Journal of Organometallic Chemistry, 228 (1982) 71—85
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE STRUCTURE AND FLUXIONAL BEHAVIOUR OF BUTADIENE IN BUTADIENE-TRANSITION METAL COMPLEXES OF Ti, Zr, Hf, Mo, W AND Co

R. BENN * and G. SCHROTH

Max-Planck-Institut für Kohlenforschung, D-433 Mülheim a.d. Ruhr, Kaiser-Wilhelm-Platz 1 (B.R.D.)

(Received July 7th, 1980)

Summary

The ^1H NMR spectra of the [(butadiene) (cyclooctatetraene)]metal complexes $[(\eta^4\text{-}C_4H_6)COT]M$ (I, M = Ti; II, M = Zr; III, M = Hf), trisbutadienemetal complexes $(\eta^4\text{-}C_4H_6)_3M$ (IV, M = Mo; V, M = W), $[(\eta^4\text{-butadiene})(\eta^5\text{-cyclopentadienyl})]$cobalt (VI), and [(butadiene) (cyclopentadienyl)$_2$]metal complexes $(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)_2M$ (VII, M = Zr; VIII, M = Hf) in toluene-d_8 solvent were measured at various temperatures. Sub-spectral analysis and iterative computer simulation were carried out to yield chemical shifts and coupling constants. These parameters provide direct evidence for a s-*cis*-η^4-butadiene conformation in I—VI and a s-*trans*-η^4-butadiene conformation in VII, VIII. Furthermore, the ^1H NMR data confirm an increasing sp^3 rehybridisation at the terminal carbon atoms in I—V and VII, VIII when descending the relevant groups of the periodic table. II, III and V have temperature dependent ^1H NMR spectra. In III the terminal butadiene protons begin to equilibrate above 30°C (80 MHz) and the transition of an AA'MM'XX' spin system to an $AA'X_2X_2'$ spin system is observed and calculated by line shape analysis including all the couplings. Whilst II and V are also fluxional the rate constant for equilibration of the terminal protons is low (compared to III) and the exchange process can be demonstrated only by magnetisation transfer experiments at temperatures above +40 and +90°C, respectively (80 MHz). The exchange process in II, III, and V is interpreted as proceeding through a metallacyclopentene transition state. Parallels to the fluxional behaviour of η^3-allyl-transition metal compounds are briefly pointed out.

Introduction

Nuclear magnetic resonance has been found to be a valuable method for elucidating the structure of transition metal complexes, and among the first

0022-328X/82/0000—0000/$02.75

organometallic compounds which were investigated by proton NMR was [(butadiene)(tricarbonyl)]iron [1]. Its crystal structure [2] showed that the complexed ligand exists in an s-*cis* conformation with four coplanar carbon atoms and nearly equal C—C bond lengths. However, the positions of the H atoms were not obtained. The NMR data were completely analysed and interpreted in terms of a non-planar C,H-skeleton with some rehybridisation of the terminal carbon atoms towards sp^3 [1]. In the meantime a full analysis of the corresponding [(butadiene)(tricarbonyl)]ruthenium complex has been published [3] and the NMR data reveal a distortion of the diene ligand similar to that in the corresponding iron complex. In addition, the crystal structure and ^{1}H NMR data of s-*cis*- and s-*trans*-η^4-butadiene osmium complexes [4] have been reported. In order to obtain information about the structural changes which occur on complexation of the butadiene ligand to transition metals, we have analysed the ^{1}H NMR spectra of the series [(η^4-butadiene)(cyclooctatetraene)]-metal, (I, M = Ti; II, M = Zr; III, M = Hf), tris(η^4-butadienemetal (IV, M = Mo; V, M = W) and [(η^4-butadiene) (η^5-cyclopentadienyl)]cobalt(VI), as well as [(η^4-butadiene) bis(η^5-cyclopentadienyl)]metal (VII, M = Zr; VIII, M = Hf) *. For IV [6] and VII ** a crystal structure has been obtained and this allows a comparison with the parameters derived from the ^{1}H NMR analysis.

Although a large number of transition metal complexes have been shown to be fluxional [8], to our knowledge fluxional behaviour of η^4-butadiene-transition metal complexes has been reported in only one case: the cationic complex [(dicarbonyl)(η^5-cyclopentadienyl)(η^4-piperilene)]molybdenum$^+$, which exhibits dynamic ^{1}H NMR spectra [9]. The ^{1}H NMR parameters of II, III, and V encouraged us to investigate the NMR spectra of these complexes at various temperatures; they revealed fluxional behaviour of the butadiene ligand either by line shape analysis [8] or magnetisation transfer techniques [10]. In the present paper the dependence of the ^{1}H NMR parameters for monometal complexes with butadiene either in s-*cis* or in s-*trans* conformation is demonstrated. Furthermore, it will be emphasized that η^4-butadiene-transition metal complexes in general may be as fluxional as many other transition metal complexes.

Experimental

Complexes I—III were prepared by Stehling and Wilke [11], IV, V by Gausing and Wilke [12,13], VI by Habermann [14], VII by Erker [7], and VII, VIII by Stehling and Wilke [11]. Solutions of I—VIII in purified toluene-d_8 (concentrations about 1% v/v) were prepared under argon and sealed in 5 mm sample tubes (Wilmad PS 505).

The ^{1}H NMR spectra of I—VI were recorded on a Bruker WP 80 spectrometer operating in the FT mode and equipped with a BNC-28 computer with

---

* The structure and the fluxional behaviour of II, III and V has been reported previously [5].

** A series of complexes of the type [(η^4-$C_4H_4R^1R^2$)(η^5-C_5H_5)$_2$]Zr has been prepared by Erker and coworkers [7]. [(η^4-C_4H_6)(η^5-C_5H_5)$_2$]M (M = Zr, Hf) were also prepared by Wilke and Stehling [11]. The structures of [(*cis*-η^4-C_4H_6)(η^5-C_5H_5)$_2$]Zr (VIIa) and [(*trans*-η^4-C_4H_6)(η^5-C_5H_5)$_2$]Zr (VII) were determined by means of ^{1}H NMR in our laboratory. Later the result of this analysis were confirmed by X-ray analysis (Krüger [7]).

16 K memory, using a spectral width of 1500 Hz with an acquisition time of 5.5 s, which corresponds to 5.4 data points per Hz in the Fourier transformed spectra. VII, VIII were studied at 270 MHz (32 K memory, spectral width 3000 Hz). The chemical shifts are determined relative to the solvent (toluene-d_8 $\delta \equiv 2.08$ at +30°C) and converted to the TMS scale.

The homo-decoupling experiments were performed using the standard decoupling unit. In the magnetisation transfer experiments the terminal protons were saturated for 10 s followed by a delay between 0.1 and 1 s and a final H_1 pulse (flip angle $\alpha \sim 20°$) with 2.7 s acquisition time. The total repetition time was 30 s. The proton NMR spectra (80 MHz, +30°C: II—VI AA'MM'XX'; I, VII, VIII AA'BB'XX'; +110°C: III $AA'X_2X_2'$) were calculated by an iterative procedure using a modified LAME program [15] on a PDP 10 computer.

The temperature dependent spectra of III were calculated by line shape analysis [8]. A strongly modified version of the DNMR III Program [16] was established which allowed inclusion of all the couplings of III in the calculation. In particular, the temperature dependent splittings of the AA' pattern could be calculated. Details of this program will be given in a forthcoming paper, in which the temperature dependent ^{1}H NMR spectra of [(s-*cis*-η^4-butadiene) bis(η^5-cyclopentadiene)]metal) VIIa, M = Zr [7,11]; VIIIa, M = Hf [11]) will also be discussed with the help of line shape analysis.

Results

^{1}H NMR spectra of transition metal complexes with butadiene in s-*cis* conformation are shown in Fig. 1, Fig. 3 (lower trace), and Fig. 4 (lower trace). The six-proton spectrum of I is of the type AA'BB'XX'. Subspectral analysis and iterative computer simulation on 28 experimental line frequencies then gave the final set of parameters. For all the complexes the relative sign of the geminal coupling constant was taken from ref. 1. VII and VIII also exhibit an AA'BB'XX' spectral pattern. The number of lines used for the iteration of VII was 59 and for VIII was 52. A typical spectrum for a mono-metal complex with η^4-butadiene in s-*trans* arrangement is shown in Fig. 2. II—VI exhibit ^{1}H NMR spectra which are of the type AA'MM'XX'. The number of lines used for iteration of II was 53, for III 37 at +30°C and 25 at +110°C, for IV 36, for V 38, and for VI 39 lines. The NMR data and the rms error of the final set of parameters of I—VIII are listed in Table 1.

Solutions of II, III and V in toluene-d_8 exhibit temperature dependent spectra. In III it is the transversal relaxation time T_2 which reveals the temperature dependence (line shape). In Fig. 3 spectra of III between +30 and +110°C are shown. With increasing temperature the spectrum changes from AA'MM'XX' pattern (+30°C lower trace, Fig. 3) to an $AA'X_2X_2'$ pattern (+110°C upper trace, Fig. 3). These spectral changes correspond to an exchange of the terminal protons b and c and of b' and c', respectively. This is confirmed by the averaged chemical shifts and coupling constants which are found in the high temperature spectrum of III: in particular for the $AA'X_2X_2'$ spin system a long range coupling $^4J(a, c')$ 0.03 Hz is found, which is (within limits of experimental error) the averaged value of $^4J(a, b')$ +2.03 Hz and $^4J(a, c') = -2.14$ Hz.

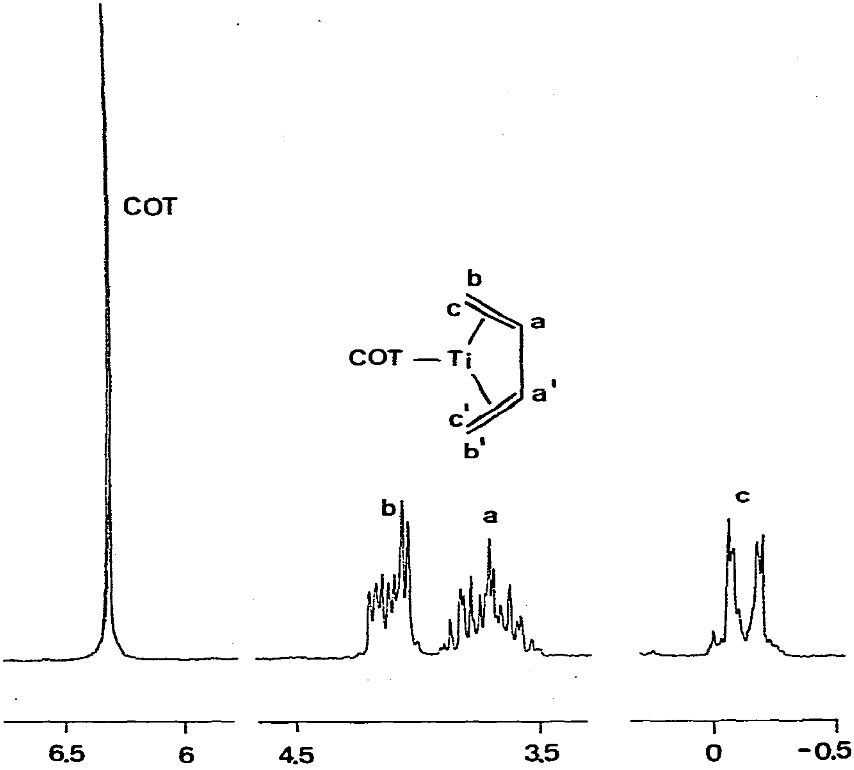


Fig. 1. 80 MHz ^{1}H NMR spectrum of I at +30°C in toluene-d_8. The protons a,a' resonate at higher fields than b and b'. In general for *cis*-η^4-butadiene complexes the reverse is observed. For the assignment in full cf. Table 1.

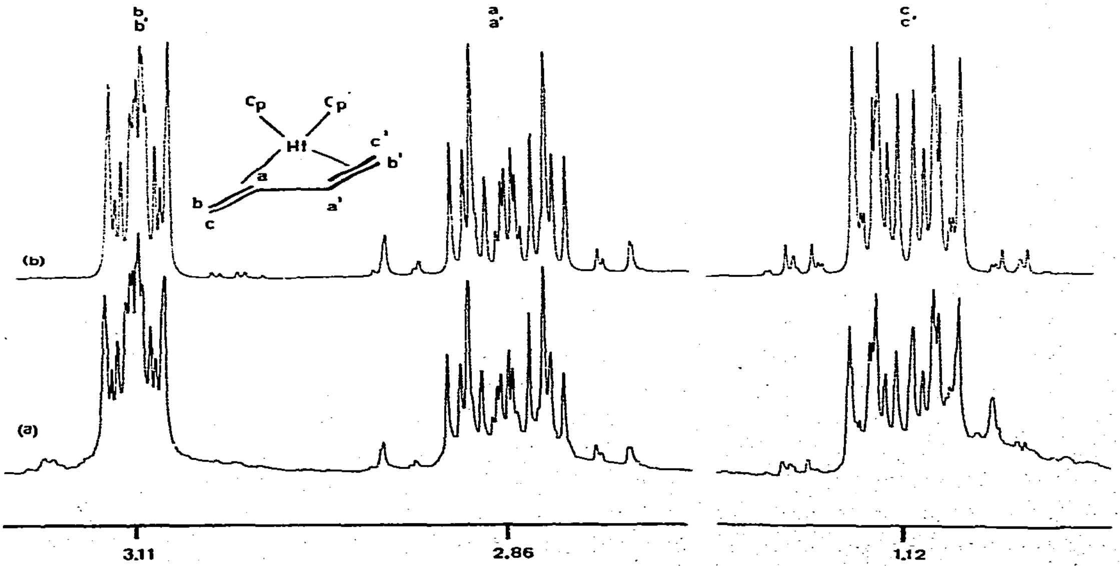
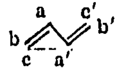


Fig. 2. 270 MHz ^{1}H NMR spectrum of VIII at 0°C in toluene-d_8: (a) experimental spectrum, and (b) calculated spectrum. The singlet for η^5-cyclopentadienyl is omitted for clarity.

TABLE 1

^{1}H NMR DATA FOR I–VIII. (The chemical shifts (δ scale (ppm)) and coupling constants (Hz) for free butadiene (*s-trans*) are taken from ref. 17.)

	I +30°C	II +30°C	III +30°C	III +110°C	IV +30°C	V +30°C	VI +30°C	VII +30°C	VIII +30°C	
aa'	7.13	7.90	7.47	7.80	6.22	6.17	4.64	15.87	16.48	10.41
ab	8.37	9.41	9.63	9.43	7.65	7.61	6.79	7.05	6.92	10.17
ac	10.70	11.09	9.55		9.19	8.09	9.36	16.63	16.70	17.05
bc	−1.31	−4.14	−5.70	—	−2.98	−4.46	−1.46	−3.88	−4.87	+1.74
a'b	1.94	2.10	2.03	0.03	1.23	1.44	0.95	−0.37	−0.39	−0.86
a'c	−0.93	−1.42	−2.14		−1.37	−1.57	−1.01	−1.14	−1.25	−0.83
bb'	−0.33	0.09	−0.04	0.02	0.06	−0.10	−0.12	0.80	0.81	0.60
cc'	−1.27	0.22	−0.05		−0.05	0.24	−0.15	−0.04	−0.07	0.60
b'c	0.51	0.08	−0.04	—	0.00	0.03	−0.07	−0.12	−0.08	1.30
rms	0.141	0.062	0.064	0.076	0.056	0.077	0.047	0.043	0.042	
δ(a)	3.72	4.31	4.85	4.76	4.52	4.61	4.91	2.85	2.83	6.26
δ(b)	4.12	2.60	1.79	1.05	1.50	1.35	1.69	3.18	3.13	5.05
δ(c)	−0.19	0.37	0.45		0.37	0.26	−0.37	1.16	1.13	5.16
δ(COT)	6.32	6.16	6.20	6.20	—	—	—	—	—	—
δ(Cp)	—	—	—	—	—	—	4.57	4.84	4.78	—

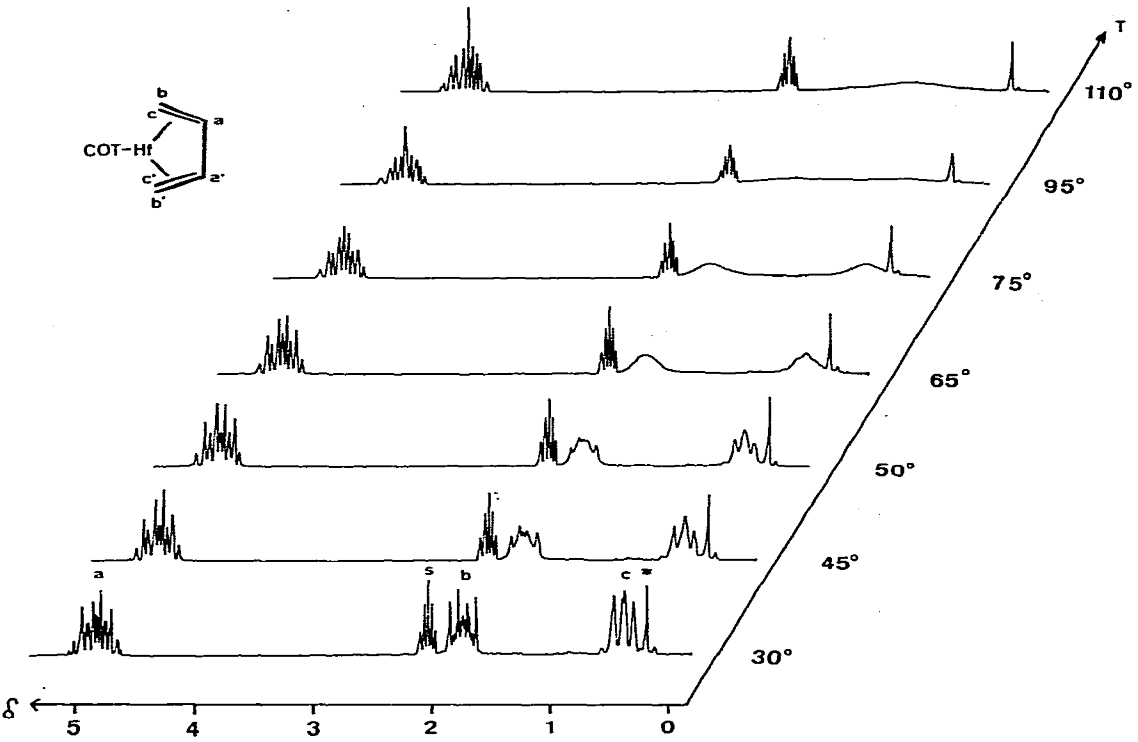


Fig. 3. 80 MHz ^{1}H-NMR spectra of III at temperatures between +30°C and +110°C (s denotes the solvent toluene-d_8).

Since the frequency differences in the AA′ pattern are smaller than those between the MM′ and XX′ patterns, the fast exchange limit of the AA′ multiplet is observed at lower temperatures than that of the averaged X_2X_2' subspectrum (cf. Fig. 3, upper trace). The line shape analysis (temperature range +45 to 101°C) including all the couplings of III yielded E_a = 17.6 ± 0.3 kcal mol^{-1}, ln A = 29.1 ± 0.4, $\Delta H^{\ddagger}$ = 16.9 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −3.1 ± 0.8 e.u. The limits of error result from regression analysis, the standard deviations are smaller than 0.05 kcal mol^{-1}; the correlation coefficients for the Arrhenius and Eyring diagrams are higher than 0.99938.

In II and V the exchange of the terminal butadiene protons was confirmed by magnetisation transfer experiments which allow the study by NMR of slower exchange processes than accessible to line shape analysis since the rate constant for the exchange process is compared to the inverse longitudinal relaxation time T_1^{-1} and not to T_2^{-1} (in general $T_1^{-1} < T_2^{-1}$ holds). Saturating the high field protons of II at δ 0.37 ppm leads to an intensity decrease of the resonances around δ 2.60 ppm by chemical exchange of the terminal protons (cf. Fig. 4, spectrum (b)). The intensities of the protons at δ 4.31 ppm as well as the signals from impurities and the solvent s remain unaffected. This confirms that exclusively the protons at δ 0.37 ppm have been saturated. The reverse experiment, saturation of the protons at δ 2.60 ppm leads exclusively to decreased intensity of the protons at δ 0.37 ppm (cf. Fig. 4, spectrum (c)). This

(Continued on p. 79)

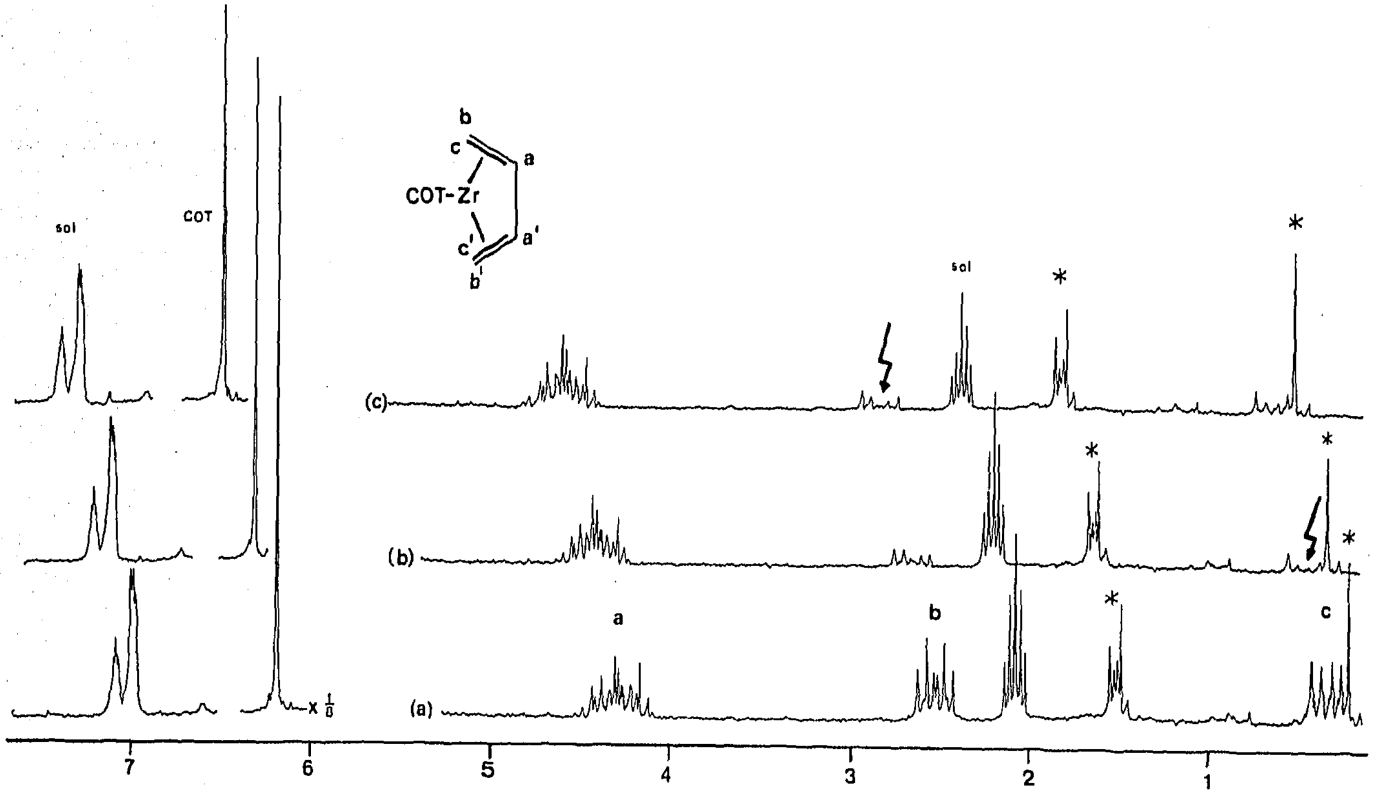


Fig. 4. 80 MHz ^{1}H NMR spectra of II at +90°C (a) normal spectrum, (b) spectrum after saturation of the protons at δ 0.37, and (c) spectrum after saturation of the protons at δ 2.60 (sol denotes the solvent and * impurities).

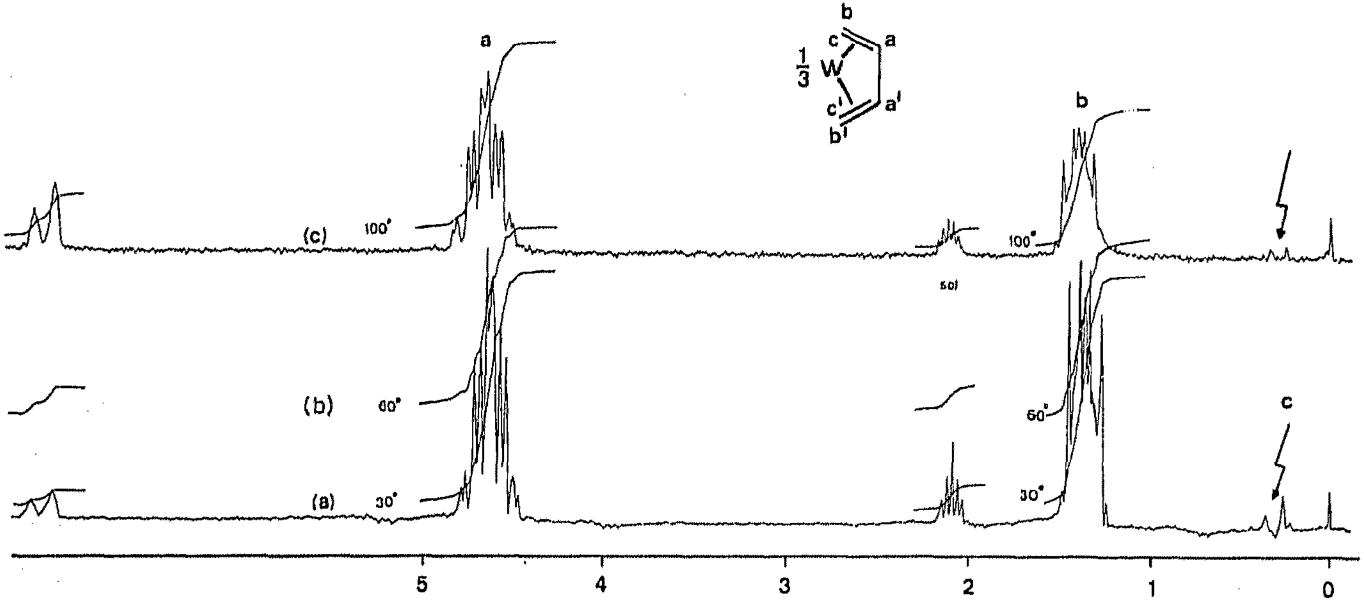


Fig. 5. 80 MHz ^{1}H NMR spectra of V at various temperatures after saturation of the protons at δ 0.26. (a) spectrum and integral at +30° C, (b) integral +60° C, (c) spectrum and integral at +100° C.

exchange process can be observed at temperatures above +40°C (80 MHz). The effects of the saturation transfer become larger with increasing temperature. At +90°C the intensity is reduced by more than 80%.

Similar experiments have been carried out with V. However, significant transfer of saturation is observed only at temperatures above +90°C (10% loss in intensity) (cf. Fig. 5). At 110°C an intensity decrease of the protons at δ 1.35 ppm (δ 0.26 ppm) of more than 25% is observed on saturating the protons at δ 0.26 ppm (δ 1.35 ppm). As for II and III these experiments confirm a chemical exchange of the terminal protons b and c and of b′ and c′, respectively.

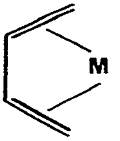
Discussion

1. Bonding of COT in I—III

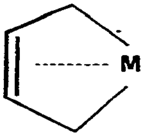
Several types of bonding are known for cyclooctatetraene (COT) to transition metals. In a number of complexes [18] COT retains its polyene nature, e.g. in COTFe(CO)$_3$ [19] it is bonded as a fluxional η^4-system. However, there are some molecules in which it acts as a planar aromatic ligand: in COTZr(η^3-allyl)$_2$ [20] COT has this dianionic type of bonding. Another example of symmetrical COT—M bonding for a *d*-block metal is found in (COT)$_3$Ti$_2$ [21]. In I—III COT is assumed to have this dianionic type of bonding. This interpretation is based on the ^{1}H NMR chemical shifts of COT in I—III, which are found at lower fields (compared to free COT), in contrast to η^4-COT-systems where high field shifts of COT are observed [22].

2. Bonding of butadiene in I—VI

The type of bonding of the s-*cis*-butadiene ligand to the transition metal [23, 24] is generally described in terms of resonance hybrids of the forms (A) and (B). In a simple picture, which has only conceptual validity, representation (A) implies that the electrons are localized as in butadiene, whereas (B) suggests that there is considerable σ-character of the bonding electrons between metal and the terminal carbons of butadiene. Representation (B) must also take account of the fact that there may be some bonding between the metal and the C(2), C(3) carbons of the diene. In other terms (MO), (A) implies that there is major bonding to the metal by the ψ_1 and ψ_2 orbitals of butadiene whilst (B) suggests that bonding between the metal and the ψ_3 MO is also very important.



(A)



(B)

The relative weighting of these forms, i.e. the degree of occupation of the ψ_3 orbital of the butadiene ligand, is reflected by particular structural features, e.g. relative C(1)—C(2) and C(2)—C(3) bond lengths and the bond angles associated with the position of protons at C(4), implying sp^3 or sp^2 character. A comparison of the coupling constants and the chemical shifts of I—VI reveals a general trend towards increasing participation of (B) in the series I—III and IV, V, respectively. A quantitative calculation of the contribution of the resonance hybrids based on NMR data was not attempted. In order to confirm the increasing participation of the presentation (B) the expected changes of spectral parameters are listed and compared to the experimental parameters (cf. Table 1) in the following sections (i—iii). The differences in the electronegativities * of Ti, Zr, and Hf on the one hand and Mo and W on the other hand do not appear to be reflected in the variations of the coupling constants.

(i) The absolute value of the geminal coupling constant ^2J(a, b) increases in the series I—III (IV, V). Similar, but smaller effects have been found for the butadiene-iron, -ruthenium, and -osmium complexes [1,3,4]. If we assume a negative sign for ^2J(b, c) in I—V as found for (η^4-C_4H_6)Fe(CO)$_3$ (^2J(b, c) —2.42 Hz) [1] the value of ^2J(b, c) in III (^2J —5.70 Hz) and V (^2J —4.46 Hz) approaches the range of what is generally found for geminal sp^3 proton couplings in five-membered rings ($^2J \sim$ —9.1 Hz) **. Therefore a large geminal coupling $|^2J$(b, c)$|$ can be interpreted as indicating significant rehybridisation of the terminal carbons of butadiene towards sp^3.

(ii) The changes of the vicinal "*cis*" ^3J(a, b) and "*trans*" ^3J(a, c) couplings in I—V are in line with this interpretation. In general these couplings are reduced on complexation. This may be rationalised in terms of increase of C—C bond length resulting from π-electron donation and back donation and of bond torsion leading to optimum orbital overlap. For our interpretation it is important that the $^3J(trans)/^3J(cis)$ ratio decreases ($^3J^t/^3J^c$ = 1.28 (I), 1.18 (II), 0.99 (III), 1.20 (IV), and 1.06 Hz (V)). This may be explained by twisting the terminal protons more and more out of the plane of the carbon skeleton.

(iii) Furthermore, the changes of chemical shifts substantiate this interpretation, as can readily be seen by comparing the ratio of the complexation shifts $\Delta\delta$(a)/$\Delta\delta$(b) and $\Delta\delta$(a)/$\Delta\delta$(c). $\Delta\delta$ denotes the difference in chemical shift of complexed and free ligand of the corresponding protons. In this calculation the ratio $\Delta\delta$(a)/$\Delta\delta$(b) decreases (2.73 (I), 0.80 (II), 0.43 (III), and 0.49 (IV), 0.45 (V), respectively; $\Delta\delta$(a)/$\Delta\delta$(c) = 0.47 (I), 0.41 (II) 0.30 (III), 0.36 (IV), and 0.34 (V). Differences in conformation of the complexed (s-*cis*) and free (s-*trans*) butadiene have been neglected; this may be justified, since within the series I—V the difference due to changes of conformation (*cis* vs. *trans*) are expected to be constant. The decreasing ratios indicate a stronger complexation of the terminal than of the C(2), C(3) carbons. Again, this is exactly what is expected for increasing participation of representation (B). Moreover, this interpretation is in accord with the results of an X-ray analysis of IV [6].

The H,H coupling constants of VI are close to what is found for I (cf. Table 1) (with the exception of ^3J(a, a$'$). In particular in VI it is $^3J(trans)/^3J(cis)$ 1.40 Hz and $|^2J$(b, c)$|$ 1.29 Hz. Thus it can be assumed that the bonding of s-*cis*-η^4-butadiene in VI is largely described by the resonance hybrid (A) and

---

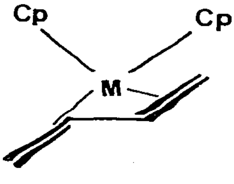
* Ti (1.3). Zr (1.2). Hf (1.2). Mo (1.3). W (1.4). Co (1.7) Allred—Rochow.

** To our knowledge no complete ^{1}H NMR data (including all couplings) have been reported so far for metallacyclopentene. Some NMR data for these systems are mentioned by Barker et al. [25]. The most convincing reference material seems to be bis(tetramethyldiaminelithium)(η^4-butadiene)(cyclopentene)metal (M = Mo [12], M = W) where ^2J—9.1 is found.

presentation (B) is involved only to a minor extent. If the NMR data of the s-*cis*-η^4-butadiene complexes of iron [1], ruthenium [3], and osmium [4] are included in our discussion, then the participation of the limiting form (B) can be suggested to increase in the series I,VI < complexes of the iron group < IV, V < II, III. Apparently the resonance hybrid (A) is especially involved in those transition metal complexes where the ability of the metal orbitals for back-bonding is high (that is, at least in general, it is more pronounced for the late transition metals). In addition, in the complexes of the iron group the vicinal ^3J(a, a′) coupling is remarkable small. This corresponds to a short bond length between carbon atom C(2) and C(3) (*d*(C(2)—C(3) 1.41 Å for $[(\eta^4\text{-}C_4H_6)(CO)_3]Fe$). On the other hand, for IV a relatively large C(2)—C(3) bond length has been found [6] (*d*(C(2)—C(3)) 1.55 Å) and this corresponds to a larger ^3J(a,a′) coupling ^3J(aa′) 6.22 Hz. How far the valence angles H—C(2)—C(3) and C(2)—C(3)—H influence this coupling constant remains unresolved. A correlation between ^3J(a,a′) and the bond length C(2)—C(3) in s-*cis*-η^4-butadiene-transition metal complexes probably can be established when further reference material is available. In particular, the influence of the ligands (CO, COT, Cp) has to be considered [24]. A linear correlation between the vicinal H,H coupling constant ^3J and the bond length has been found in unsaturated six-membered rings [26].

3. *Bonding of butadiene in VII and VIII*

The complexes VII and VIII are monomeric as has been shown by molecular weight determinations [11]. In the temperature range +30 to −80°C the ^{1}H NMR spectra of VII (VIII) show one singlet for the two cyclopentadienyl units and three temperature independent multiplets for the butadiene ligand. The shifts indicate that all the carbons of butadiene are complexed to the metal (cf. Fig. 2): the number of signals confirm that there is an element of symmetry in VII and VIII. The coupling constants (cf. Table 1) differ significantly from those of I—VI. They are close to that what was found for s-*trans*-η^4-butadiene-osmium complexes [4] and uncomplexed s-*trans*-butadiene [17]. In particular, the coupling constants ^3J(a,a′) and ^3J(a,c) are about 16 Hz, which is close to the range generally observed for *trans*-couplings and also for *anti*-couplings in η^3-allyl complexes of Zr and Hf [11,27]. Furthermore, in VII and VIII the long range coupling ^4J(a′ b) is negative, as was also found for free s-*trans*-butadiene, whereas in the s-*cis*-η^4-butadiene complexes I—VI the relative sign of ^4J(a′ b) is positive. It can be concluded that the ligand adopts a s-*trans* conformation in VII, VIII, as qualitatively illustrated.



VII, M = Zr; VIII, M = Hf

The crystal structure of VII is discussed in detail by Krüger (cf. ref. 7). The geminal coupling $|^2J(b, c)|$ is remarkably large in VII and VIII. Again, the relative sign of these couplings was taken from ref. 1. These couplings indicate that there is significant rehybridisation towards sp^3 at the terminal carbon atoms. It must be emphasized that to our knowledge VII and VIII are the first mono-metal transition metal complexes in which the butadiene is η^4 complexed to the metal and adopts a s-*trans* conformation.

From the ^{1}H NMR data of I—VIII several general trends are apparent:

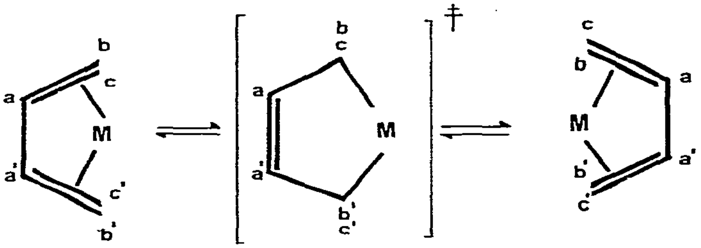
(i) The coupling constants $^3J(\mathrm{a, a'})$ and $^4J(\mathrm{a', b})$ are highly sensitive parameters which can be used to distinguish a s-*cis*-η^4-butadiene arrangement clearly from an s-*trans* conformation.

(ii) In a series of s-*cis*-η^4-butadiene-metal complexes the participation of the resonance hybrids (A) and (B) can be discussed in terms of $^2J(\mathrm{b, c})$, $^3J(trans)/{}^3J(cis)$, $\Delta\delta(\mathrm{a})/\Delta\delta(\mathrm{b})$ and $\Delta\delta(\mathrm{a})/\Delta\delta(\mathrm{c})$ (cf. section 2). Caution, however, is necessary, in the interpretation of the chemical shifts. The sequence $\delta(\mathrm{b}) > \delta(\mathrm{a}) > \delta(\mathrm{c})$ holds for the s-*trans* complexes VII, VIII and also for the corresponding osmium complex [4], but this sequence is also found in I, in which the ligand adopts an s-*cis* conformation. Thus the sequence of chemical shifts is not an unequivocal indicator of the conformation of the butadiene ligand.

4. *Fluxional behaviour of butadiene in II, III and V*

The interconversion of the terminal protons in II, III and V (cf. Fig. 3,4,5) may be achieved by passage through a metallacyclopentene intermediate followed by collapse to the η^4-butadiene structure (cf. Scheme 1). A clear distinction between a concerted (cf. Scheme 1) and other (e.g. stepwise or bimolecular) mechanisms has not yet been possible. However, we favour a concerted mechanism of the type depicted above (at least for III) for the following reasons:

SCHEME 1



(i) It was possible to establish rate constants for the concerted exchange of the bb′ and cc′ protons by line shape analysis. With the help of these rate constants the temperature dependent splittings of the AA′ subspectral multiplets could be calculated by assuming also a simultaneous exchange of the proton b with c and b′ with c′. The calculated line shape due to this permutational scheme (two configurations 1 (a,a′, b,b′, c,c′) and 2 (a,a′, c,c′, b,b′)) is in accord with what is observed in the experimental spectra (cf. Fig. 6). In the case of a stepwise mechanism at least three configurations have to be included in the permutational scheme (1 (a,a′, b,b′, c,c′), 2 (a,a′, c,b′, b,c′), 3 (a,a′, c,c′, b,b′)) and we would expect a different splitting of the AA′ spectral pattern. In fact, for the *syn—anti*-rearrangement in (η^3-allyl)$_4$Zr (A MM′XX′ spin system)

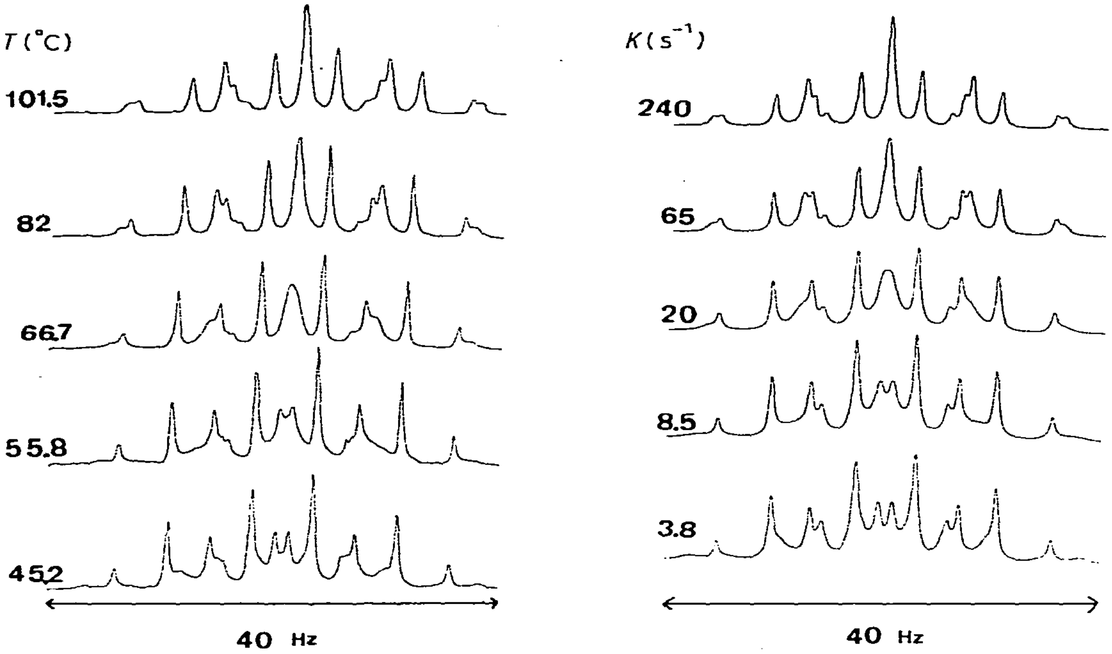


Fig. 6. Experimental (left) and calculated (right) splittings of the AA′ multiplet of III at various temperatures. The rate constants result from the line shape analysis of the exchange of proton b with c, and b′ with c′ assuming a concerted mechanism.

[28,29] it has been shown [29] that a concerted and a stepwise mechanism can be distinguished with the help of line shape analysis if all the couplings are included in the calculation. The similar should be true for III (AA′MM′XX′ spin system), but due to limited computer capacity (the program exceeds 250 K in this case) the stepwise exchange has not yet been stimulated.

(ii) The exchange process in III was revealed by line shape analysis, whereas in II and V by magnetisation transfer experiments. Thus, the exchange process is most rapid ($V < II < III$) in those cases where the rehybridisation of the terminal carbons of butadiene is most evident.

A similar mechanism as depicted in Scheme 1 has sometimes been invoked to account for the fluxional behaviour of η^3-allyl in η^3-allyl-transition metal complexes (η^1, η^1-flip mechanism) [8]. To our knowledge there is no experimental evidence for such a mechanism for η^3-allyl compounds. In the light of our results for the corresponding η^4-butadiene complexes we would expect that the η^1, η^1-flip mechanism for the η^3-allyl complexes would be indicated by a significant negative geminal H,H coupling constant of the respective allyl protons. In general, however, these couplings are in the range of (±) 1.5 Hz [20,30,31].

The variety of complexes for which this fluxional behaviour can be demonstrated (II, III, V) suggests that butadiene-transition metal complexes may in general be fluxional, as for example η^3-allyl-transition metal complexes. The tendency of the complex to show temperature dependent NMR spectra is evident particularly in those cases in which backbonding does not play such an important role (as for the early transition metals of Group IVB—VIB). The activation parameters for the fluxional process in butadiene complexes, however, seem to be significantly higher than for the corresponding η^3-allyl compounds (e.g. COTZr(η^3-C_3H_5)$_2$ $\Delta G^{\ddagger}$ = 8.1 ± 0.3 kcal mol^{-1} [32]; COTZr(η^4-C_4H_6) $\Delta G^{\ddagger} > \sim 20$ kcal mol^{-1}). Comparing the activation parameters for the fluxional behaviour of the corresponding η^3-allyl and η^4-butadiene complexes as the metal is varied shows that for both types of complexes the activation parameters decrease when descending the relevant groups of the periodic table (e.g. E_a(Zr(η^3-C_3H_5)$_4$ > E_a (Hf(η^3-C_3H_5)$_4$) [32] and E_a (COT Zr(η^4-C_4H_6)) > E_a (COT Hf(η^3-C_4H_6))).

Conclusion

It has been shown that H,H spin coupling constants are valuable parameters for structural and dynamic properties of butadiene-transition metal complexes. These parameters can provide detailed information about the conformation of the complexed organic ligand in solution. They permit a clear distinction between *cis*-η^4-butadiene (I—VI) and *trans*-η^4-butadiene (VII, VIII). The nature of the transition metal has been shown to have a significant influence on the arrangement of the butadiene ligand. Moreover, for different butadiene complexes fluxional behaviour of the butadiene could be clearly demonstrated, revealing a novel and general property of η^4-butadiene-transition metal complexes is solution.

References

1 K. Bachmann and W. von Philipsborn, Org. Magn. Res., 8 (1976) 648.
2 (a) O.S. Mills and G. Robinson, Acta Crystallogr., 16 (1963) 758; (b) O.S. Mills and G. Robinson, Prog. Chem. Soc. London, (1960) 421.
3 S. Ruh and W. von Philipsborn, J. Organometal. Chem., 127 (1977) C59.
4 M. Tachikawa, J.R. Shapley, R.C. Haltiwanger and C.G. Pierpart, J. Amer. Chem. Soc., 98 (1976) 4651.
5 R. Benn and G. Schroth GDCh Fachgruppe Magnetische Resonanzspektroskopie, Steinhagen October 1979.
6 (a) P.S. Skell and M.J. McGlinchey, Angew. Chem., 87 (1975) 215; (b) P.S. Skell, E.M. Van Dam and M.P. Silvon, J. Amer. Chem. Soc., 96 (1974) 626.
7 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and C. Krüger, submitted 1980.
8 Dynamic Nuclear Magnetic Resonance Spectroscopy Academic Press, New York, 1975.
9 F.W. Faller and Rosan, J. Amer. Chem. Soc., 99 (1977) 4858.
10 S. Forsen and R.A. Hoffmann, J. Chem. Phys., 39 (1963) 2892.
11 G. Wilke et al., in preparation.
12 W. Gausing, Ph. D. Thesis Ruhr-Universität Bochum, 1979.
13 G. Wilke et al., to be published.
14 Gmelins Handbuch, Vol. 5, No. 1, 1973, p. 314. R.B. is indebted to D. Habermann for providing a sample of VI.
15 C.W. Haigh, Dept. Chem. Univ. Coll. Swansea, SA 28PP (England).
16 (a) Binsch in DNMR cf. ref. [8], p. 45; (b) G. Binsch and D.A. Kleier, Quantum Chemical Program Exchange 140 (1969), Indiana University, Bloomington.
17 R.T. Hobgood, Jr. and J.H. Goldstein, J. Molecul. Spectr., 12 (1964) 76.
18 (a) F.A. Cotton, J.W. Faller, and A. Musco J. Amer. Chem. Soc., 90 (1968) 1438; (b) F.A. Cotton A. Davidson, T.J. Marks and A. Musco, ibid., 91 (1969) 6598.
19 G. Rigatti, G. Boccalon, A. Ceccon and G. Giacometti, J. Chem. Soc. Chem. Commun., (1972) 1165.
20 H.J. Kablitz and G. Wilke, J. Organometal. Chem., 51 (1973) 241.
21 (a) H. Breil and G. Wilke, Angew. Chem., 78 (1966) 942; (b) H. Dierks and H. Dietrich, Acta Cryst. B, 24 (1968) 58.
22 W. Geibel, Ph. D. Thesis, Ruhr-Universität, Bochum, 1978.
23 M.R. Churchill and R. Mason, Advan. Organometal. Chem., 5 (1967) 93.

24 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Interscience, New York, 1972, p. 731.
25 G.K. Barker, M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton, 12 (1978) 1839.
26 J.B. Pawliczek and H. Günther, Tetrahedron, 26 (1970) 1755.
27 R. Kallweit, Ph. D. Thesis, Ruhr-Universität Bochum, B.R.D., 1974, p. 111.
28 E.G. Hoffmann, R. Kallweit, G. Schroth, K. Seevogel, W. Stempfle and G. Wilke, J. Organometal. Chem., 97 (1975) 183.
29 J.K. Krieger, J.M. Deutsch and G.M. Whitesides, Inorg. Chem., 12 (1973) 1535.
30 P.W. Jolly and G. Wilke, The organic Chemistry of Nickel, Vol. 1, Academic Press, New York, 1974, Ch. VI.
31 R. Benn and G. Schroth, Org. Mag. Resonance, in press.
32 R. Benn and E.G. Hoffmann, J. Organometal. Chem., 193 (1980) C33.