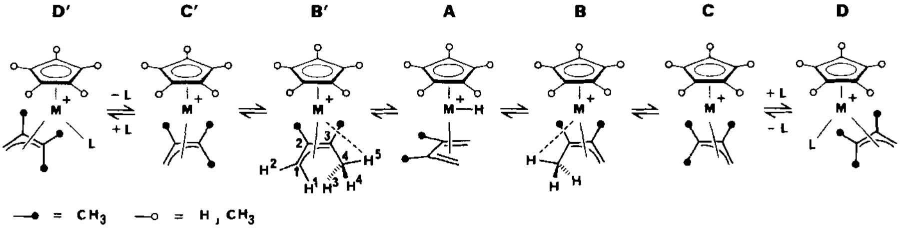


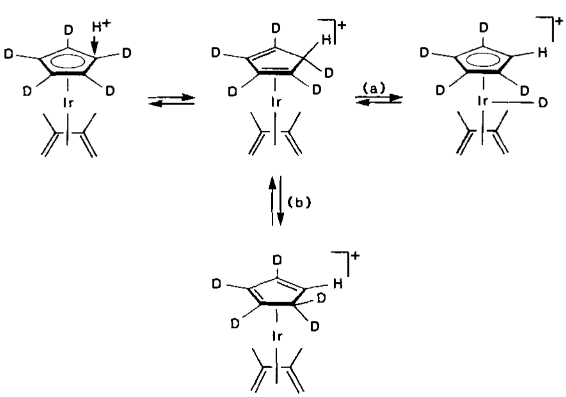
Table 1. *^1H Chemical Shifts* ([ppm]; 400 MHz, CD_2Cl_2) *of Complexes* **2a–c**, **2a'–c'**

	T/K	C_5H_5	$C_5(CH_3)_5$	$CH_3(C(2,3))$		H(1)	H(2)	H(3)	H(4)	H(5)
2a	178	5.86	–	2.60		1.72	3.61	3.61	1.72	–14.70
2a'	173	–	2.02	2.12		1.49	2.89	2.89	1.49	–14.70
2b	173	5.41	–	2.55	2.12	0.61	3.75	0.92	–2.51	–13.18
2b'	258	–	1.78	2.32	1.94	0.80	2.92		–4.41	
2b'	178	–	1.80	2.33	1.95	0.77	2.92	0.56	–2.19	–11.48
2c[a])	154	5.64	–	2.46	2.06	1.22	3.77	1.77	–0.93	–8.40
2c[b])	193	5.64	–	2.23	1.97	2.51	4.86		0.81	
2c[c])	193	5.55	–	2.14	1.93	2.42	4.78		0.91	
2c'	183	–	1.87	2.10	1.70	1.30	2.87		–2.20	
2c'	154	–	1.78	2.13	1.73	1.29	2.80	1.2	–0.75	–7.05

[a]) Form **B**, in dry CD_2Cl_2. [b]) Form **D** in dry $(CD_3)_2O$. [c]) Form **D** in CD_2Cl_2 with traces H_2O.

Deuteration experiments indicate that other exchanges processes, although with a slower reaction rate, have to be considered. Protonation of $[Ir(C_6H_{10})(C_5D_5)]$ with HBF_4 and immediate recording of the low-temperature ^{1}H-NMR spectrum shows statistical incorporation of the five D-atoms of the C_5D_5 ring into the position Ir-H and the terminal CH_2 groups, but not into the CH_3 groups of the olefinic ligand. For this process, two mechanisms can be proposed *(Scheme 9)*, analogous to those discussed for the electrophilic substitution of molecules like ferrocene. *a*) exo-*Protonation of the C_5D_5 ring and*

Scheme 9



endo-*deuterium shift to give the Ir—D group, with concurrent fast equilibrium* **A** ⇄ **B** ⇄ **C**. *b*) exo- *or* endo-*Protonation of the* C_5D_5 *ring and redistribution within the intermediate cyclopentadiene complex by 1,5-H or deuterium shifts.* The second process appears less likely, as it requires a relatively long lifetime for the intermediate cyclopentadiene complex. It also seems uncertain, whether 1,5-H shifts in a metal-coordinated cyclopentadiene are rapid (compare the very slow and incomplete deuteration of ferrocene [5]).

In contrast to the Ir complexes, a different ground state is observed for the Co complexes **2b** and **2b'**. At 173 K and 178 K, ^{1}H-NMR spectra show form **B** with M··H··C bridges *(Scheme 8)*. The rotation of the three H-atoms at C(4) is hindered, so that in the slow-exchange limit three separate signals are observed *(Table 1, Fig. 2)*. On warming, two distinct dynamic processes occur: *1.* CH_3 rotation (which leads to the equivalence of protons H(3), H(4), H(5), and presumably proceeds through intermediate **C**). *2.* Interconversion of the enantiomers **B**⇄**B'**, which most likely involves an intermediate of structure **A** *(Scheme 8)*. This process can be described as an 1,2-allyl or 1,4-H shift.

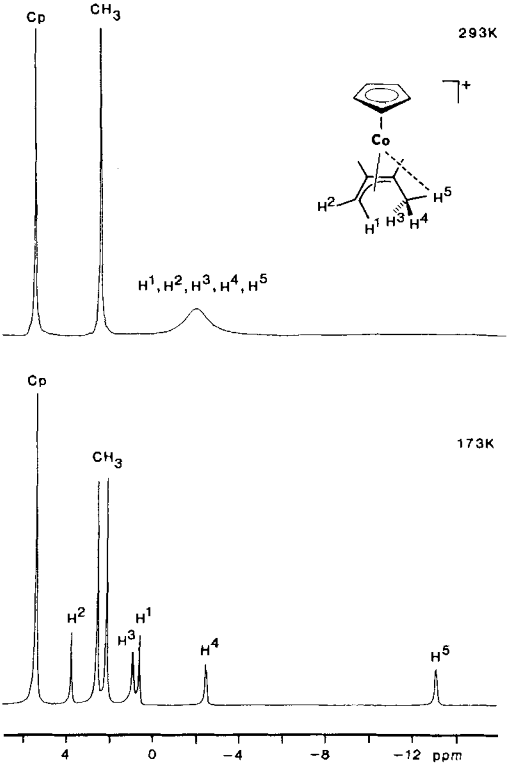
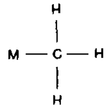


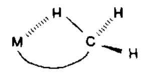
Fig. 2. ^{1}H-NMR Spectrum (CD_2Cl_2, 400 MHz) *of* **2b** *at 293 K* (top) *and 173 K* (bottom)

As a consequence, a signal corresponding to five protons is observed at elevated temperatures. For **2b'**, the resonances of the three CH_3 protons coalesce, before the 1,4-H shift strongly affects the spectrum, so that both dynamic processes can be observed consecutively. The resonances for H-atoms H(5) bridging to Co are highly shielded and appear at −13.18 and −11.48 ppm in **2b** and **2b′**, respectively (*Table 1*). These shifts seem to be typical for a state in which coordinatively unsaturated species achieve coordinative saturation through bonding to an aliphatic H-atom [14] [18].

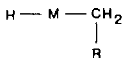
^{1}H-NMR Chemical-shift arguments alone do not suffice, however, for clear distinction between an M–H and an M· ·H· ·C group as seen by comparison of the low-frequency signals in **2a**, **2a′** and **2b**, **2b′**. In our case, the different symmetries of **A** and **B** help to distinguish between the two different ground states for the Ir and Co complexes. An additional confirmation for ground state **B** is also seen in the ^{13}C,^{1}H-coupling constants of C(4) (*Table 2*), which show a characteristic reduction of ^1J(C(4), H(5)) [14] [18]. One of the most reliable indications for the presence of a C· ·H· ·M bridged system appears to be these substantially diminished values for ^1J(C,H) (75–100 Hz), which arise from the reduced bond order in the two-electron three-centre C· ·H· ·M bond. They are significantly lower than typical ^1J(C,H) values for normal saturated (sp^3)C–H bonds (120–130 Hz). The coupling constant data also allow distinction between a C· ·H· ·M system and a C–M–H alkyl hydride group, since ^2J(C,H) in this case is normally less than 10 Hz [18]. This distinction, however, requires that spectra of the static species can be measured, as for fluxional systems only average values for J(C,H) and chemical shifts are obtained.



^1J(C,H) = 120–130 Hz



^1J(C,H) = 75–100 Hz



^2J(C,H) < 10 Hz

Table 2. *^{13}C-NMR Data for Complexes* **2a–c**, **2a′–c′**[a])

	T/K	C_5H_5	*C*$_5$(CH$_3$)$_5$	C$_5$(*C*H$_3$)$_5$	C(1)	C(4)	C(2)	C(3)	*C*H$_3$–C(2,3)
2a	200	88.0	–	–	35.2		98.9		19.6
2a′	173	–	99.8	9.0	34.2		94.4		15.6
2b	238	86.9	–	–	51.8	−2.0[b])	106.9	94.0	20.2
2b′	220	–	95.8	9.6	53.0	−1.5[c])	105.5	87.2	18.3, 16.9
2c	152	87.5	–	–	53.0	6.3	105.2	94.2	20.5, 19.2
2c′	169	–	100.1	9.4	55.8	6.9[d])	106.7	88.7	17.1, 18.2

[a]) Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in CD_2Cl_2 at 100.6 MHz.
[b]) 173 K, J(C(4), H(3), H(4)) = 150 Hz, J(C(4), H(5)) = 80 Hz.
[c]) 173 K, J(C(4), H(3), H(4)) = 147 Hz, J(C(4), H(5)) = 87 Hz.
[d]) J(C(4), H(3,4,5)) = 123 Hz.

The ^{13}C-NMR spectra, when measured with proton-noise decoupling, have the additional advantage of being only sensitive to the second exchange process. The chemical shifts observed in the slow-exchange limit are collected in *Table 2*. As an example, the ^{13}C-NMR spectra of the Rh complex **2c′** are illustrated in *Fig. 3*. If carefully dried CD_2Cl_2 is used as solvent, **2c** and **2c′** show similar temperature-dependent spectra as in the case of the Co complexes, which are in agreement with a 1,4-H shift which is fast on the ^{13}C-NMR time scale at room temperature. The CH_3 group involved in agostic bonding to

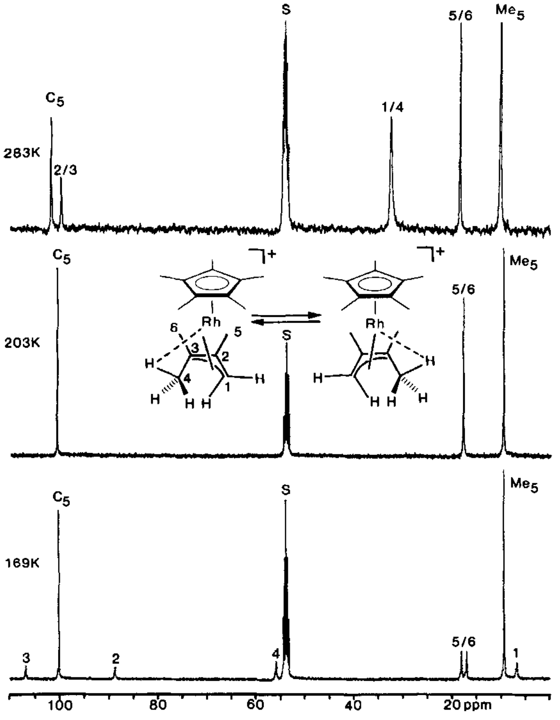


Fig. 3. *^{13}C-NMR Spectrum* (CD_2Cl_2, 100.6 MHz) *of* **2c′**. 283 K: fast exchange, 203 K: coalescence of signals 1⇄4, 2⇄3 (very br.), 169 K: slow exchange.

the metal exhibits a very high shielding value (**2b**: −2.0; **2b′**: −1.5; **2c**: 6.3; **2c′**: 6.9 ppm). For the ^{1}H-NMR spectrum of **2c′**, the coalescence temperature for CH_3 rotation is lower than for **2c**, which, even at the lowest temperature reached (154 K), results in very broad lines for H(3), H(4), and H(5). The low-frequency shift for the H-atom bridging to Rh is considerably less in this case *(Table 1)*, and this also applies to the CH_3 ^{13}C-shift *(Table 2)*. On protonation of $[Rh(C_6H_{10})(C_5D_5)]$, no rapid incorporation of deuterium into the olefinic ligand is observed.

The activation parameters for the two exchange processes discussed above were obtained from complete line-shape analyses of the temperature-dependent ^{1}H- and ^{13}C-NMR spectra of the Co and Rh complexes **2b**, **2b′**, and **2c**, **2c′**, respectively. Three pairs of ^{13}C sites (C(1)/C(4); C(2)/C(3); $\mathit{C}H_3$–C(2)/$\mathit{C}H_3$–C(3)) and two pairs of proton groups (CH_3(1)/CH_2(4); CH_3–C(2)/CH_3–C(3)) are exchanged in the course of the interconversion of the enantiomers **B** ⇄ **B′**. Therefore, this rate constant can be extracted from five sources characterised by different chemical shifts $\Delta\nu$ and, consequently, different line shapes. Details of the analysis are given in *Experimental*. The kinetic data for the CH_3-rotation process were obtained from the ^{1}H-NMR spectra by line-shape simulation of the coupled three-spin system using the geminal H,H-coupling constants reported in [25] [26]. The free enthalpies of activation *($\Delta G^{\neq}$)* for the two processes are collected in *Table 3*. The $\Delta G^{\neq}$ values for the CH_3-rotation barrier (28–40 kJ/mol) are *ca.* four times larger than in uncomplexed allylic systems, *e.g.* $CH_3CH{=}CH_2$ (E_a = 8.9 kJ/mol [27]). On the other hand, the interconversion barrier for $\mathbf{B} \rightleftarrows \mathbf{B'}$ (31–47 kJ/mol) is low when compared with H shifts in free olefinic systems [28]. Clearly, the first process is hindered, while the second one is facilitated by the M···H interaction. Furthermore, a data comparison of the C_5H_5 and the C_5Me_5 complexes reveals that an increase in the rotational barrier is associated with a decrease in the H-shift barrier. There is also a significant effect of the metal on the energy barriers of the two processes, whereby the decrease in $\Delta G^{\neq}$ for the 1,4-H shift in the Rh complexes is most pronounced (*cf. Table 3* and *Footnote a* and *c*). Our results are in good agreement with those of *Kreiter* and coworkers obtained on Cr complexes of (*Z*)-penta-1,3-diene, in which hindered CH_3 rotation and a 1,5-H shift are observed [25] [26].

Table 3. *Kinetic Data for the Two Dynamic Processes and NMR Parameters of the Agostic H-Atom*

Compound	CH_3 Rotation $\Delta G^{\neq}$ [kJ/mol]	1,4-H Shift $\Delta G^{\neq}$ [kJ/mol]	δ(H) [ppm]	^1J(C,H) [Hz]
2b	40.6 ± 1.0 (193 K)	44.5 ± 1.0[a]) (193 K)	–13.18	80[b])/150/150
2b'	37.2 ± 1.0 (188 K)	47.1 ± 1.0[c]) (188 K)	–11.48	87[b])/147/147
2c	32.0 ± 1.0 (156 K)	31.3 ± 1.0 (156 K)	–8.40	–
2c'	28.3 ± 1.0 (154 K)	34.9 ± 1.0 (154 K)	–7.05	123[d])

[a]) $\Delta G^{\neq}_{156}$ = 43.4 ± 1.0 kJ/mol.

[b]) Agostic proton.

[c]) $\Delta G^{\neq}_{154}$ = 45.9 ± 1.0 kJ/mol.

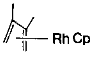
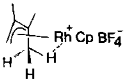
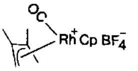
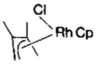
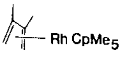
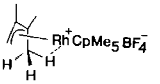
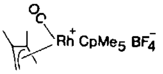
[d]) Average coupling constant in C(4) CH_3 group.

The $\Delta G^{\neq}$ values for the CH_3 rotation in our Co and Rh complexes may be correlated with the chemical shifts of the agostic proton and the ^1J(C,H) values of the CH_3 protons. Thus, the lowest ^1J(C,H) value (80 Hz) is associated with the highest shielding (–13.18 ppm) for the agostic proton and with a high rotation barrier ($\Delta G^{\neq}$ = 40.6 kJ/mol) in the Co complex **2b**. The strength of the agostic bond appears to decrease in the order $Co(C_5H_5) > Co(C_5Me_5) > Rh(C_5H_5) > Rh(C_5Me_5)$. A similar trend illustrating a decrease of the strength of the agostic bond with increasing electron density (*i.e.* decreasing electrophilicity) at the metal was demonstrated in $[FeL_3(\eta^3\text{-butenyl})]^+$ complexes using rotational barriers and the magnitude of ^1J(C,H) [14] [29].

The trends in the activation parameters of our cationic Co and Rh complexes may be rationalised assuming that the 2e,3-centre bond gives a better ground-state stabilisation for the Co complexes than in the Rh cases, and this increases $\Delta G^{\neq}$ for both exchange processes. In addition, the different basicities of the $M(C_5H_5)$ and $M(C_5Me_5)$ systems have an opposite influence on the transition state energies with the result that, in going from C_5H_5 to C_5Me_5, $\Delta G^{\neq}$ for the CH_3 rotation decreases, while for the 1,4-H shift $\Delta G^{\neq}$ increases. This result is reasonable, since in the first process the M–H bond is cleaved, whereas in the second one the C–H bond is broken.

The agostic structures of the Rh complexes **2c** and **2c'** were also characterized by ^{103}Rh chemical shifts (*Table 4*), together with the corresponding data of the neutral complexes **1c** and **1c'**. As expected, the protonated species exhibit strongly deshielded Rh resonances

Table 4. *^{103}Rh-NMR Data*

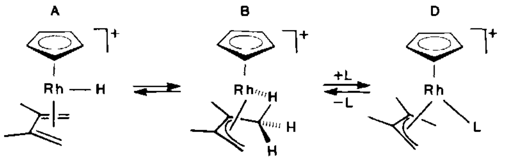
Compound		Solvent (conc.)	T [K]	$\delta(^{103}\text{Rh})^{a})$ [ppm]	t_1 [s]
	**1c**	C_6D_6 (0.1 M)	296	-1108.7	–
	**2c**	CD_2Cl_2 (0.24 M)	196	– 597.1	–
	**3c**	CD_3NO_2 (0.43 M)	296	– 942.7	–
		$CDCl_3$ (0.12 M)	296	+ 686.8	–
	**1c′**	C_6D_6	203	–1063.6	0.7
		(0.1 M)	296	–1004.5	6.5
	**2c′**	CD_2Cl_2	203	– 426.8	0.8
		(0.09 M)	296	– 344.1	5.6
	**3c′**	CD_2Cl_2 (0.36 M)	296	– 837.3	–

[a] ppm relative to the arbitrary standard $\nu(\text{Rh})(\text{ref})/\nu(\text{H})(\text{TMS}) = 0.0316$; from variable-temperature measurements, an average temperature coefficient of +0.8 ppm/K was determined. The accuracy of the chemical shifts: ± 1.0 ppm.

($\Delta\delta \approx$ 600–700 ppm), however, the chemical shifts are not typical for cationic Rh complexes [30]. This indicates that the positive charge is delocalized between the metal and the allylic ligand. The chemical shifts of the agostic 16e species **2c** and **2c′** appear to be characteristic for Rh involved in a two-electron, three-centre bond and lie in between the data for the relatively shielded 18e cationic CO complexes and the 18e chloride complex with a strongly ionic Rh–Cl bond. Furthermore, the agostic bonding does not lead to a significant dipolar relaxation of the Rh nucleus in **2c′** as shown by a negligible Rh-NOE observed upon irradiation at the $CH_3(4)$ protons at 220 K and by a very similar ^{103}Rh spin-lattice relaxation of **1c′** and **2c′**.

When small traces of a *Lewis*-base (*e.g.* solvent molecules such as H_2O, acetone, or pyridine) are present in CH_2Cl_2 solutions of **2c**, variable amounts of a coordinatively saturated allyl complex **D** competing with the agostic species are observed in the ^{1}H-NMR spectra *(Scheme 10)*. If the spectra are recorded in acetone instead of CD_2Cl_2, only

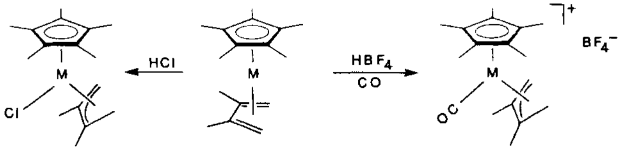
Scheme 10



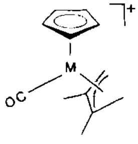
L = H_2O, C_5H_5N, $(CD_3)_2O$

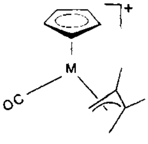
form **D** is observable at low temperatures (L = acetone). A Co(allyl) complex of type **D** with coordinated H_2O had previously been described and characterized [31]. **B** and **D** are in equilibrium, since the signals for the two species coalesce on warming of the samples ($\Delta G^{\neq}$ = 44 kJ/mol, L = H_2O) pointing to a very weak coordination of the solvent molecule. Form **D** (L = acetone) also becomes fully fluxional on warming. This structure is unique for **2c** and is not observed for **2c′** or any of the other complexes. In Form **D**, the three CH_3 protons are equivalent and show normal ^{1}H-NMR chemical shifts, ($\delta(CH_3(4))$ = 0.81–0.91 ppm depending on L), as no M··H··C interaction takes place. More than equimolar amounts of a basic solvent result in slow deprotonation of **2c** with recovery of the starting complex **1c**. This behaviour is also seen in all other protonated complexes.

Scheme 11



If complexes **1a–c** or **1a′–c′** are protonated in presence of CO, stable allyl complexes **3a–c**, **3a′–c′** of type **D** (L = CO) are formed in very high yields *(Scheme 11)*. They can also be prepared from previously isolated **2a–c** and **2a′–c′** by ready displacement of M··H··C or M–H bonds. This reaction is irreversible. Co complexes of this general structure had previously been prepared by reaction of $[Co(CO)_2(C_5H_5)]$ with allyl halides [32] [33] in low yields. The reaction principle outlined here seems to be more generally applicable and proceeds without any side reactions. The reactivity of this group of cationic allyl CO complexes, especially in regard to nucleophilic additions, is currently under investigation. The orientation of the allylic moiety in respect to the other ligands merits a further comment. It is well known, that $[M(allyl)(C_5H_5)L_x]$ complexes exhibit *exo*/*endo* isomerism [34]. They undergo slow intramolecular rearrangement, which interconverts conformers arising from two orientations of the η^3-allyl moiety with respect to the η^5-cyclopentadienyl ring.



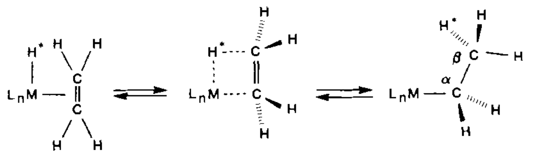


Only in the case of the $Ir(C_5H_5)$ complex **3a**, we observe by ^{13}C-NMR a mixture of *exo*/*endo* isomers. This suggests that in the other complexes one conformation is strongly preferred or that the rate of *exo*/*endo* interconversion is extremely slow, so that only the conformer initially formed by kinetic control is actually observed. Protonation of **1a–c** with HCl, where the halide ion acts as a coordinating anion, generates the well-known neutral $[MCl(allyl)(C_5H_5)]$ complexes [35]. Protonation of **1b** with DCl shows after longer reaction times (2 days) slow incorporation of deuterium at C(1) and C(4) as well as into the C_5H_5 ring. Similar halide complexes with the C_5Me_5 ligands are not very stable. They readily react with further HCl to give 2,3-dimethylbut-2-ene and the complexes $[MCl_2(C_5Me_5)]_2$. They also easily lose HCl on reaction with weak bases and regenerate the starting complexes **1a′–c′**. This is in agreement with mechanistic studies by *Lee* and *Maitlis*, which showed that allyl-halide complexes are labile intermediates in the synthesis of $[Rh(C_5Me_5)(diene)]$ from $[RhCl_2(C_5Me_5)]_2$ [36].

The protonated diolefin complexes of Co, Rh, and Ir **2a–c** and **2a′–c′**, while similar in their dynamic behaviour to complexes of Fe [13], Mo [37] as well as Mn [17] recently described in the literature, are nevertheless unique in exhibiting three different structures **A**, **B**, and **D** in the ground state, depending on the metal or the substituents at the auxiliary ligand. The fluxional behaviour (1,4-H shift) is only observed for the coordinatively unsaturated 16e species, while for the CO and Cl^- adducts only the static form **D** is observed at room temperature, indicating that the suprafacial 1,4-H shift can only take place *via* a free coordination site at the metal, thus confirming the proposed mechanism. As the fluxional behaviour observed in solution is independent of the ground state, this indicates that the energies of ground state and low-lying intermediates are very close and also, as indicated by $\Delta G^{\neq}$, separated by low activation barriers. These protonated olefin complexes and their dynamic behaviour, while instructive in the discussion of the M··H··C bonding mode and the conditions under which it can occur, also help to illustrate some general aspects of the interaction of alkenes and transition metal hydrides.

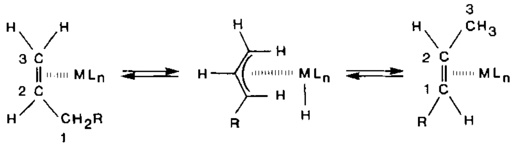
The reaction of transition-metal hydrido complexes with alkenes or other unsaturated organic substances is of prime importance in catalytic reactions such as hydrogenation or hydroformylation, and one of the major methods for the synthesis of M–C bonds [20] [38]. This reaction involves the H transfer from the M- to the C-atom, which becomes the β-C-atom of the new alkyl substituent. This reaction step, which is often rate-determining in the catalytic cycle, may be designated as a *1,2-hydride shift* or as an insertion of an olefin into a M–H bond. For this process, a four-centre transition state with a M··H··C interaction is commonly postulated [19]. The reverse of that reaction, the so-called β-hydride elimination, is responsible for the decomposition of many metal alkyls [20] [38]. Comparison of *Scheme 12* with the ground states observed in our systems **2a–c** and **2a′–c′** as illustrated in *Schemes 8* and *10* shows remarkable similarities. The reversible H transfer from a M–H group to a metal-coordinated olefin is responsible for the dynamic behaviour of **2a** and **2a′**. This corresponds to the key step in the homogenous catalytic hydrogenation of olefins [38]. In this process, the intermediacy of complexes, in which vacant coordination sites are occupied by solvent molecules, is commonly assumed. The H transfer in our system becomes irreversible, when the vacant coordination site is occupied by a CO ligand. The reverse reaction is observed in the interconversion of the enantiomeric forms **D** and **D′** *via* form **B** and **B′** in **2c**, which corresponds to a reversible β-elimination and proceeds most likely *via* a metal-hydride transition state of type **A**.

Scheme 12



A second type of hydride shift, where again the intermediacy of M· ·H· ·C species may play an important role, is the metal-assisted *1,3 shift* [38], which is observed in the isomerization of alkenes and which most likely proceeds *via* π-allyl-hydride intermediates *(Scheme 13)*.

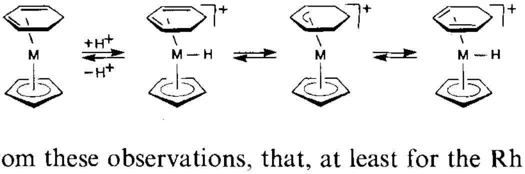
Scheme 13



As mentioned earlier, one dynamic process observed in our as well as related systems is best described as a metal-assisted *1,4-H shift*, which takes place in coordinatively unsaturated metal-allyl complexes with an H-bearing α-alkyl substituent. This arrangement also appears to be the most favourable for M· ·H· ·C interaction, as most isolable species with this bonding mode belong to this class. As already mentioned, C–H activation has also been observed in Cr complexes of (*Z*)-substituted pentadienes, where dynamic processes corresponding to *1,5-H shifts* are observed. The M· ·H· ·C interactions in the ground state are evident from spectroscopic as well as structural data [25] [26].

2.2. *Protonation of Complexes [M(cyclohexadiene)(C_5Me_5)] (M = Co, Rh, Ir).* The protonation of the cyclohexadiene analogues of **1a–c** had earlier been investigated by *Lewis* and coworkers [24]. It was reported, that the protonated Ir complex had a diolefin-hydride structure at lower temperatures, but became fluxional on warming. The corresponding Rh complex was fluxional down to 223 K and a static structure could not be observed by ^{1}H-NMR at 100 MHz. The following conclusions were drawn from the averaged spectra as well as deuteration studies with CF_3CO_2D: *a*) *Initial protonation (or deuteration) of the metal takes place followed by reversible transfer of the proton to the cyclohexadiene ligand to form a cationic 16e allyl complex. This will equilibrate three protons between* endo-*CH_2 and metal-hydride environments* (Scheme 14). *b*) *In the fast exchange limit only two proton resonances are observable for the olefinic ligand, one for the three* endo-*protons involved in the proton transfer and one for the six other protons permanently bonded to the six-membered ring and equilibrated between allylic and* exo-*CH_2 environments. c*) *Slow exchange of H^+ or D^+ between the solvent and metal hydride eventually leads to incorporation of three D-atoms into the protonated product. After quenching with D_2O and $NaHCO_3$, two* endo-*D-atoms are left in the CH_2 positions of the cyclohexadiene ligand.*

Scheme 14



We concluded from these observations, that, at least for the Rh complex, a ground state with M· ·H· ·C bonding was also fully compatible with the dynamic behaviour in solution. We, therefore, investigated the protonation of the corresponding C_5Me_5 complexes, including also the Co complex, under the assumption, that the more basic C_5Me_5 ligand might allow the detection of the slow-exchange limit and also lead to the stabilization of the protonated product, as $[Co(C_6H_8)(C_5H_5)]$ decomposed in acid solution [24].

Complexes **4a'–c'** were protonated with equimolar amounts of HBF_4 in propionic anhydride and precipitated with Et_2O in almost quantitative yields.

Scheme 15

$$[M(C_6H_8)(C_5Me_5)] + HBF_4 \rightarrow [M(C_6H_9)(C_5Me_5)]\,[BF_4]$$

4' **5'**

a M = Ir **b** M = Co **c** M = Rh

All complexes of type **5'** are again fluxional at room temperature, the Ir complex **5a'** showing only broad lines in the 400-MHz ^{1}H-NMR spectrum at room temperature. In CD_3NO_2 at 368 K, two signals at 3.91 and −3.77 ppm in the ratio of 6:3 appeared, typical for the fast-exchange process described earlier. In the slow-exchange spectrum of **5a'** at 208 K, the classical symmetrical diolefin-hydride structure **A** became evident, which showed a low frequency multiplet at −14.92 ppm for the M–H moiety *(Table 5)*.

Table 5. *^{1}H-NMR Data for Complexes* **5a'–c'**[a])

	T/K	$C_5(CH_3)_5$	H(1)	H(3)	H(2)	H(4)	H(6)	H(5)	H(8)	H(7)	H(9)
5a'	368[b])	2.27			3.91					−3.77	
	208	2.27	4.25	5.47	5.47	4.25	2.25		1.90		−14.92
5b'	296	1.84		3.21						−3.39	
	216	1.84	5.33		4.92	1.52		0.21	1.16	−5.70	
	141	1.72	4.37	6.17	4.87	1.12	1.7	0.17	1.17	1.35	−12.88
5c'	293	1.98			3.42					−1.67	
	166	1.85	5.10		5.10	2.01		0.55	1.38	−3.40	

[a]) ^{1}H Chemical shifts [ppm] in CD_2Cl_2, 400 MHz, **5a'**: 200 MHz. [b]) CD_3NO_2.

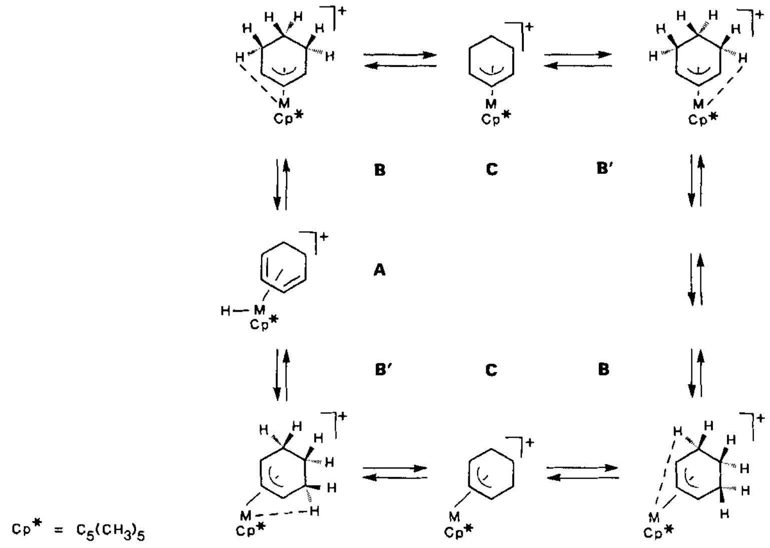
The Co complex **5b'**, while showing at room temperature similar chemical shifts as **5a'** and a similar averaged spectrum for the olefinic ligand with two signals in the ratio of 6:3, nevertheless revealed totally different ^{1}H- and ^{13}C-NMR spectra on cooling (*Table 5* and *6*), compatible only with an unsymmetrical ground state of type **B** *(Scheme 16)*.

Table 6. *^{13}C-NMR Data for Complexes* **5a'–c'**[a])

	T/K	$C_5(CH_3)_5$	$C_5(\mathit{C}H_3)_5$	C(3)	C(1)	C(2)	C(6)	C(4)	C(5)
5a'	213	100.4	10.1	83.0	59.7	83.0	26.1	59.7	26.1
5b'	155	97.7	11.0	81.1	81.1	95.6	30.0	16.2	17.1
5c'	293	102.6	10.5			55.7			
	173	102.3	11.2	82.6		92.5	27.8		17.9

[a]) ^{13}C Chemical shifts [ppm] obtained from proton-noise-decoupled spectra in CD_2Cl_2 at 100.6 MHz, **5a'**: $CDCl_3$, 25.2 MHz.

Scheme 16



As in **2b**, **2c** and **2b′**, **2c′**, form **B** must be an enantiomeric pair. On warming of **5b′**, two exchange processes can be observed separately *(Fig. 4): 1. Interconversion of the enantiomeric pair* **B** ⇄ **B′** via *a coordinatively unsaturated intermediate of structure* **C** *(Scheme 16).*

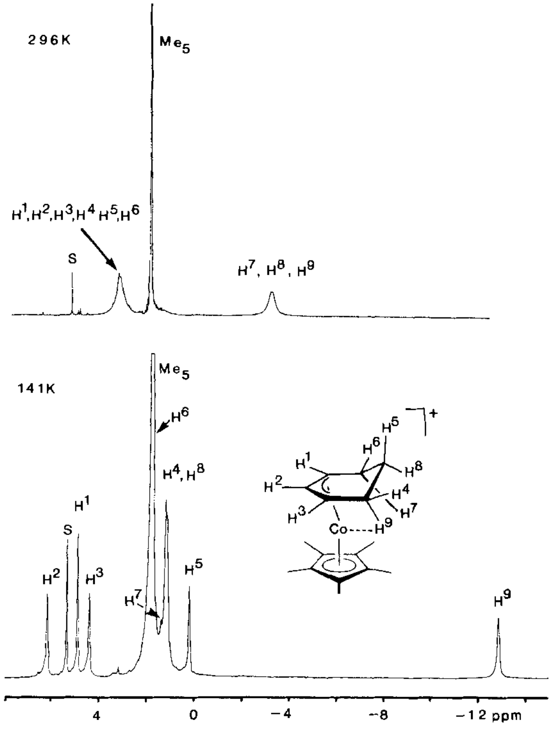


Fig. 4. *^{1}H-NMR Spectrum* (CD_2Cl_2, 400 MHz) *of* **5b′** *at 296 K* (top) *and 141 K* (bottom)

In this process, H(7) and H(9) alternate as bridging hydride in the M· ·H· ·C moiety and in the fast exchange the molecule has an apparent plane of symmetry going through C(2), H(2), and C(5), H(5), H(8). This process has a low coalescence temperature, and fast exchange is observed at 216 K. 2. Interconversion of enantiomeric pairs **B** $\rightleftarrows$ **B′** via *a metal hydride* **A**. *This can again be described as a 1,2-allyl or 1,4-H shift. As this exchange has a higher energy of activation, process* 1 *and* 2 *are coupled and in the fast-exchange limit only two types of protons in the ratio 3:6 are observed and all ring C-atoms become equivalent.*

While this work was in progress, **5b′** was also prepared and characterized by *Spencer* and coworkers [39]. The ground-state structure with M· ·H· ·C bonding was confirmed by X-ray and neutron-diffraction studies.

The Rh complex **5c′** proved again to have lower energies of activation for internal rearrangement than the Ir and Co analogues. Full fluxionality was observed at room temperature with equivalence of all six ring-C-atoms. At 166 K, the exchange *via* the metal hydride is sufficiently slow to observe the spectra of the symmetrical intermediate in which H(9), H(7), and C(4), C(6) become equivalent *(Fig. 5)*. H(9) and H(7) are again bridging H-atoms, and the averaged signal for the two protons appears at −3.40 ppm *(Table 5)*. This value may be compared with the average δ value of H(7) and H(9) (−5.7 ppm) of **5b′** and clearly indicates that the agostic bond is weaker in the Rh complex.

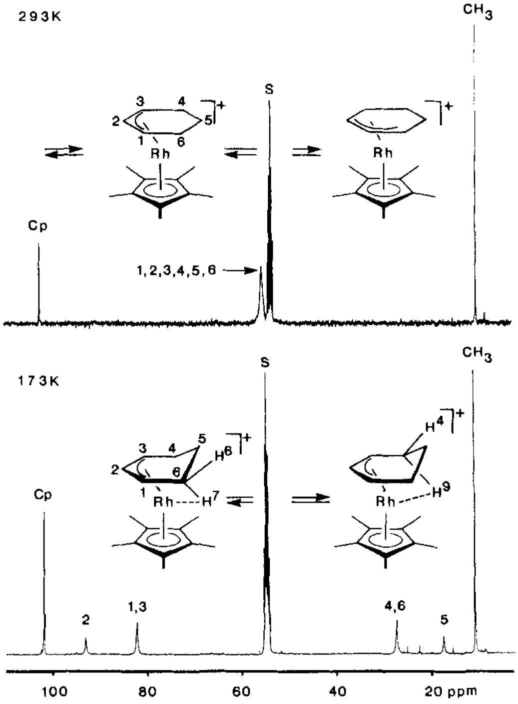


Fig. 5. *^{13}C-NMR Spectrum* (CDCl$_2$, 100.6 MHz) *of* 5c′ *at 293 K* (top) *and 173 K* (bottom)

Therefore, there is no doubt that **5c′** also has ground state **B**, although the slow-exchange limit for the ^{1}H-NMR spectrum could not be reached. The dynamic behaviour and ground-state structures for **5b′** and **5c′** are, therefore, similar to the cyclohexenyl complexes described by *Brookhart et al.* [16], but probably with lower activation energies for the rearrangement processes in solution. Within the three homologous metals, the Rh complexes investigated in this study have invariably the lowest activation energies. It is perhaps not surprising that in many catalytic processes involving hydride transfer between metals and olefins, Rh catalysts are also generally more reactive than those of other metals.

The protonation of **4a′** and **4c′** with HCl had already been investigated by *Maitlis* and coworkers [40]. No intermediate allyl-halide complexes could be isolated and the reaction yielded cyclohexene and $[MCl_2(C_5Me_5)]_2$ by double addition of HCl. Preliminary results indicate, that on protonation with HBF_4 in the presence of CO stable $[M(C_5Me_5)(cyclohexenyl)CO]^+$ complexes are formed. The general reactivity of these complexes as electrophilic allyl synthons is currently under investigation, an extension of our previous work in this field [1] [10] [41].

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Experimental. – All reactions were carried out under N_2, using dry and deoxygenated solvents. Photochemical reactions were conducted in a 300-ml vessel (with quartz finger) using a 125-W *Philips* quartz Hg-vapour lamp.

The following compounds were synthesized by the respective literature procedure: $[RhCl(C_2H_4)_2]_2$ [42]; $[RhCl_2(C_5Me_5)]_2$ [43]; $[Co(CO)_2(C_5H_5)]$ [44]; $[Co(CO)_2(C_5Me_5)]$ [45]; $[IrCl(C_8H_{14})_2]_2$ [46]; $[IrCl_2(C_5Me_5)]_2$ [47]. Pentamethylcyclopentadiene and cyclopentadienyl thallium were purchased from *Strem Chemicals*, 2,3-dimethylbutadiene and cyclohexadiene from *Fluka*. IR: *Perkin-Elmer 983* spectrophotometer. ^{1}H-NMR: *Bruker AM 400* at 400.13 MHz. ^{13}C-NMR: *Varian XL 100-12* at 25.2 MHz or *Bruker AM 400* at 100.6 MHz. Typical acquisition parameters on the *AM-400:* ^{1}H-NMR: spectral width 8000 Hz, number of spectral data points 16000, pulse angle 8 µs; ^{13}C-NMR: spectral width 20000 Hz, number of spectral data points 32000, pulse angle 13 µs; ^{13}C,^{103}Rh-coupling constants [Hz] are given in parentheses following the chemical shifts and were obtained with an accuracy of ±0.3 Hz from the proton-noise-decoupled spectra at 25.2 MHz. ^{103}Rh-NMR: in 20 mm sample tubes, *Bruker AM-400* spectrometer at 12.64 MHz. The temp. adjustments were made by the variable-temperature unit of the *Bruker AM-400* using N_2 and the temp. were measured by the thermocouple located below the bottom of the sample tube. Because of sample warming due to high-power proton irradiation (^{13}C-NMR) a calibration curve was taken by placing a second thermocouple, located in the NMR tube filled with the same amount of solvent as the sample tubes, at the height of the receiver coil. The temp. indicated by the *Bruker* temp.-measuring device were thus related to the true temp. in the dummy tube by least-squares adaptation und then appropriately corrected. For the proton measurements, no noticeable difference between the temp. indicated by the two thermocouples was observed and the temp. were taken without any correction. Before temp. measurements, the system was allowed to reach thermal equilibrium within 15–20 min. Under these conditions, temp. were accurate to ±1°.

The exchange-broadened ^{1}H- and ^{13}C-NMR spectra were evaluated by complete band-shape analysis, whereby for the Co compounds **2b** and **2b′** quadrupolar relaxation was treated as an additional broadening included in the natural linewidth. Theoretical spectra were calculated using the DNMR3 program [48] by entering the chemical shifts, natural linewidth, population, and trial rate values. The latter were obtained from the halfwidth of the lines above and below coalescence by means of the usual approximations. The natural linewidth data were derived from the C_5H_5 and C_5Me_5 signals assuming that the ring rotation is very fast even at the lowest temp. To obtain the rate constant, calculated and experimental spectra were then compared to the best fit.

Free enthalpies of activation for the 1,4-H shift were derived from least-squares fits including both the ^{1}H and ^{13}C data by means of the *Eyring* equation. Errors in $\Delta G^{\neq}$ are not only of statistical origin, but include i.a. the possible temp. inaccuracy of ±1 K. $\Delta G^{\neq}$ for the CH_3 rotation was evaluated from the line shapes by substraction of the broadening due to the 1,4-H shift at the given temp. and assuming the same geminal H,H-coupling constants as reported by *Kreiter* and coworkers [25] for the pentadienyl system; ^{1}H,^{103}Rh coupling was neglected.

(Cyclopentadienyl)(dimethylbutadiene)iridium (**1a**). An excess of the diene was added to a suspension of $[\mathrm{IrCl(C_8H_{14})_2}]_2$ in hexane. The mixture was stirred until the orange colour had disappeared. An equimolar amount of $\mathrm{Tl(C_5H_5)}$ was added and stirring was continued for 3 h. After removal of the solvent the residue was chromatographed with hexane on Alox (grade IV). Yield: 60%. ^{13}C-NMR ($\mathrm{C_6D_6}$): 76.5 ($\mathrm{C_5H_5}$); 26.1 (C(1,4)); 80.7 (C(2,3)); 20.7 ($\mathrm{CH_3}$).

(Cyclopentadienyl)(dimethylbutadiene)rhodium (**1c**). An excess of the diene (5 mmol) was added to a suspension of $[\mathrm{RhCl(C_2H_4)_2}]_2$ (0.5 mmol) in hexane at −50°. After refluxing for 10 min, the soln. was cooled to r.t. and an equimolar amount of $\mathrm{Tl(C_5H_5)}$ was added. The mixture was stirred for 4 h, TlCl was filtered off and the solvent evaporated. Chromatography with hexane (Alox, grade IV) yielded **1c** (95%). ^{13}C-NMR ($\mathrm{C_6D_6}$): 83.4 (5.2) ($\mathrm{C_5H_5}$); 36.6 (17.0) (C(1,4)); 91.7 (7.8) (C(2,3)); 20.8 (1.0) ($\mathrm{CH_3}$).

General Preparation of [M(diene)(C_5Me_5)] Complexes (M = Rh, Ir; **1a′**, **1c′**, **4a′**, **4c′**) [36] [49]. An excess of the appropriate diene (5 mmol) and $\mathrm{Na_2CO_3}$ (5 mmol) were added to a suspension of $[\mathrm{MCl_2(C_5Me_5)}]_2$ (0.5 mmol) in EtOH. The mixture was refluxed for 3 h, the solvent evaporated and the residue chromatographed with hexane (Alox, grade IV). Yields: **1a′**: 90%; **1c′**: 95%; **4a′**: 79%; **4c′**: 82%. ^{13}C-NMR ($\mathrm{C_6D_6}$): **1a′**: 88.8 ($\mathit{C}_5\mathrm{Me}_5$); 10.8 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 29.7 (C(1,4)); 77.7 (C(2,3)); 18.2 ($\mathrm{CH_3}$). **1c′**: 93.8 (5.8) ($\mathit{C}_5\mathrm{Me}_5$); 10.8 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 40.8 (17.3) (C(1,4)); 87.6 (7.3) (C(2,3)); 18.2 ($\mathrm{CH_3}$). **4a′**: 88.8 ($\mathit{C}_5\mathrm{Me}_5$); 11.1 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 46.8 (C(1,4)); 67.1 (C(2,3)); 28.3 (C(5,6)). **4c′**: 94.1 (6.0) ($\mathit{C}_5\mathrm{Me}_5$); 11.0 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 58.5 (16.6) (C(1,4)); 76.1 (6.9) (C(2,3)); 26.3 (1.7) (C(5,6)).

General Preparation of C_5H_5 and C_5Me_5 Co-Diolefin Complexes (**1b**, **1b′**, **4b′**). A soln. of $[\mathrm{Co(CO)_2(C_5H_5)}]$ or $[\mathrm{Co(CO)_2(C_5Me_5)}]$ and a 5-fold excess of the appropriate diene in hexane was irradiated at 5°, until no further CO evolved. The soln. was evaporated and the residue chromatographed on Alox (grade IV). Yields: **1b**: 81%; **1b′**: 70%; **4b′**: 65%. ^{13}C-NMR ($\mathrm{C_6D_6}$): **1b**: 80.6 ($\mathrm{C_5H_5}$); 34.9 (C(1,4)); 91.3 (C(2,3)); 20.5 ($\mathrm{CH_3}$). **1b′**: 88.6 ($\mathit{C}_5\mathrm{Me}_5$); 10.0 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 38.6 (C(1,4)); 87.6 (C(2,3)); 17.3 ($\mathrm{CH_3}$). **4b′**: 89.1 ($\mathit{C}_5\mathrm{Me}_5$); 10.6 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 57.1 (C(1,4)); 79.1 (C(2,3)); 25.6 (C(5,6)).

Protonation of Diolefin Complexes. a) *With HBF_4.* An equimolar amount of $\mathrm{HBF_4}$ (50% aq. soln.) in propionic anhydride at 0° was added dropwise to a soln. of the appropriate diolefin complex in propionic anhydride at 0°. After addition of cold $\mathrm{Et_2O}$ the precipitated products were filtered off, washed with cold $\mathrm{Et_2O}$ and dried. ^{1}H-NMR of **2a–c**, **2a′–c′**: see *Tab. 1;* ^{1}H-NMR of **5a′–c′**: see *Tab. 5.* ^{13}C-NMR of **2a–c** and **2a′–c′**: see *Tab. 2;* ^{13}C-NMR of **5a′–c′**: see *Tab. 6.*

b) *With HCl.* An equimolar amount of conc. HCl was added to a soln. of the appropriate diolefin complex in MeOH at 0°. After 5 min, the products were precipitated with $\mathrm{Et_2O}$ and filtered off. ^{13}C-NMR ($\mathrm{CDCl_3}$): (**1c**·HCl): 89.2 (5.5) ($\mathrm{C_5H_5}$); 55.0 (10.0) (C(1)); 99.7 (6.6) (C(2)); 83.8 (10.0) (C(3)); 29.0, 22.1, 25.8 ($\mathrm{CH_3}$). ^{13}C-NMR: **1c′**·HCl: 98.5 (5.8) ($\mathit{C}_5\mathrm{Me}_5$); 9.3 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 58.7 (10.5) (C(1)); 101.0 (C(2)); 94.0 (9.5) (C(3)); 26.9, 25.9, 19.5 ($\mathrm{CH_3}$).

Addition of CO to **2a–c**, **2a′–c′**, *and* **5c′**. CO was bubbled into a soln. of the protonated complexes **2a–c**, **2a′–c′**, **5c′** in $\mathrm{CH_2Cl_2}$. After 30 min, the products were precipitated with $\mathrm{Et_2O}$, filtered and dried.

3a: IR ($\mathrm{CH_2Cl_2}$): 2061. ^{13}C-NMR ($\mathrm{CD_3NO_2}$): Isomer **A**: 91.2 ($\mathrm{C_5H_5}$); 35.5 (C(1)); 114.0 (C(2)); 79.8 (C(3)); 28.9, 28.0, 19.1 ($\mathrm{CH_3}$); 164.0 (CO). Isomer **B**: 90.4 ($\mathrm{C_5H_5}$); 35.6 (C(1)); 99.2 (C(2)); 78.4 (C(3)); 29.1, 26.2, 21.3 ($\mathrm{CH_3}$); 165.3 (CO).

3a′: IR ($\mathrm{CH_2Cl_2}$): 2047. ^{13}C-NMR ($\mathrm{CDCl_3}$): 102.0 ($\mathit{C}_5\mathrm{Me}_5$); 9.16 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 37.0 (C(1)); 96.7 (C(2)); 69.3 (C(3)); 27.6, 25.6, 17.9 ($\mathrm{CH_3}$); 168.7 (CO).

3b: IR ($\mathrm{CH_2Cl_2}$): 2070. ^{13}C-NMR ($\mathrm{CD_3NO_2}$): 93.5 ($\mathrm{C_5H_5}$); 37.0 (C(1)); 96.7 (C(2)); 69.3 (C(3)); 27.6, 17.9, 25.6 ($\mathrm{CH_3}$); 199.1 (CO).

3b′: IR ($\mathrm{CH_2Cl_2}$): 2048. ^{13}C-NMR ($\mathrm{CD_3NO_2}$): 104.5 ($\mathit{C}_5\mathrm{Me}_5$); 9.8 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 50.5 (C(1)); 105.2 (C(2)); 90.6 (C(3)); 28.9, 26.0, 18.8 ($\mathrm{CH_3}$); 204.8 (CO).

3c: IR ($\mathrm{CH_2Cl_2}$): 2078. ^{13}C-NMR ($\mathrm{CD_3NO_2}$): 95.7 (4.4) ($\mathrm{C_5H_5}$); 49.5 (9.7) (C(1)); 107.9 (5.4) (C(2)); 100.0 (7.6) (C(3)); 29.7, 28.5, 22.6 ($\mathrm{CH_3}$); 187 (79.0) (CO).

3c′: IR ($\mathrm{CH_2Cl_2}$): 2061. ^{13}C-NMR ($\mathrm{CDCl_3}$): 106.0 (5.0) ($\mathit{C}_5\mathrm{Me}_5$); 9.5 ($\mathrm{C_5(}\mathit{C}\mathrm{H_3)_5}$); 51.5 (9.7) (C(1)); 104.6 (5.1) (C(2)); 88.2 (7.6) (C(3)); 28.5 (0.8), 25.1 (0.6), 18.7 (0.5) ($\mathrm{CH_3}$); 189.4 (80.4) (CO).

5c′·CO: IR ($\mathrm{CH_2Cl_2}$): 2057. ^{13}C-NMR ($\mathrm{CDCl_3}$): 93.3 (4.3) ($\mathrm{C_5H_5}$); 77.6 (7.6) (C(1,3)); 84.2 (5.3) (C(2)); 27.6 (C(4,6)); 16.9 (C(5)); 187.3 (83.3) (CO).

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