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METAL π-COMPLEXES OF BENZENE DERIVATIVES

XXVIII *. STRAINED ANELLATED ARENES AS π-LIGANDS: SYNTHESIS AND MAGNETIC RESONANCE PROPERTIES OF BIS(CYCLOBUTA-η^6-BENZENE)CHROMIUM$^{0,+1}$ AND BIS([1,2:4,5]-DICYCLOBUTA-η^6-BENZENE)CHROMIUM$^{0,+1}$

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Summary

Bis(cyclobuta-η^6-benzene)metal complexes of chromium(0) (**4**), molybdenum(0) (**14**) and tungsten(0) (**15**) as well as bis([1,2:4,5]-dicyclobuta-η^6-benzene)chromium(0) (**5**) have been prepared by metal atom ligand vapor cocondensation techniques. The ^{1}H NMR coordination shifts $\Delta\delta$ for the *endo*- and *exo*-protons of the cyclobutene ring are discussed in the context of anisotropic shielding in the periphery of bis(η^6-arene)chromium. The ESR spectra of the chromium centered radical cations $\mathbf{4}^{\ddagger}$ and $\mathbf{5}^{\ddagger}$ are also reported. In conjunction with hyperfine coupling data for (η^{12}-[2.2]paracyclophane)chromium‡ ($\mathbf{16}^{\ddagger}$), which also possesses monitor protons at defined positions, and for bis(η^6-paraxylene)chromium‡ ($\mathbf{17}^{\ddagger}$), containing freely rotating methyl groups, the contributions of conformation dependent, and conformation independent pathways of metal ligand electron-spin transfer are assessed.

Introduction

Considerable effort has been invested into experimental and theoretical study of small ring anellated arenes like cyclobutabenzene (**1**), [1,2:4,5]dicyclobutabenzene (**2**) and [1,2:3,4:5,6]tricyclobutabenzene (**3**). The work aimed at proving or dispro-

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* Part XXVII see ref. 1.

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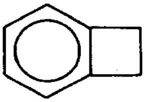
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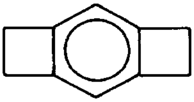
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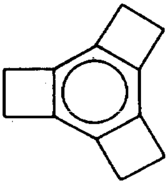
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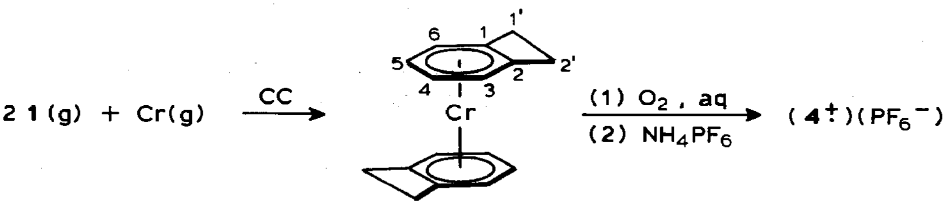
ving the Mills–Nixon hypothesis [2–4] and was also triggered by curiosity as to the influence of ring strain on chemical reactivity [5,6,7]. A characteristic feature of arenes is their coordination to transition metals in complexes of the half sandwich as well as the sandwich type, (η^6-Ar)M(CO)$_n$ and (η^6-Ar)$_2$M respectively. Whereas slight bond angle alternation in the arene as demonstrated in the case of [1,2 : 4,5]dicyclobutabenzene [8] should not prevent complex formation [9], synthesis of bis(arene)metal complexes containing fused cyclobutene and cyclopropene rings might be hampered by ring opening reactions. This will certainly be the case if the reducing Friedel–Crafts synthesis [10] is applied and should at least be considered a possibility for the path of metal atom ligand vapor cocondensation. In addition to the latter quest, availability of complexes (η^6-**1**)$_2$M, (η^6-**2**)$_2$M and (η^6-**3**)$_2$M would be attractive to the magnetic resonance spectroscopist since the axial disposition of the methylene C–H bonds in the periphery of these sandwich molecules should aid in interpretations of the ^{1}H NMR coordination shift (neutral diamagnetic species) as well as the mechanism of metal ligand electron spin transfer (radical cations). In this paper we report on the cocondensation of **1** and **2** with chromium atoms. The potential ligand **3** [11] is not yet accessible in sufficient quantities for a metal ligand cocondensation.

Results and discussion

From cocondensations (CC) of **1** and **2** with chromium vapor, the complexes **4** and **5** were obtained as reddish-brown, air-sensitive materials. Whereas aqueous solutions of the radical cations **4**$^{+\cdot}$ and **5**$^{+\cdot}$ are stable for extended periods, samples of the solid hexafluorophosphates **4**$^{+\cdot}$ (PF$_6$)$^-$ and **5**$^{+\cdot}$ (PF$_6$)$^-$, are occasionally generated in pyrophoric form.



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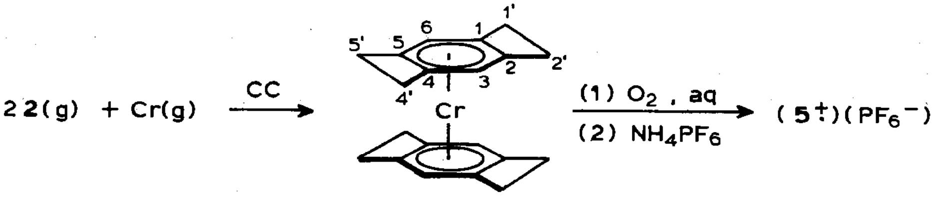

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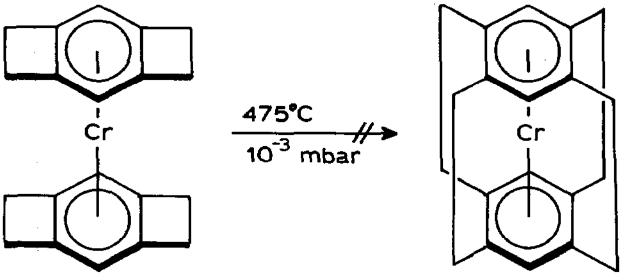
Complexes **4** and **5** can be sublimed (120° C, 10^{-3} mbar) without decomposition or rearrangement. In order to further investigate the latter aspect, **5** was exposed to vacuum flash pyrolysis conditions (475° C, 10^{-3} mbar), since it was conceivable that **5** might undergo an interannular sigmatropic rearrangement to yield (η^{12}-[2_4](1,2,4,5)cyclophane)chromium (**6**) in analogy to the reported conversion of 1,2-bis([1,2 : 4,5]dicyclobutaphenyl)ethane to [2_5](1,2,3,4,5)cyclophane [12].



(5) (6)

However, the pyrolysis tube displayed a chromium mirror, indicative of metal–ligand cleavage and in the condensate of the pyrolysis experiment only free ligand and unrearranged **5** (MS, ^{1}H NMR; ESR of $\mathbf{5}^{\overset{+}{\cdot}}$) could be identified. Apparently, the molecular dimensions of boat-shaped [2_4](1,2,4,5)cyclophane (**7**) (4 pairs of ring carbon atoms at an interannular distance of 269 pm, 2 pairs at 295 pm [13]) would impose excessive compression strain on the hypothetical complex **6** favoring the reverse of the above reaction [14].

H/D exchange reactions. The sandwich complexes **4** and **5** contain different types of protons $H_{CH_2,endo}$, $H_{CH_2,exo}$, $H_{Ar,ortho}$, $H_{Ar,meta}$ which should differ in their kinetic CH acidity. In the case of (indan)(tricarbonyl)chromium which also holds benzylic protons in *exo*- and *endo*-positions attached to an η^6-arene, it has been demonstrated, that base-catalyzed hydrogen/deuterium exchange selectivity occurs in *exo*-position [16]. We therefore placed **4** in a 0.5 *M* solution of potassium t-butoxide in dimethyl-d_6 sulfoxide (DMSO-d_6) and checked the behavior by means of ^{1}H NMR. Whereas (indan)(tricarbonyl)chromium exchanges the *exo*-protons with a half-life of ca. 15 min at ambient temperature [17a], not surprisingly, exchange in the case of the bis(arene) complex proceeds at a much slower rate. In Fig. 1 ^{1}H NMR spectra taken after reaction times of 15 min (20° C) and 72 h (110° C) respectively are depicted [17b]. It clearly emerges, that the relative rates of hydrogen/deuterium exchange in **4** follow the sequence $H_{Ar,ortho} \gg H_{Ar,meta} > H_{CH_2,exo} > H_{CH_2,endo}$. This order complies with the regioselective metalation of free cyclobutabenzene by butylpotassium [19] and may be traced to the increased CH acidity of aryl positions adjacent to fused strained rings [20]. In the case of the complex **4**, however, H/D exchange occurs to a small degree in the cyclobutene ring as well. To the extent that preferential attack of t-butoxide is expected to take place at the more accessible position, the decrease in intensity of the signal at δ 2.76 ppm provides evidence for the assignment of this signal to $H_{CH_2,exo}$.

Nuclear magnetic resonance. ^{1}H NMR spectroscopic data are collected in Table 1, the corresponding ^{13}C NMR parameters are given in Table 2. For comparison we

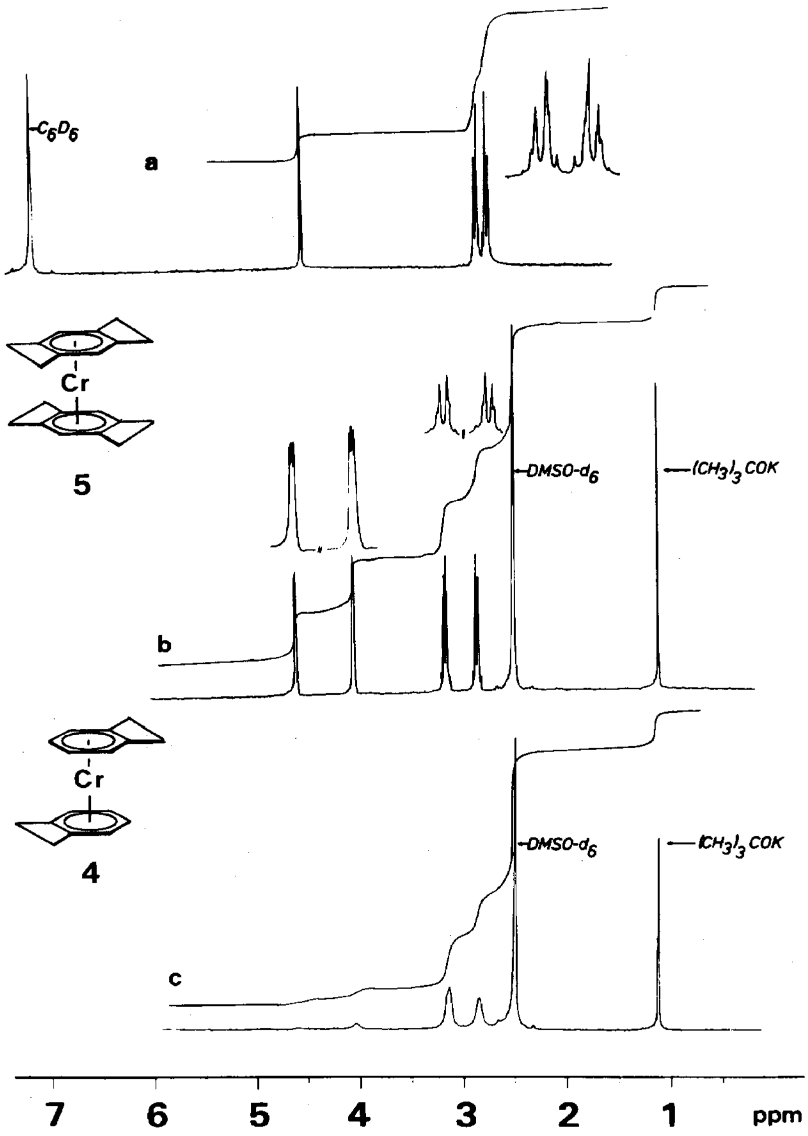
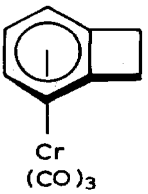


Fig. 1. ^1H NMR spectra (400 MHz) of the complexes **5** (**a**, in benzene-d_6) and **4** (**b**, **c**, in dimethylsulfoxide-d_6, 0.5 M t-BuOK) **b**: after 15 min at 20 °C, **c**: after 72 h at 110 °C.

have included NMR data for the related (arene)(tricarbonyl)chromium complexes **8–10** [21] and for bis(η^6-durene)chromium (**12**).



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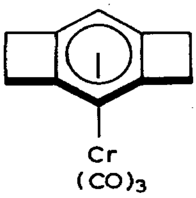

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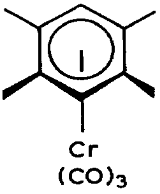

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TABLE 1

^{1}H NMR DATA FOR (η^6-ARENE)CHROMIUM COMPLEXES OF CYCLOBUTABENZENE, [1,2:4,5]DICYCLOBUTABENZENE AND DURENE [a]

Ligand complex	$\delta(^1H_{Ar})$ (position)	$\Delta\delta(^1H_{Ar})$ [b]	$\delta(^1H_{CH_2})$	$\Delta\delta(^1H_{CH_2})$ [b]
1 [c]	7.09(1,4)		2.92	
	6.92(2,3)			
4	4.47(1,4)	−2.62	2.76(*exo*)	−0.16(*exo*)
	3.96(2,3)	−2.96	2.98(*endo*)	+0.06(*endo*)
8	4.58(1,4)	−2.34	2.25(*exo*)	−0.67(*exo*)
	4.17(2,3)	−2.92	2.54(*endo*)	−0.38(*endo*)
2 [c]	6.78		3.12	
5	4.53	−2.25	2.70(*exo*)	−0.42(*exo*)
			2.82(*endo*)	−0.30(*endo*)
9	4.90	−1.88	2.26(*exo*)	−0.86(*exo*)
			2.48(*endo*)	−0.64(*endo*)
11 [c]	6.84		2.07	
12	3.89	−2.95	1.99	−0.08
10	4.65	−2.19	1.66	−0.41

[a] C_6D_6 solutions, measured relative to internal Me_4Si at 0.00 ppm. [b] Coordination shift. [c] Free ligand.

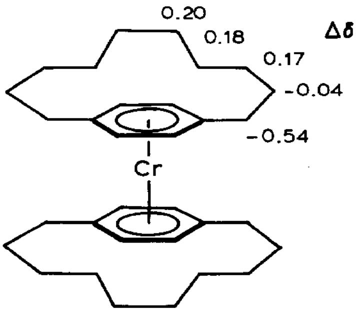
TABLE 2

^{13}C NMR DATA FOR (η^6-ARENE)CHROMIUM COMPLEXES OF CYCLOBUTABENZENE, [1,2:4,5]DICYCLOBUTABENZENE AND DURENE

Ligand complex	$\delta(^{13}C_{Ar})$ (position)	$\Delta\delta(^{13}C_{Ar})$	$\delta(^{13}C_{CH_2})$	$\Delta\delta(^{13}C_{CH_2})$	$\delta(^{13}C_{co})$	Coupling constants ^1J(C,H) (Hz)
1 [a]	145.90(1,2)		29.78(1′,2′)			137.0(1′,2′)
	121.89(3,6)					168.0(3,6)
	126.40(4,5)					159.0(4,5)
4	99.29(1,2)	−46.61	30.09(1′,2′)	+0.31		
	73.82(3,6)	−48.07				
	76.04(4,5)	−50.36				
8	115.86(1,2)	−30.04	29.60(1′,2′)	−0.18	233.86	140.0(1′,2′)
	89.53(3,6)	−32.36				172.0(3,6)
	91.25(4,5)	−35.15				172.0(4,5)
2 [a]	143.40(1,2,4,5)		29.30(1′,2′,4′,5′)			138.2(1′,2′,4′,5′)
	117.30(3,6)					160.0(3,6)
5	99.53(1,2,4,5)	−43.87	29.56(1′,2′,4′,5′)	+0.26		
	73.92(3,6)	−43.38				
9	113.55(1,2,4,5)	−29.85	28.98(1′,2′,4′,5′)	−0.32	234.49	137.9(1′,2′,4′,5′)
	87.14(3,6)	−30.16				165.4(3,6)
11 [a]	133.80(1,2,4,5)		19.20(1′,2′,4′,5′)			
	131.20(3,6)					
12	87.19(1,2,4,5)	−46.61	18.30(1′,2′,4′,5′)	−0.90		
	83.22(3,6)	−47.98				
10	106.30(1,2,4,5)	−27.50	17.88(1′,2′,4′,5′)	−0.42	235.03	161.0(3,6)
	97.90(3,6)	−33.30				138.0(1′,2′,4′,5′)

[a] Free ligand.

The crucial assignment of the *endo*- and *exo*-proton signals rests on studies of the rates of H/D exchange in **4** as described above, and on previous experience concerning related [3] (1,2)-ferrocenophane derivatives [24]. Whereas the magnitude of the coordination shift $\Delta\delta$ (H_{Ar}) for the arene protons of **4** is as expected, the shifts $\Delta\delta$ ($H_{CH_2,exo}$) and $\Delta\delta$ ($H_{CH_2,endo}$) in the four-membered ring differ conspicuously, and furnish information with regard to anisotropy of the shielding in the periphery of bis(benzene)chromium.



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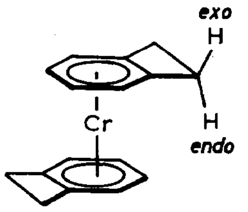

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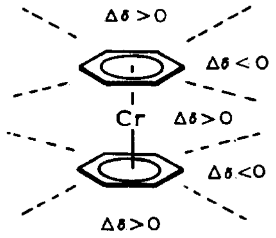

As we have shown recently for bis(η^6-[10]paracyclophane)chromium(0) (**13**) [25], the coordination shifts above the plane of an η-arene, remote from the central metal, change their magnitudes and signs as anticipated from coordination induced diminution of the aromatic ring-current. The ^{1}H NMR data for **4**, reported here, indicate that $\Delta\delta$ experiences an additional change in sign in the region between the two rings. Therefore the periphery of bis(η^6-benzene)chromium is to be divided into areas of positive and negative coordination shift $\Delta\delta$ such that tori in the circumference of the two η^6-arenes define zones of $\Delta\delta < 0$, whereas in the interannular (*endo*) region and in the *exo* regions on top of and below the sandwich structure, $\Delta\delta > 0$ applies. A more detailed description of the surfaces where $\Delta\delta$ changes sign must await the synthesis and ^{1}H NMR analysis of further complexes containing monitor protons at specified positions. The data available may, however, be discussed qualitatively at this stage.

The observation that the protons $H_{CH_2,exo}$ and $H_{CH_2,endo}$ display coordination shifts $\Delta\delta$ varying in sign and in magnitude may be traced to one or to a combination of the following effects: (a) Movements of the center of electron circulation from the ring plane to a position between the ring and the central metal atom; (b) the aggregate action of the two loops of electron circulation bearing different geometric relations to the proton under observation; and (c) unequal shielding caused by different dispositions of the *endo*- and *exo*-protons relative to the central metal. With regard to alternative (c) it had been suggested, that close proximity to the central metal would place the proton in a strongly shielding region [24], leading to $\Delta\delta < 0$ for $H_{CH_2,endo}$ contrary to observation. Obviously metal proton distances for the complexes considered here, are not yet in the realm where direct interactions with the central metal become significant. Since shielding of this kind should be strongly dependent upon atomic number, we have also prepared bis(cyclobuta-η^6-benzene)molybdenum (**14**), and bis(cyclobuta-η^6-benzene)tungsten (**15**). As shown in Fig. 2, the coordination shifts for the analogous Cr, Mo, and W

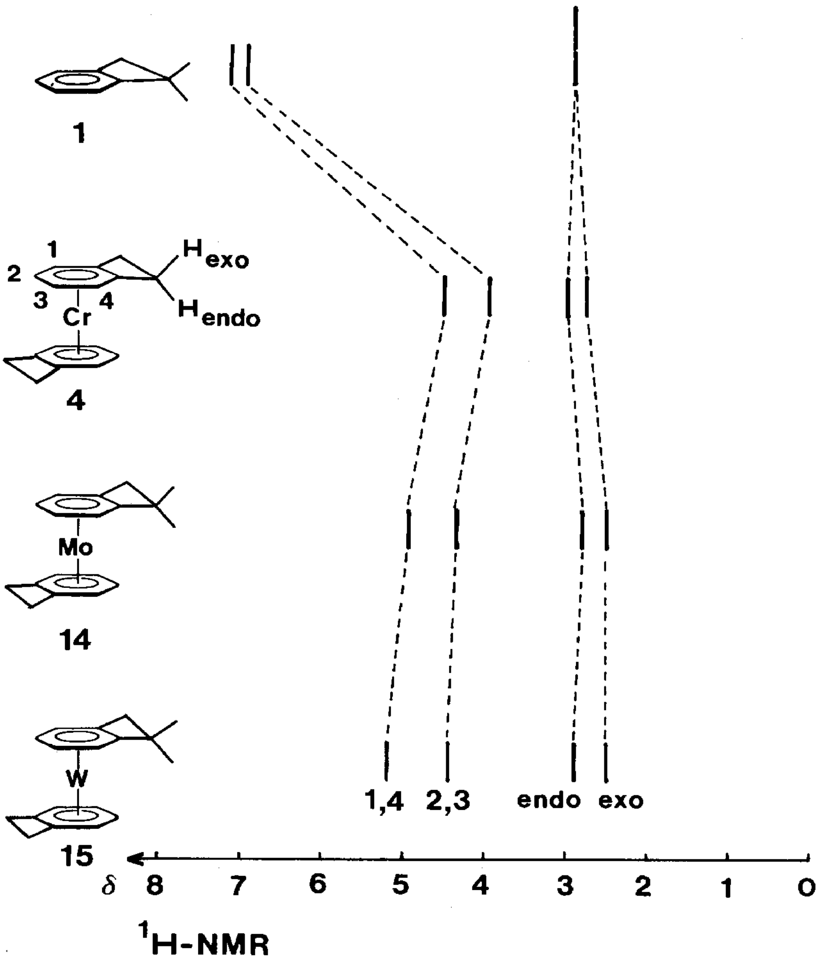

Fig. 2. ^{1}H NMR chemical shifts for the ligand **1** and for the complexes **4**, **14** and **15** in benzene-d_6 (+25°C).

complexes are very similar and direct metal proton interaction as a factor governing $\Delta\delta$ may be discounted.

The problems involved in alternative (a) have been discussed recently [26] for the related case of (arene)(tricarbonyl)chromium. Specifically, the appropriate choice for the center of anisotropy, required for an application of McConnels formula $\sigma = \chi(1 - \cos^2\theta)/(N \cdot 3R^3)$ [27] which relates the chemical shift increment σ to the molar diamagnetic anisotropy χ and a geometric term, is not immediately apparent. In the case of **4**, the differing coordination shifts $\Delta\delta(\mathrm{H}_{\mathrm{CH_2},exo})$ and $\Delta\delta(\mathrm{H}_{\mathrm{CH_2},endo})$ may however be explained qualitatively under the assumption that the center of anisotropy, which coincides with the ring center for the free arene, moves towards the metal upon coordination. The *endo*- and *exo*-protons of the fused four-membered ring then bear different geometric dispositions relative to that center and consequently experience different shielding (Fig. 3) [28]. During this translocation, the *exo*-protons effectively move into a region of decreased deshielding (closer to the zero shift surface) and the *endo*-protons into a region of increased deshielding

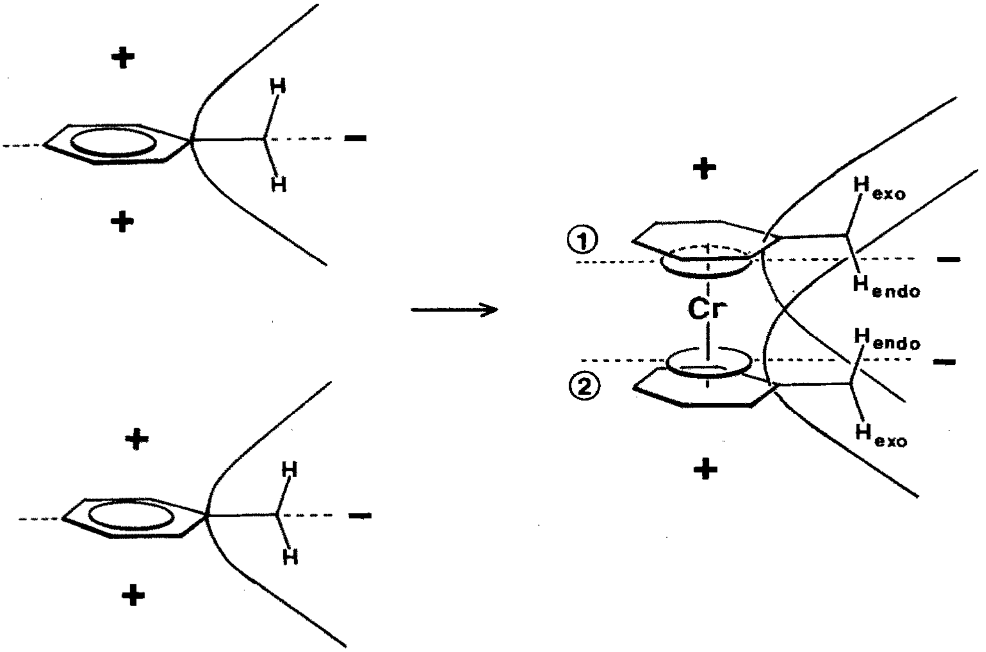

Fig. 3. Movements of the centers of diamagnetic anisotropy of two benzene rings upon formation of a bis(η^6-arene)metal complex. The curves represent cross sections through the conical surfaces separating shielding (+) from deshielding (−) regions which are associated with diamagnetic ring currents. The molecular dimensions are roughly to scale and the positions of H_{exo} and H_{endo} apply to bis(cyclobuta-η^6-benzene)chromium, (**4**).

(closer to the equatorial plane of the deshielding torus). This complies with the experimental finding $\Delta\delta(H_{CH_2,exo}) < 0$ and $\Delta\delta(H_{CH_2,endo}) > 0$. The same type of shielding difference for $H_{CH_2,exo}$ and $H_{CH_2,endo}$ on ring ① will be caused by addition of ring ②. This is, because $H^{①}{}_{CH_2,endo}$ will be located in the deshielding torus and $H^{①}{}_{CH_2,exo}$ in the shielding cone defining the magnetic anisotropy of the bond between the central metal and ring ② [29]. The considerations detailed above may not be directly applied to η^6-[1,2:4,5]dicyclobutabenzene (**2**) since in the case of complex **5** $\Delta\delta(H_{CH_2})$ is negative for the *exo*- as well as for the *endo*-protons. A comparison of the data in Table 1 shows, that the values of $\Delta\delta(H_{CH_2})$ for complexes of **2** differ from those pertaining to respective complexes of **1** by ca. −0.2 ppm. This applies to the sandwich complexes **4** and **5** as well as to the arene(tricarbonyl) complexes **8** and **9**. An explanatory hint is provided by the coordination shift $\Delta\delta(H_{CH_2},\mathbf{12})$ −0.08 ppm for the freely rotating methyl group of durene **11**. This value represents an average of the coordination shifts $\Delta\delta(H_{CH_2,exo},\mathbf{4})$ and $\Delta\delta(H_{CH_2,endo},\mathbf{4})$, suggesting that the complexes **12** and **4** belong to the same category. The anomalously large coordination shifts for complexes of the ligand **2**, on the other hand, must be related to severe distortion from hexagonal geometry [8] which benzene experiences upon fusion on opposite sides to cyclobutene rings. This has the effect of moving the protons H_{Ar} away from and the protons H_{CH_2} closer to the center of diamagnetic anisotropy in **2**. Therefore, the coordination shifts for complexes of **2** are probably not representative for bis(arene)chromium complexes in general.

Electron spin resonance. Hyperfine coupling in paramagnetic bis(arene)transition metal complexes has been studied extensively in the past employing NMR [30] as well as ESR [31] techniques. A question that has remained unresolved is the mechanism of spin transfer to the protons of methyl substituents in these complexes. The experimental finding that the proton hyperfine coupling constants $a(^1H_{Ar})$ and $a(^1H_{CH_2})$ for $(CH_3\text{-}\eta^6\text{-}C_6H_5)_2Cr^{+}$ (**14**) differ in magnitude by ca. 5/1 as well as in sign [30c] could not be accommodated with either one of the suggested mechanisms π_1, π_2 and σ [30b] for metal ligand spin transfer and the aggregate action of at least two of these mechanisms had to be assumed. Since it had been proposed, that negative spin density on the methyl protons in **14**$^{+}$ might arise from polarization of the filled MO e_{2g} by the singly occupied orbital a_{1g} (mainly Cr $3d_{z^2}$) followed by transfer of negative spin density from the ring carbon to the attached methyl group via hyperconjugation [30c] we felt that the weight of this contribution should be probed via comparison of the $a(^1H_{CH_2})$ values for the radical cations **4**$^{+}$, (η^{12}-[2.2]paracyclophane)chromium^{+} (**16**$^{+}$) and bis(1,4-dimethyl-η^6-benzene)chromium^{+} (**17**$^{+}$).

The extent of hyperconjugation is governed by the geometrical relation between the axis of a singly occupied π-orbital and the neighbouring C–H bond. Since this

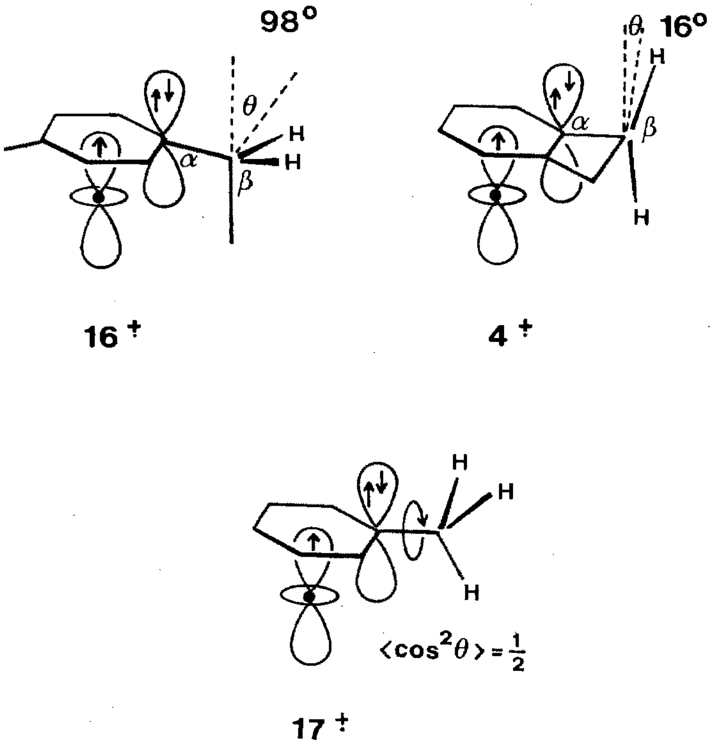

Fig. 4. Geometric relation between the C_β–H bond and the $C_\alpha(p_z)$ orbital for the rigid structures of **4**$^{+}$ and **16**$^{+}$ and for the freely rotating methyl group in **17**$^{+}$. θ is the dihedral angle between the plane containing the C_α–C_β–H bonds and that containing the C_α–C_β bond and the axis of the p_z orbital and C_α. The single occupancy of the Cr $3d_{z^2}$ orbital and the spin polarization of the filled orbital $C_\alpha(p_z)$, which contributes to the MO e_{2g}, are also shown.

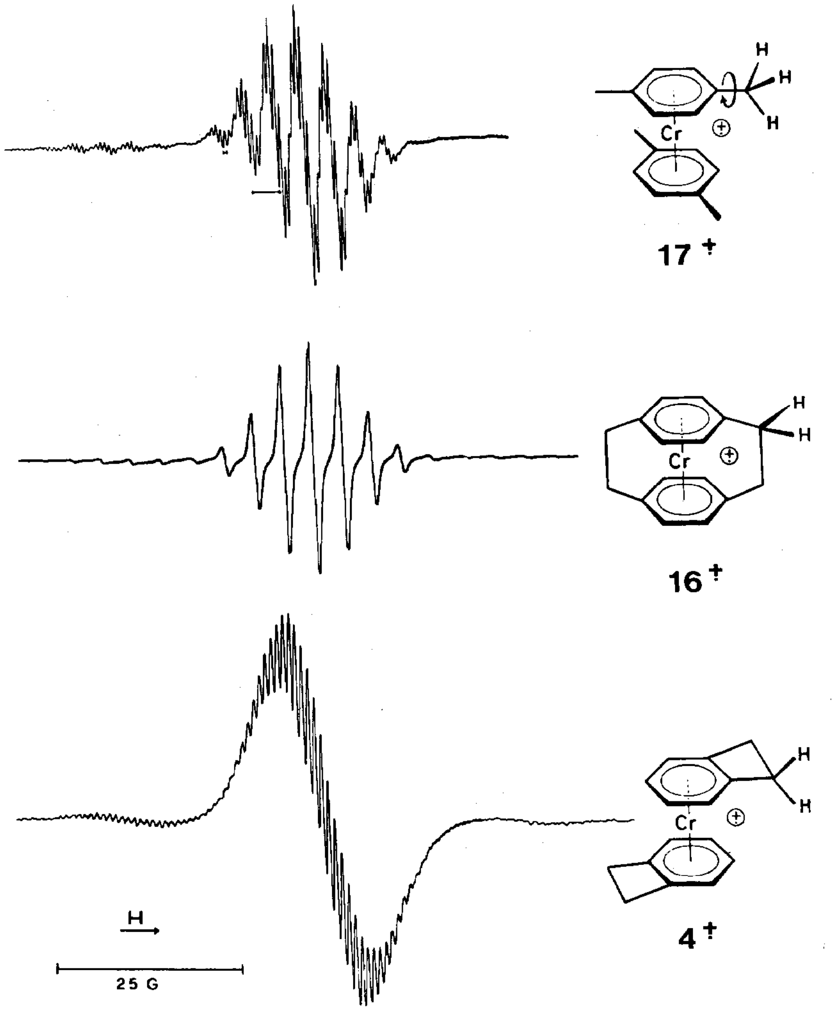

Fig. 5. ESR spectra of the radical cations **4**$^+$, **16**$^+$ and **17**$^+$ in fluid solution (methanol, −43°C). Mode of generation: air oxidation.

angle is well defined for the complexes of cyclobutabenzene and [2.2]paracyclophane (Fig. 4) the respective coupling constants $a(^1\mathrm{H}_{\mathrm{CH}_2},\mathbf{4}^+)$ and $a(^1\mathrm{H}_{\mathrm{CH}_2},\mathbf{16}^+)$ may be apportioned into a conformation-dependent and a conformation-independent part, thereby yielding information as to the importance of hyperconjugation in the spin transfer process. The division is based on the Heller–McConnell formula (eq. 1) [32], which relates the experimental hyperfine coupling constant $a(^1\mathrm{H}_\beta)$ to a

$$a\left(^1\mathrm{H}_\beta\right) = B_0 + \cos^2\theta B_2 \qquad (1)$$

conformation independent part B_0 and a conformation dependent part $\cos^2\theta B_2$ where θ is the angle of twist between the α-carbon $2p_z$ orbital and the plane containing the β-proton C–H bond.

In Fig. 5, isotropic ESR spectra of **4**$^+$ and **16**$^+$ are depicted together with the spectrum of $(1,4\text{-}\mathrm{Me}_2\text{-}\eta^6\text{-}\mathrm{C}_6\mathrm{H}_4)_2\mathrm{Cr}^+$ (**17**$^+$), a complex which contains freely rotating

TABLE 3

ESR PARAMETERS OF BIS(CYCLOBUTA-η^6-BENZENE)CHROMIUM$^{+\cdot}$ ($\mathbf{4}^{+\cdot}$), (η^{12}-[2.2]PARACYCLOPHANE)CHROMIUM$^{+\cdot}$ ($\mathbf{16}^{+\cdot}$) AND BIS(1,4-DIMETHYL-η^6-BENZENE)CHROMIUM$^{+\cdot}$ ($\mathbf{17}^{+\cdot}$)

	$\mathbf{4}^{+\cdot\, a}$	$\mathbf{16}^{+\cdot\, a,b}$	$\mathbf{17}^{+\cdot\, a,b}$
$a(^1H_{Ar})$ [c]	+3.30 (8H)	+4.05 (8H)	+3.70 (8H)
$a(^1H_{CH_2,CH_3})$ [c]	−0.83 (8H) [d]	−0.25 (8H)	−0.57 (12H)
$a(^{53}Cr)$ [c]	17.5	16.5	17.8
$\langle g \rangle$	1.9828	1.9905	1.9867

[a] Methanol, −50°C. [b] Ref. 31a. [c] Coupling constants in Gauss. [d] Within the resolution attained, the alternative analysis $a_1(4\ ^1H_{CH_2})$ −0.83 G, $a_2(^1H_{CH_2})$ −1.66 G cannot be excluded.

methyl groups [32]. g-Values and proton hyperfine coupling constants, which were confirmed by computer simulation, are collected in Table 3.

Whereas the negative sign of the coupling constants $a(^1H_{CH_3})$ for $\mathbf{17}^{+\cdot}$ has been established by means of the upfield direction of the ^{1}H NMR contact shift, the assignment of a negative sign for $a(^1H_{CH_2}, \mathbf{16}^{+\cdot})$ rests on linewidth arguments which have been presented in detail elsewhere [31a]. Insertion of the data for $\mathbf{4}^{+\cdot}$ and $\mathbf{16}^{+\cdot}$ into eq. 1, employing angles θ derived from molecular models, leads to the parameters B_0 −0.24 G and B_2 −0.65 G. It is pleasing to note, that these parameters, if applied to $\mathbf{17}^{+\cdot}$ ($\langle \cos^2\theta \rangle = \frac{1}{2}$ for a freely rotating methyl group) yield $a(^1H_{CH_3}, \mathbf{17}^{+\cdot})_{calc}$ −0.56 G in agreement with the experimental value of −0.57 G which was derived from the ^{1}H NMR contact shift [30c]. Therefore, it may be concluded that conformation independent and dependent pathways pertain in a ratio of ca. 1/3. This result lends support to the original proposal of hyperconjugative spin transfer which was put forward to explain the sign and magnitude of the coupling constant $a(^1H_{CH_3})$ for methyl substituted bis(η^6-arene)chromium$^{+\cdot}$ cations [30c].

It remains to rationalize the negative sign of B_0 by relating this parameter to a spin transfer process which is invariant to rotation about he C_{Ar}–C_β bond. For organic π-radicals, coupling constants $a(^1H_{Ar}) < 0$ and $a(^1H_{Me}) > 0$ of comparable magnitude are generally accepted as evidence for positive π spin density on the ring carbon atom bearing the proton or the methyl group, respectively. In the case of the bis(arene)chromium complexes $\mathbf{4}^{+\cdot}$, $\mathbf{16}^{+\cdot}$ and $\mathbf{17}^{+\cdot}$, however, the inverted signs $a(^1H_{Ar}) > 0$ and $a(^1H_{Me}) < 0$ hold and the magnitudes differ considerably ($|a(^1H_{CH_2})| \approx 0.2\,|a(^1H_{Ar})|$). First of all, it should be emphasized, that a coupling constant $a(^1H_{Ar})$ of 3–4 G cannot be traced to a spin polarization process of the McConnell type alone since even if one unpaired electron were to occupy a pure ligand π-orbital encompassing both η^6-arenes, $a(^1H_{Ar})$ of negative sign and smaller magnitude would be expected. Rather, direct delocalization $Cr(3d_{z^2}) \rightarrow$ arene(a_{1g}) is thought mainly to be responsible for the positive spin density on the protons H_{Ar} [31c] or on the β-carbon atoms C_{Me} in case of methyl derivatives. This positive spin density is augmented by spin polarization of filled MO's e_{2g} by singly occupied $Cr(3d_{z^2})$ to create negative spin density on the ring carbon atoms which in turn polarizes the C_{Ar}–H or C_{Ar}–C_{Me} bonds, respectively. Positive spin density on C_{Me}, caused by the two mechanisms described above, may then polarize the C_{Me}–H_{Me} bond leading to negative spin density on H_{Me}. This would account for the negative value of B_0 derived from experiment. The larger negative value of B_2, on the other hand, arises from transfer of negative spin density from C_{Ar} to H_{Me} by means of hyperconjugation.

Experimental

The air sensitivity of the products **4**, **5**, **14** and **15** requires manipulations to be carried out under an atmosphere of purified nitrogen. Spectra were recorded with the instruments Bruker WH 400 (^{1}H NMR, ^{13}C NMR) and Varian EE12 (ESR). The ligands cyclobutabenzene (**1**) [35] and [1,2 : 4,5]dicyclobutabenzene (**2**) [36] were prepared as described in the literature.

*1. Bis(cyclobuta-η⁶-benzene)chromium(0) (**4**)*

Chromium vapor (0.5 g, 9.6 mmol) and cyclobutabenzene (25 g, 96 mmol) were cocondensed at 10^{-3} mbar during 2 h in a 4 l static reactor which was immersed in liquid nitrogen. Chromium was evaporated from a resistively heated conical coil of tungsten wire and the vapor of the ligand was introduced from an external reservoir. The dark brown cocodensate was allowed to reach room temperature and was filtered over a 4 cm layer of silica gel in order to remove unreacted chromium slurry. After removal of excessive ligand in vacuo, the reddish-brown raw material was purified by means of sublimation (80 °C, 10^{-4} mbar). Yield: 300 mg (1.2 mmol), 12% based on chromium evaporated. M.p. 122 °C (Found: C, 72.18; H, 6.24. $C_{16}H_{16}Cr$ (260.40) calcd.: C, 73.26; H. 6.92%). MS (EI, 70 eV) *m/e* (rel. Int.): 261(10.7), 260(39.0), 157(12.6), 156(65.0), 104(66.0), 103(29.1), 78(22.4), 77(12.6), 53(11.3), 52(100).

*2. Bis([1,2 : 4,5]dicyclobuta-η⁶-benzene)chromium(0) (**5**)*

Chromium (0.5 g, 9.6 mmol) and [1,2 : 4,5]-dicyclobutabenzene (3 g, 2.3 mmol) vaporized at 10^{-3} mbar from a resistively heated tungsten coil and a small electrically heated furnace respectively, both within the interior of the reactor, were cocondensed at the cooled surface (−196 °C). The matrix initially took a deep red color which turned to reddish brown at later stages. After warming up to room temperature, the cocondensate was collected in 100 ml of toluene, filtered over silicagel and taken to dryness. From the dark red residue, excess ligand was removed at 80 °C/10^{-4} mbar. Pure **5** may be obtained via sublimation at 130 °C/10^{-4} mbar. Yield: 60 mg (0.2 mmol), 2% referred to chromium evaporated. M.p. 138 °C (Found: C, 75.60; H, 6.54. $C_{20}H_{20}Cr$ (312.46) calcd.: C, 76.88; H, 6.41%). MS (EI, 70 eV) *m/e* (rel. Int.): 312(11.14), 281(18.37), 182(11.12), 131(10.81), 130(100.0), 52(18.60).

*3. ([1,2 : 4,5]Dicyclobuta-η⁶-benzene)(tricarbonyl)chromium(0) (**9**)*

[1,2 : 4,5]Dicyclobutabenzene (1 g, 7.7 mmol) and (trisacetonitrile)(tricarbonyl)chromium (1.98 g, 7.7 mmol) were treated in boiling di-n-butyl ether during 12 h. From the filtered yellow solution upon cooling to −20 °C, **9** was obtained as yellow needles. The material may be recrystallized from low boiling petrol ether. Yield: 1.6 g (6 mmol), 78%. M.p. 125 °C (Found: C, 58.46; H, 4.03. $C_{13}H_{10}CrO_3$ (266.3) calcd.: C, 58.64; H, 3.76%). MS (EI, 70 eV) *m/e* (rel. Int.): 266(18.72), 210(8.43), 182(97.3), 154(3.61), 52(100).

4. *Bis(cyclobuta-η^6-benzene)molybdenum(0)* (**14**)

14 was prepared via cocondensation whereby molybdenum was vaporized by means of electron beam heating from a water cooled copper block which was held at positive potential [37]. The 10 l reactor was of the stationary type, it was built from stainless steel and the ligand was introduced from an external reservoir. In a typical run, 1.3 g (13.5 mmol) of molybdenum was evaporated (electron beam: 3.5 kV, 0.4 A; tungsten emitter filament: 12 V, 48A) during 2 h at an internal pressure of $< 10^{-5}$ mbar and cocondensed with 4 g (38.5 mmol) of cyclobutabenzene at the reactor surface which was cooled to -196 °C. After switching off the power supplies, the reactor was filled with argon and the reaction mixture was filtered through a 3 cm layer of silicagel. From the green filtrate, excess ligand was removed in vacuo and **14** was obtained as a dark green material. Yield: 110 mg (0.36 mmol), 2.7% referred to molybdenum evaporated. Sublimation (80 °C/10^{-3} mbar) or recrystallization from low boiling petrol ether affords green needles of **14** which decompose at 160 °C before melting. (Found: C, 63.45; H, 5.33. $C_{16}H_{16}Mo$ (304.2) calcd.: C, 63.17; H, 5.30%). MS (EI, 70 eV) *m/e* (^{96}Mo, rel. Int.): 306(100), 200(24.5), 173(11.7), 153(28.6), 138(12.2) 104(96.9), 96.0(18.8). ^{13}C NMR (100.6 MHz, C_6D_6): δ 30.45, 72.61, 76.10, 100.21.

5. *Bis(cyclobuta-η^6-benzene)tungsten(0)* (**15**)

This compound was synthesized in an analogous way employing an electron beam of higher energy (4.8 kV). Although evaporation of tungsten was satisfactory (ca. 1.2 g W/h) only very small amounts of reddish-brown **15** (ca. 5 mg per run) could be isolated. They were used to record the ^{1} NMR spectra (Data: Fig. 2).

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References

1 Ch. Elschenbroich, J. Kroker, W. Massa, and M. Wünsch, Angew. Chem., 98 (1986) 562; Angew. Chem. Int. Ed. Engl., 25 (1986) 571.
2 W.H. Mills and I.G. Nixon, J. Chem. Soc., (1930) 2510.
3 R.M. Mitchell, P.D. Slowey, T. Kamada, R.V. Williams, and P.J. Garratt, J. Am. Chem. Soc., 106 (1984) 2431.
4 P.C. Hiberty, G. Ohanessian, and F. Delbecq, J. Am. Chem. Soc., 107 (1985) 3095.
5 I. Klundt, Chem. Rev., 70 (1970) 471.
6 R.P. Thummel, Acc. Chem. Res., 13 (1980) 70.
7 B. Halton, Chem. Rev., 73 (1973) 113.
8 J.L. Lawrence and S.G.G. MacDonald, Acta Cryst. B, 25 (1969) 978.
9 Note, that various η^6-cycloheptatriene complexes have been prepared and characterized structurally, e.g. $(\eta^6\text{-}C_7H_8)Mo(CO)_3$ J.D. Dunitz and P. Pauling, Helv. Chim. Acta, 43 (1960) 2188.
10 (a) E.O. Fischer and J. Seeholzer, Z. Anorg. Allg. Chem., 312 (1961) 244. (b) E.O. Fischer, G. Huttner, and Ch. Elschenbroich, J. Organomet. Chem., 3 (1965) 230.
11 W. Nutakul, R.P. Thummel, and A.D. Taggart, J. Am. Chem. Soc., 101 (1979) 770.
12 P.F.T. Schirch and V. Boekelheide, J. Am. Chem. Soc., 103 (1981) 6873.
13 A.W. Hanson, Acta Cryst. B, 33 (1977) 2003.

14 For comparison: $(\eta^6\text{-}C_6H_6)_2Cr$, interannular distance 322 pm, E. Keulen and F. Jellinek, J. Organomet. Chem., 5 (1966) 490. However, $[2_2]$(1,4)cyclophane (four pairs of ring carbon atoms at 309 pm, two pairs at 278 pm interannular distance [15]) forms the very stable complex $(\eta^{12}\text{-}[2_2]$(1,4)cyclophane)chromium, albeit in minute yield, Ch. Elschenbroich, R. Möckel and U. Zenneck, Angew. Chem. Int. Ed. Engl., 17 (1978) 870.

15 H. Hope, J. Bernstein and K.N. Trueblood, Acta Cryst. B, 28 (1972) 1733.

16 W.S. Trahanowsky and R.C. Card, J. Am. Chem. Soc., 94 (1972) 2897.

17 (a) We use (indan)(tricarbonyl)chromium for comparison because in this case stereoselective H/D exchange at the *exo*-position has been unequivocally established by means of exchange experiments on the respective 1-methylindan complexes of known stereochemistry. In response to the suggestion of a reviewer, we have also studied H/D exchange for (cyclobutabenzene)(tricarbonyl)chromium (**8**) and observed a decrease in exchange rate in the sequence *exo* > *ortho* > *meta* > *endo* (assignment of the *exo*- and *endo*-proton signals in analogy to that worked out for (indan)(tricarbonyl)chromium). (b) Line-broadening effects stemming from $Ar_2Cr^{0/+}$ electron exchange [18] can be excluded since the ^1H NMR sample was shown by ESR to be free of radical cations.

18 Ch. Elschenbroich and U. Zenneck, J. Organomet. Chem., 160 (1978) 125.

19 R.A. Finnegan, J. Org. Chem., 30 (1965) 1333.

20 A. Streitwieser, Jr., G.R. Ziegler, P.C. Mowery, A. Lewis, and R.G. Lawler, J. Am. Chem. Soc., 90 (1968) 1358.

21 The preparation of **8** [22] and **10** [23] and partial NMR data have been reported.

22 D.E.F. Gracey, W.R. Jackson, W.B. Jennings, S.C. Rennison, R. Spratt, J. Chem. Soc. B, (1969) 1210.

23 (a) J.T. Price and T.S. Sorensen, Can. J. Chem., 46 (1968) 515. (b) B.E. Mann, J. Chem. Soc., Chem. Commun., (1971) 976.

24 T.D. Turbitt and W.E. Watts, Tetrahedron, 28 (1972) 1227.

25 Ch. Elschenbroich, B. Spangenberg, and H. Mellinghof, Chem.Ber., 117 (1984) 3165.

26 M.J. McGlinchey, R.C. Burns, R. Hofer, S. Top and G. Jaouen, Organometallics, 5 (1986) 104.

27 H.M. McConnell, J. Chem. Phys., 27 (1957) 226

28 In a crude way, the change accompanying η^6-coordination may be pictured as a transformation of the contour diagram describing the shielding in the periphery of an arene into a pattern typical for an element–element multiple bond. An analogy between the metal ring bond in sandwich complexes and a carbon–carbon triple bond has drawn previously (P.C. Lauterbur and R.B. King, J. Am. Chem. Soc., 87 (1965) 3266). The chemical shift difference for proximal and distal methyl groups in $Mo_2(NMe_2)_6$ is also a case in point (M.M. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive, and B.R. Stults, J. Am. Chem. Soc., 98 (1976) 4469).

29 Additivity of contributions from both rings may also serve to explain the sizeable coordination shifts ($\Delta\delta > 0$) for protons in a plane midway between two η^6-arenes (Ch. Elschenbroich, J. Schneider, H. Prinzbach, and W.D. Fessner, Organometallics, in press.

30 (a) For leading references: M.F. Retting in G.N. LaMar, W. DeW. Horrocks, Jr., and R.H. Holm, (Eds), NMR of Paramagnetic Molecules, Academic Press, New York, 1973, p. 217–242; (b) R. Prins, J. Chem. Phys., 50 (1969) 4804; (c) S.E. Anderson, Jr. and R.S. Drago, J. Am. Chem. Soc., 92 (1970) 4244; (d) S.E. Anderson, Jr. and R.S. Drago, Inorg. Chem., 11 (1972) 1564; (e) Ch. Elschenbroich and F. Gerson, J. Organomet. Chem., 49 (1973) 445. (f) A.d. Krivospitskii and G.K. Chirkin, Zh. Strukt. Khim., 15 (1974) 25.

31 (a) For leading references: Ch. Elschenbroich, R. Möckel, U. Zenneck, and D.W. Clack, Ber. Bunsenges. Phys. Chem., 83 (1979) 1008; (b) K.D. Warren, Struct. Bond., 27 (1976) 45. (c) R. Prins and F.J. Reinders, Chem. Phys. Lett., 3 (1969) 45; (d) M.F. Rettig, C.D. Stout, A. Klug, P. Farnham, J. Am. Chem. Soc., 92 (1970) 5100. (e) G. Henrici-Olivé, S. Olivé, Z. Phys. Chem. NF, 56 (1967) 223.

32 (a) C. Heller and H.M. McConnell, J. Chem. Phys., 32 (1960) 1575; (b) E.W. Stone and A.H. Maki, J. Chem. Phys., 37 (1962) 1326; (c) J.R. Morton, Chem. Rev., 64 (1964) 453; (d) D. Lazdins and M. Karplus, J. Chem. Phys., 44 (1966) 1600.

33 No ^1H hyperfine structure was resolved in the spectrum of 5^+. A simulation of the ESR spectrum of 5^+, employing the coupling constants obtained for 4^+ but changing the numbers of equivalent protons also lead to a single, broad trace.

34 In this context, the bathochromic shift and the greatly enhanced extinction in the UV spectrum of **2** in contrast to **1** should be mentioned (C. Santiago, R.W. Gandour, K.N. Houk, W. Nutakul, W.E. Cravey, and R.P. Thummel, J. Am. Chem. Soc., 100 (1978) 3730).

35 M.P. Cava and D.R. Napier, J. Am. Chem. Soc., 80 (1958) 2255.

36 (a) M.P. Cava, A.A. Deana, and K. Muth, J. Am. Chem. Soc., 82 (1960) 2524; (b) R.P. Thummel and W. Nutakul, J. Org. Chem., 42 (1977) 300.

37 F.G.N. Cloke and M.L.H. Green, J. Chem. Soc., Dalton Trans., (1981) 1938.