# (5,12:6,11-Dimethano-5,5a,6,11,11a,12-hexahydro-$\eta^{12}$-tetracene)chromium—A Model Compound To Study $^1$H NMR Coordination Shift Anisotropy in the Periphery of Bis($\eta^6$-arene)metal Complexes[1]

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The title compound **4**, a sandwich complex of a bridged [3.3]orthocyclophane derivative with an internally coordinated chromium atom and sterically fixed protons in the periphery, was synthesized by means of metal atom ligand vapor cocondensation. Analysis of the $^1$H NMR spectrum of **4** provides data describing the spatial variation of the coordination shift $\Delta\delta$. In conjunction with proton chemical shift data for bis($\eta^6$-[10]paracyclophane)chromium and bis(cyclobuta-$\eta^6$-benzene)chromium, a graph is drawn, which depicts radial and angular dependence of $\Delta\delta$. Whereas positive coordination shifts are observed for the regions above and between the rings, tori in the circumference of the $\eta^6$-arenes define regions of negative coordination shift. These features are in accord with coordination-induced attenuation of diamagnetic ring currents in the aromatic ligands. An extended version of the graph presented in this paper will be of heuristic value in deducing configurational and conformational information in the field of sandwich complex chemistry. The ESR spectra of the radical cation **4**$^{•+}$ display pronounced inequivalence of the ring proton hyperfine coupling constants (fluid solution) but no discernible splitting of the component $g_\perp$ (rigid solution). This denotes that tilting of the bis($\eta^6$-arene)metal (d$^5$) sandwich structure strongly affects metal ligand spin delocalization while the overall electronic structure of the complex is perturbed only insignificantly.

## Introduction

Irrespective of details in the physical explanation, the diamagnetic anisotropy, and the attendant spatial variation of shielding on the vicinity of benzene rings, commonly regarded as a consequence of induced ring currents,[2] has been transformed into a widely applied $^1$H NMR spectroscopic tool for structure elucidation.[3] On the basis of Mulay's determination of the magnetic anisotropy of ferrocene,[4] it was recognized that a division of the periphery of metallocenes into shielding and deshielding regions, analogous to the Waugh–Fessenden–Johnson–Bovey graphs[2] for benzene, should be possible. Since the calculation of secondary magnetic fields in the vicinity of a bis(arene) transition-metal species would be exceedingly difficult, we prefer to empirical approach of synthesizing model complexes containing protons at well-defined positions in their periphery. The chemical shifts of these protons may then serve to map the diamagnetic anisotropy of bis($\eta^6$-benzene)chromium (**1**) which will be useful in future applications of $^1$H NMR to structural problems

concerning this class of compounds.[6c] Furthermore, from a spatial dependence of the sign of the coordination shift [$\Delta\delta = \delta$(complex) $- \delta$(free ligand)] the importance of "ring-current quenching" as a contributing factor may be assessed.[6] With regard to the latter point, our observation for bis(1,4-decano-$\eta^6$-benzene)chromium (**2**),[7] $\Delta\delta$[H⑦] < 0 (−0.54), $\Delta\delta$[H⑧] ≈ 0 (−0.04), and $\Delta\delta$[H⑨, ⑩, ⑪] > 0 (0.17, 0.18, 0.20), would be in line with a disruption of ring current accompanying complex formation. The monitor protons in **2** mainly cover the axial region above and below the sandwich complex. In order to obtain complementary information concerning the equatorial periphery of the parent complex **1**, we have now prepared the title compound **4**. In the context of the present investigation, the ligand **3**,[8] which may be regarded as a triply bridged [3.3]orthocyclophane, has a number of attractive features: the average inter-arene distance (341 pm) approaches the respective distance in **1** (322 pm), the alkane framework is only moderately strained, there are no overcrowded protons, and unambiguous $^1$H NMR assignment is possible. Furthermore, in the case of **4** the coordination shift may be studied in pure form since **3** and **4** differ by a neutral metal atom only,[9] and the introduction of additional ligands like CO which would influence $^1$H NMR shifts via inductive effects as encountered with the (ar-

(1) Metal π-Complexes of Benzene Derivatives. 26. Part 25: Elschenbroich, Ch.; Gondrum, R.; Massa, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 967.

(2) (a) Haigh, C. W.; Mallion, R. B. *Prog. NMR Spectrosc.* **1980**, *13*, 303. (b) Barfield, M.; Grant, D. M.; Ikenberry, D. *J. Am. Chem. Soc.* **1975**, *97*, 6956. (c) Agarwal, A.; Barnes, J. A.; Fletcher, J. L.; McGlinchey, M. J.; Sayer, B. G. *Can. J. Chem.* **1977**, *55*, 2575. (d) Dailey, B. P. *J. Chem. Phys.* **1964**, *41*, 2304. (e) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(3) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Top. Curr. Chem.* **1971**, *16*, 103.

(4) (a) Mulay, L. N.; Fox, M. E., Sr. *J. Am. Chem. Soc.* **1962**, *84*, 1308; *J. Chem. Phys.* **1963**, *38*, 760. Mulay, L. N.; Withstandley, V. *J. Chem. Phys.* **1965**, *43*, 4522. (b) Recent work: Ritchie, G. L. D.; Cooper, M. K.; Calvert, R. L.; Dennis, G. R.; Phillipps, L.; Vrbancich, J. *J. Am. Chem. Soc.* **1983**, *105*, 5215.

(5) (a) Turbitt, T. D.; Watts, W. E. *Tetrahedron* **1972**, *28*, 1227. (b) Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1971**, *27*, 4343. (c) In the case of ferrocene, diamagnetic anisotropy of the sandwich unit has been established via $^1$H NMR of mesityl substitutents which introduce endo and exo methyl groups (Fuchs, B.; Fröhlich, R.; Musso, H. *Chem. Ber.* **1985**, *118*, 1968).

(6) For a discussion of the sources of the coordination shift see: Graves, V.; Lagowski, J. J. *J. Organomet. Chem.* **1976**, *120*, 396 and references therein.

(7) Elschenbroich, Ch.; Spangenberg, B.; Mellinghoff, H. *Chem. Ber.* **1984**, *117*, 3165.

(8) Prinzbach, H.; Sedelmeier, G.; Krüger, C.; Goddard, R.; Martin, H. D.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 271. An efficient five-step route to (1α, 2α, 3α, 6α, 7α, 8α)-4,5:9,10-Dibenzotetracyclo-[6.2.1.1$^{3,6}$.0$^{2,7}$]dodeca-4,9-diene (**3**) has been developed: Fessner, W.-D. Dissertation, University of Freiburg, 1985.

(9) $\Delta\delta$($^1$H$_{Ar}$) for 18-valence-electron bis(arene)metal complexes strongly depends on central metal atom formal charge. For equal charge there is also a dependence on the nature of the central metal atom. (a) Elschenbroich, Ch.; Gerson, F. *J. Am. Chem. Soc.* **1975**, *97*, 3556. (b) Elschenbroich, Ch.; Möckel, R.; Massa, W.; Birkhahn, M.; Zenneck, U. *Chem. Ber.* **1982**, *115*, 334.

**2**

**3 (ligand)**
**4 (complex)**

**5**
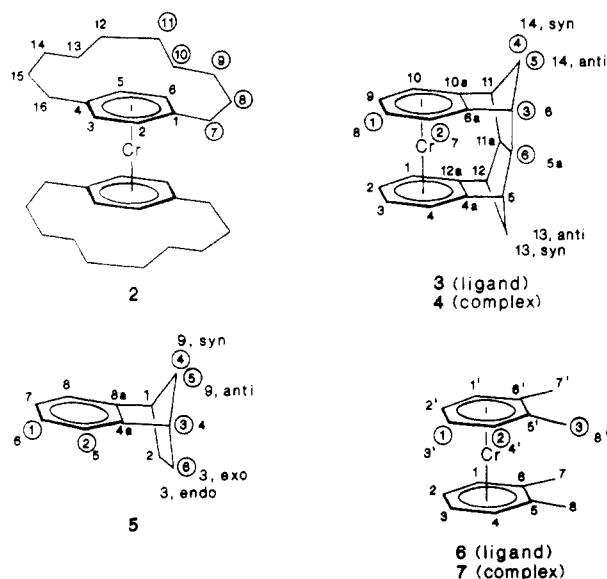
**6 (ligand)**
**7 (complex)**

ene)metal carbonyls[10] or bis(arene)metal cations[11] is avoided.

## Results and Discussion

Cocondensation of the vapor of ligand **3** with chromium atoms leads to a brown matrix from which the title compound **4** is obtained via fractional sublimation. The tendency of the complex **4** to cosublime with its ligand **3** renders this separation rather difficult. Attempts to isolate the bis exo complex $(\eta^6\text{-}3)_2\text{Cr}$, which is also formed according to field desorption mass spectroscopic evidence, were frustrated by its low solubility and the fact that, at the temperature necessary for sublimation of $(\eta^6\text{-}3)_2\text{Cr}$, extensive decomposition occurs. Air oxidation of **4** yields



**3**

**4**

$(\eta^{12}\text{-}3)\text{Cr}$

$(\eta^6\text{-}3)_2\text{Cr}$
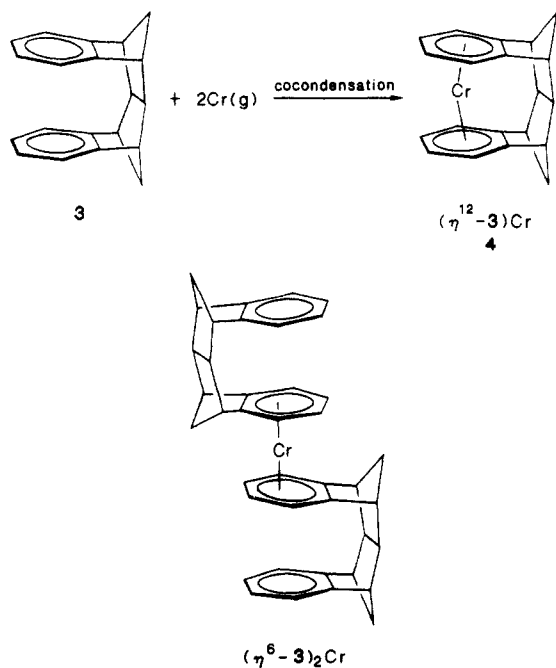
(10) (a) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Öfele, K. *J. Organomet. Chem.* **1967**, *7*, 289. (b) Khankarova, V. S.; Gubin, S. P.; Kvasov, B. A. *J. Organomet. Chem.* **1970**, *23*, 509. (c) Cristiani, F.; DeFelilipo, D.; Deplano, P.; Devillanova, F.; Diaz, A.; Trogu, E. F.; Verani, G. *Inorg. Chim. Acta* **1975**, *12*, 119. (d) Ohno, H.; Horita, H.; Otsubo, T.; Salzata, Y.; Misumi, S. *Tetrahedron Lett.* **1977**, 265. (e) Mourad, A. F.; Hopf, H. *Tetrahedron Lett.* **1979**, 1209. (f) Langer, E.; Lehner, H. *J. Organomet. Chem.* **1979**, *173*, 47.

(11) Laganis, E. D.; Voegeli, R. H.; Swann, R. T.; Finke, R. G.; Hopf, H.; Boekelheide, V. *Organometallics* **1982**, *11*, 1415.
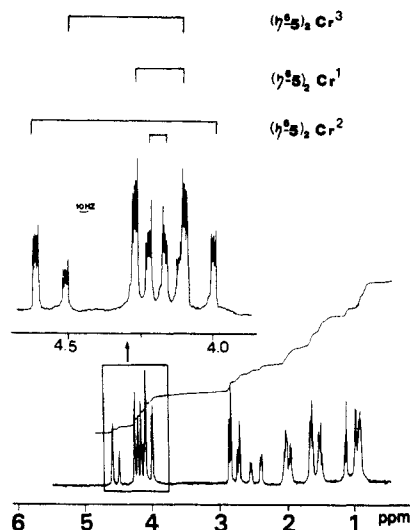


**Figure 1.** $^1$H NMR spectrum (400 MHz) of the mixture of isomeric complexes $(\eta^6\text{-}5)_2\text{Cr}^{1-3}$ in $C_6D_6$ at room temperature. The expanded part ($\eta^6$-arene region, insert) was recorded under homonuclear decoupling of H-1,4. For assignment see text.

the radical cation **4**$^{\bullet+}$; the half-wave potential $E_{1/2}(4^{0,1+})$, as determined by cyclic voltammetry, amounts to $-0.73$ V (vs. SCE, measured in dimethoxyethane). The identity of this value to the half-wave potential for the couple $7^{0,1+}$ ($E_{1/2} = -0.73$ V) suggests that the ring-tilt distortion affects the electronic structure of **4** only insignificantly.

For comparison with **4** and for a test on whether face selective complexation would occur, chromium atoms were also cocondensed with benzonorbornene **5**. According to $^1$H NMR of the product, however, the three conceivable isomers $(\eta^6\text{-}5)_2\text{Cr}$ are formed in comparable quantities.



**5**

$(\eta^6\text{-}5)_2\text{Cr}^1$

$(\eta^6\text{-}5)_2\text{Cr}^2$

$(\eta^6\text{-}5)_2\text{Cr}^3$
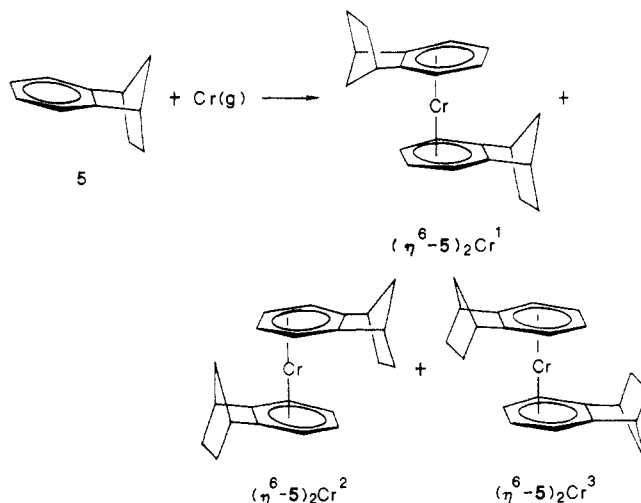
Although separation of the mixture of isomers did not yet meet with success, an estimate of the product ratio, based on the $^1$H NMR spectrum, will be given here. As shown in Figure 1, in the region $5 > \delta > 4$ eight multiplets are discernible which may be combined pairwise to yield four AA'XX' systems. Since in the $\eta^6$-arene proton region the unsymmetrical isomer $(5)_2\text{Cr}^2$ must display two different AA'XX' systems, albeit of equal intensity, the pairs $\delta$ 4.02, 4.60 and $\delta$ 4.18, 4.23 are assigned to $(5)_2\text{Cr}^2$. The pair $\delta$ 4.13, 4.50 is assigned to isomer $(5)_2\text{Cr}^3$ as suggested by the similarity with the respective data $\delta$ 4.12, 4.43 for **4** which contains two fused norbornene moieties bearing the same stereochemical relation to the sandwich unit as in $(5)_2\text{Cr}^3$. The most intense couple $\delta$ 4.11, 4.28 must then be associated with isomer $(5)_2\text{Cr}^1$. This analysis leads to the ratio

**Table I. Proton Chemical Shifts (δ) for Corresponding Positions[a] ①–⑥ in the Free Arenes 3, 5, and 6 and the Bis(η⁶-arene) Chromium Complexes 4[b] and 7[c,d]**

| | arene protons | | | | | | side chain protons | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ① | | ② | | ③ | | ④ | | ⑤ | | ⑥ | |
| | δ | Δδ | δ | Δδ | δ | Δδ | δ | Δδ | δ | Δδ | δ | Δδ |
| 5[e] | 7.04 (6,7) | | 7.09 (5,8) | | 3.12 (1,4) | | 1.65 (9syn) | | 1.23 (9anti) | | 1.07 (3 endo) 1.62 (3 exo) | |
| 6 | 7.02 (2,3,2',3') | | 7.02 (1,4,1',4') | | 2.03 (7,8,7',8') | | | | | | | |
| 3 | 6.68 (2,3,8,9) | | 6.59 (1,4,7,10) | | 2.98 (6,11,5,12) | | 1.76 (13syn,14syn) | | 1.74 (13anti, 14anti) | | 2.82 (5a,11a) | |
| 7 | 4.04 (2,3,2',3') | −2.98 | 4.13 (1,4,1',4') | −2.89 | 1.98 (7,8,7',8') | −0.05 | | | | | | |
| 4 | 4.12 (2,3,8,9) | −2.56 | 4.43 (1,4,7,10) | −2.16 | 2.40 (6,11,5,12) | −0.58 | 2.14 (13syn,14syn) | +0.38 | 1.86 (13anti, 14anti) | +0.12 | 3.19 (5a,11a) | +0.37 |

[a] Numbers in circles indicate corresponding positions of protons which bear different labels in the IUPAC numbering scheme for the respective ligands. [b] ¹H NMR of (η⁶-5)₂Cr: see text. [c] 400-MHz spectra were run at ambient temperature; solvent C₆D₆. [d] Selected coupling constants ($J_{H,H}$, Hz): ligand 3, $J_{1,2} = J_{3,4} = 7.45$, $J_{1,3} = J_{2,4} = 1.31$, $J_{2,3} = 7.0$, $J_{1,4} = 0.6$; complex 4, $J_{1,2} = J_{3,4} = 5.25$, $J_{1,3} = J_{2,4} = 0.5$, $J_{2,3} = 4.80$, $J_{1,4} = 0.0$, $J_{14syn,14anti} = 8.0$. [e] See ref 24 for assignment.

of isomers $(5)_2Cr^1 : (5)_2Cr^2 : (5)_2Cr^3 = 5.0 : 4.0 : 1.0$ which is reasonable in view of the increase in steric hindrance to complexation along this sequence and taking into account the statistical factor which favors the formation of $(5)_2Cr^2$.

The low degree of stereoselectivity in this metal ligand cocondensation contrasts with the wet chemical synthesis of an analogous ferrocene derivative wherin the least hindered isomer, containing two endo methylene groups, was obtained exclusively:[12]
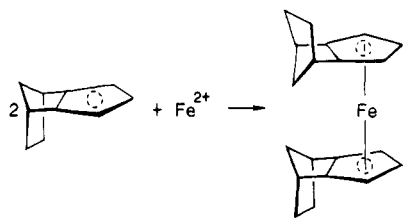
**Nuclear Magnetic Resonance.** In Figure 2, the ¹H NMR spectra of ligand 3 and complex 4 are depicted; the spectral parameters are collected in Table I. Insertion of a chromium atom into the inter-arene region in 3 causes negative (H①–H③) as well as positive (H④–H⑥) ¹H NMR coordination shifts Δδ. Although the largest upfield shifts are encountered for the arene protons H① and H②, they are considerably smaller for 4 as compared to sandwich complexes built from two independent aromatic ligands, the difference amounting to 0.6–0.7 ppm. This is readily explained by the fact that the effect of stacking two arenes[15] which contributes to the total shift Δδ does not enter into Δδ for 4.[16] Therefore, in order to interpret the
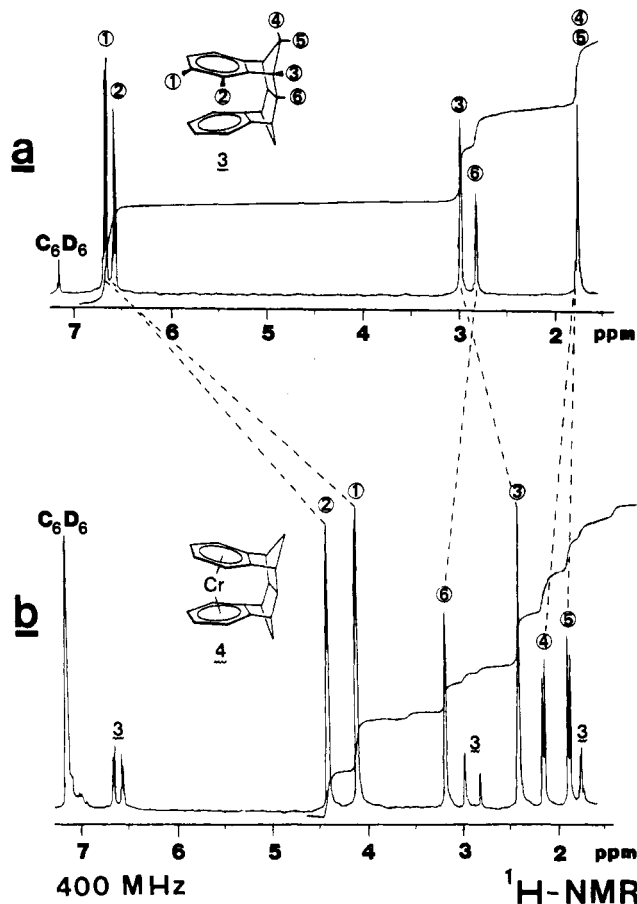


**Figure 2.** ¹H NMR spectra (400 MHz) of ligand 3 and complex 4 in C₆D₆ at room temperature. A small amount of ligand 3 was added to sample b. For labeling of the ligand protons see Table I.

changes the ¹H NMR parameters experience during the transition arene → (η⁶-arene)metal, this process should be divided into two stages:

(12) Hsu, L.-Y.; Hathaway, S. J.; Paquette, L. A. *Tetrahedron Lett.* **1984**, *25*, 259.

(13) Assignment based on the varying inter-ring distance of the non-parallel arenes in 3,[8] the experience that upfield shifts in [2ₙ]cyclophanes are a function of ring proximity,[14,15g] and on decoupling experiments.

(14) Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 3512.

(15) The high-field shift as a typical feature of face-to-face phanes has been discussed extensively. (a) Cram, D. J.; Dalton, C. K.; Knox, G. R. *J. Am. Chem. Soc.* **1963**, *85*, 1088. (b) Cram, D. J.; Helgeson, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 3515. (c) Wasserman, H. H.; Keehn, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 2374. (d) Toyoda, T.; Otsubo, I.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1972**, 1731. (e) Staab, H. A.; Haenel, M. *Chem. Ber.* **1973**, *106*, 2190. (f) Vögtle, F.; Hohner, G. *Top. Curr. Chem.* **1978**, *74*, 1. (g) Boekelheide, V. *Top. Curr. Chem.* **1983**, *113*, 87.
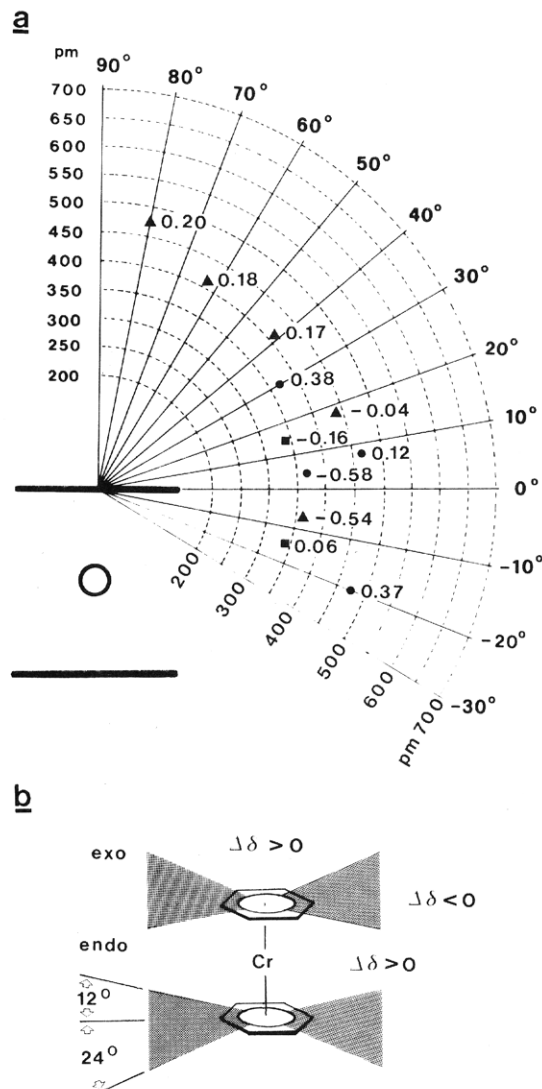
(16) This argument also explains the unusually small ¹H NMR coordination shifts for (η¹²-[2.2]paracyclophane) chromium as compared to bis(η⁶-p-xylene)chromium. (Elschenbroich, Ch.; Möckel, R.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531).
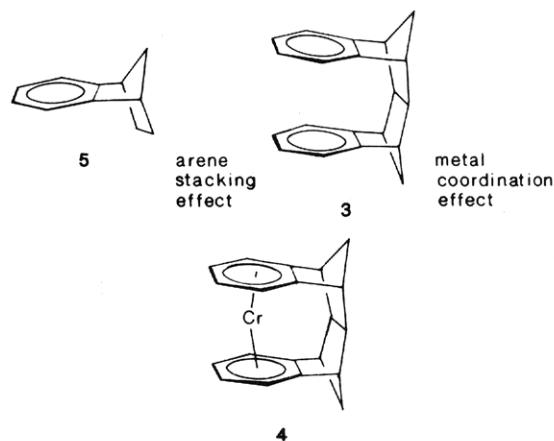
Whereas in practice the sum of the two effects is observed, a physical explanantion of the specific contribution of the metal to the overall coordination shift should only consider the second stage and in any attempt to deal quantitatively with the source of $\Delta\delta$ for bis(arene)metal complexes a value of $\Delta\delta(H_{Ar})$ of about $-2.3$ ppm only has to be accounted for. In the following only coordination shifts for protons on carbon atoms not directly bonded to the central metal will be discussed because they more faithfully reflect the overall change in the magnetic anisotropy of bis($\eta^6$-benzene)-chromium rather than the result of local chromium carbon bond anisotropies and the build-up of charge on $\eta$-carbon atoms.

The nature of the bridging framework in $\mathbf{3}$[17] is expected to effect slight tilting of the sandwich structure $\mathbf{4}$. In the following NMR discussion, this deviation of the two $\eta^6$-arenes from a parallel arrangement will be ignored, however, and $\mathbf{4}$ will be regarded representative for bis($\eta^6$-arene)metal complexes in general.

The $^1$H NMR absorption in the region $3.5 > \delta > 1.5$ can be assigned without having to resort to the model which will be used later to analyze the source for these shift differences. The assignment $\delta$ 3.19 (2 H⑥) and 2.40 (4 H③) for the protons at tertiary carbon atoms of complex $\mathbf{4}$ is unequivocal for intensity reasons. The signals $\delta$ 2.14 (2 H) and 1.86 (2 H) for complex $\mathbf{4}$ correlate with $\delta$ 1.76 (2 H) and 1.74 (2 H) for ligand $\mathbf{3}$. The assignment $\delta$ 2.14 (2 H④) and 1.86 (2 H⑤) is based on the more favorable disposition of H④) for long-range coupling to H⑥ which manifests itself in slightly larger apparent line widths. The most conspicous feature which a conceptual model to explain the coordination shifts for the bis($\eta^6$-arene)chromium complexes $\mathbf{2}$ and $\mathbf{4}$ must be able to cope with is the *change in sign of* $\Delta\delta$ *above as well as in the region between the rings.* The latter aspect suggests that the impact of the central metal on the shielding of peripheral protons is mediated via the ligands rather than being a direct effect of the transition metal. An obvious model to rationalize the $^1$H NMR results involves coordination-induced modification of the magnetic susceptibilities of the two $\pi$-bonded benzene rings and additivity of the influences of these changes on peripheral proton shielding. The $\Delta\delta$ values for complexes $\mathbf{4}$ (and $\mathbf{2}$[7]) will therefore be traced to the location of the protons H③-H⑥ and H⑦-H⑪ relative to the individual shielding cones of both $\eta^6$-arenes. In Figure 3 the approximate locations of the protons de-

(17) An X-ray structure determination for $\mathbf{3}$ revealed the distances $d(C_{4a}-C_{6a}) = 304$ pm and $d(C_3-C_8) = 382$ pm and an interplanar angle of $18.6°$.[8] This is to be compared with $d(\text{inter-ring}) = 322$ pm for ($\eta^6$-$C_6H_6)_2Cr$.[18]
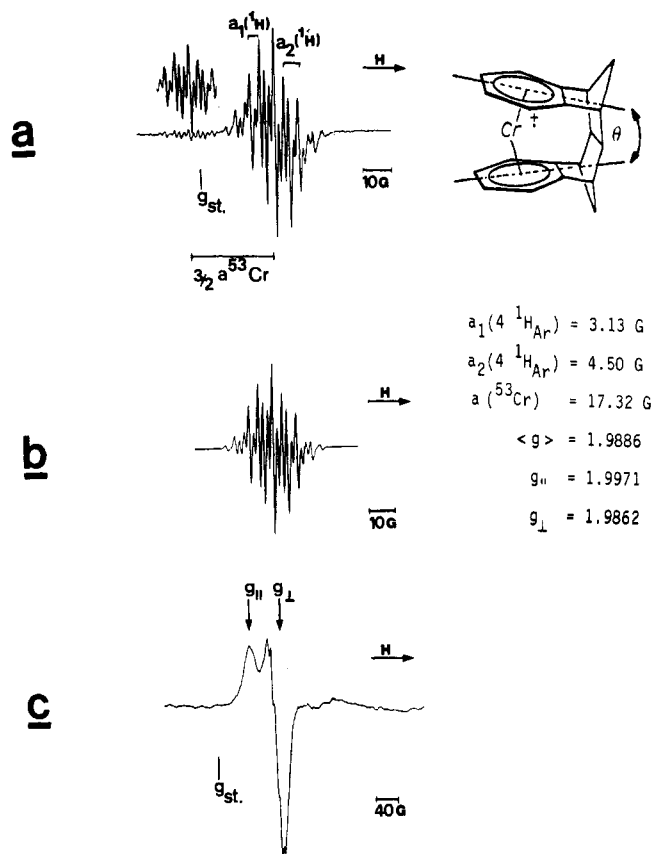
(18) (a) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41. (b) Keulen, E.; Jellinek, F. *J. Organomet. Chem.* **1965**, *5*, 490.



**Figure 3.** (a) $^1$H NMR coordination shift data for protons in the periphery of bis($\eta^6$-benzene)chromium (**1**), plotted in a polar coordinate system (origin: center of $\eta^6$-$C_6H_6$). The locations of the individual protons were derived from Dreiding models: (▲) **2**; (●) **4**; (■) **8**. (b) Regions of positive and negative coordination shift in the periphery of **1**. The angles $+24°$ (exo) and $-12°$ (endo) characterizing the conical surfaces where $\Delta\delta$ changes sign were estimated from the data in Figure 3a.

rived from Dreiding models are indicated and a schematic representation of the areas $\Delta\delta > 0$ and $\Delta\delta < 0$ in the vicinity of bis($\eta^6$-arene)chromium is given. Since in the interligand region (endo) effects related to ring currents of *both* rings operate, whereas in the exo region the influence of *one* ring current only should dominate, the shielding cones designated as endo and exo in Figure 3b cannot be expected to be symmetrical with regard to the individual rings. The border of the exo shielding cone may be inferred from the $^1$H NMR spectrum of **2** for which $\Delta\delta$ was shown to practically vanish at H⑧.[7] The disposition of this cone cannot be directly transferred to complex **4** since, as shown in Figure 3a, in the case of **4** $\Delta\delta > 0$ applies already at smaller angles. This inconsistency is only apparent, however, because in **4** the pure metal coordination effect only operates, whereas in **2** the combination of arene stacking plus metal coordination contributes to $\Delta\delta$. Since in most practical applications, the two arenes will be independent prior to complexation, we consider the exo cone at an angle of about $24°$ as derived from **2** and depiced in Figure 3b a realistic one. An estimate of the area where $\Delta\delta$ changes sign in the interligand (endo) region is based

on the ¹H NMR data for bis(cylobuta-$\eta^6$-benzene)chromium (8)[19] [$\Delta\delta$($H_{CH_2,exo}$) (−0.16), $\Delta\delta$($H_{CH_2,endo}$) (+0.06)].

The primitive model of two ring currents which are modified upon metal coordination may now be illustrated referring to complex 4. The largest upfield shift $\Delta\delta$[H③] (−0.58) meets the expectation since the respective protons are situated close to the ligand plane where the contribution of ring currents to proton deshielding is maximal.[20] The sign and the relative magnitudes of the coordination shifts $\Delta\delta$[H④] (+0.38) and $\Delta\delta$[H⑤] (+0.10) are plausible since both types of protons adopt positions exo to the zero shift surface of the neighboring ring current whereby H⑤ lies closer to this surface as compared to H④. With regard to $\Delta\delta$[H⑥] (+0.37), note that H⑥ is symmetrically disposed between the two rings and has an angular relation to each individual ring comparable to a position intermediate between H④ and H⑤. Therefore, positive contributions $\Delta\delta$ from both rings reinforce each other and a shift of $\Delta\delta$[H⑥] ≈ 2 [($\Delta\delta$[H④] + $\Delta\delta$[H⑤])/2] accrues. The coordination shift of a freely rotating methyl group as in bis($\eta^6$-o-xylene)chromium (7), $\Delta\delta$($H_{Me}$) (−0.05), may also be accommodated into the picture if it is realized that during rotation this methyl group samples contributions $\Delta\delta$ < 0 as well as $\Delta\delta$ > 0 from the connected ring and contributions $\Delta\delta$ > 0 of smaller magnitude from the opposite ring.

It remains to comment on possible causes for partial quenching of the ring current which is proposed to accompany metal coordination. Several lines of evidence suggest that bonding of a transition metal to an arene leads to a decrease of $\pi$-bond order within the ring: the C–C bond distance increases from 139 ($C_6H_6$) to 142 pm [($\eta^6$-$C_6H_6$)$_2$Cr],[18] proton coupling constants decrease considerably[9b] and the transmission of resonance effects across the $\eta^6$-arene is attenuated.[21] To the extent that ring current intensity is related to $\pi$-bond order, a decrease of the diamagnetic ring current in bis($\eta^6$-arene)chromium complexes may be traced to a depopulation of the bonding orbital $e_{1g}$ of benzene (arene → metal donation, MO $e_{1g}$) and a population of the benzene antibonding orbital $e_{2u}$ (arene ← metal back-donation, MO $e_{2g}$).

**Electron Spin Resonance.** As opposed to radical ions of free arenes, in the case of bis($\eta^6$-arene)metal ($d^5$) species substitution in the ring periphery does not perceptibly raise the equality of the hyperfine coupling constants of the remaining ring protons.[22] This is a consequence of the Cr ($3d_{z^2}$) $\xrightarrow{\sigma}$ arene ($a_{1g}$) mechanism of direct spin delocalization which is virtually unaffected by a loss of $\pi$-orbital degeneracy. However, $\sigma$-delocalization should be sensitive to overlap between the singly occupied Cr ($3d_{z^2}$) orbital and the >CH fragments of the $\eta^6$-arene and therefore should respond to tilting of the sandwich structure. This expectation is borne out by the ESR spectrum of **4**·⁺ which displays a hyperfine pattern generated by two sets of four equivalent ring protons (Figure 4).[23] Conversely, for the



$a_1(4\ ^1H_{Ar}) = 3.13\ G$
$a_2(4\ ^1H_{Ar}) = 4.50\ G$
$a\ (^{53}Cr) = 17.32\ G$
$<g> = 1.9886$
$g_\| = 1.9971$
$g_\perp = 1.9862$

**Figure 4.** ESR spectra of the radical cation **4**·⁺ in fluid solution (a) and in rigid solution (c) (mode of generation: air oxidation): a, methanol, −25 °C; b, simulated trace, $^{53}$Cr satellites not considered; c, methanol, −114 °C. $g_{st}$(perylene(·+)) = 2.0026.

cation **6**·⁺ where tilting is absent, coupling to eight equivalent ring protons is observed. A note of caution should be sounded, however, concerning the assignment of the coupling constants $a_1$ and $a_2$. Although in **4** the interannular C–C distance is smaller for the ortho positions than for the meta positions, an assignment of the larger coupling constant $a_2$ to the ortho protons is not warranted in the absence of X-ray structural data since the possibility that a shift in the position of the chromium atom might lead to a shorter distance between the central metal and the meta positions cannot be excluded. Finally, it is worth mentioning that the sensitive response of proton hyperfine structure on tilting is not complemented by a corresponding splitting of $g_\perp$ into two components $g_x$ and $g_y$. As shown in Figure 4, the ESR spectrum of **4**·⁺ in rigid solution suggests an axially symmetric species. Apparently, the degeneracy of the unoccupied orbitals $e_{2u}$ and $e_{1g}$ (symmetry labels for the parent complex **1**) is raised by tilting to an extent which is unsufficient to manifest itself in the resolution of three **g** tensor components.

## Concluding Remark

As shown above, model compounds of the type **4** may serve the dual purpose of providing evidence in support of the contribution, partial quenching of the ring current adds to the ¹H NMR coordination shift $\Delta\delta$ and of laying the foundation for a systematic study of its spatial variation. For a more complete picture of coordination shift anisotropy to be gained, the search for further bis(arene)metal complexes which possess peripheral protons

(19) Elschenbroich, Ch.; Schneider, J.; Spangenberg, B.; Schiess, P., submitted for publication in *J. Organomet. Chem.*
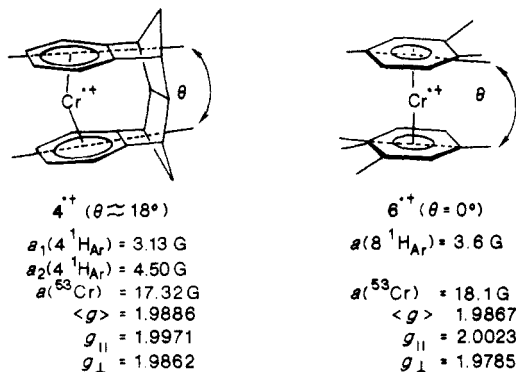
(20) Inclusion of the arene stacking effect [$\delta$[H③, **3**] − $\delta$[H③, **5**] = −0.14] would lead to the composite value $\Delta\delta$ = −0.72.

(21) (a) Graves, V.; Lagowski, J. J. *Inorg. Chem.* **1976**, *15*, 577. (b) Burdorf, H.; Elschenbroich, Ch. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1981**, *36B*, 94.

(22) (a) Prins, R.; Reinders, F. *J. Chem. Phys. Lett.* **1969**, *3*, 45. (b) Elschenbroich, Ch.; Möckel, R.; Zenneck, U.; Clack, D. W. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 1018. (c) Li, T. T.-T.; Kung, W.-J.; Ward, D. L.; McCulloch, B.; Brubaker, C. H. *Organometallics* **1982**, *1*, 1229.

(23) The influence of tilting on ESR hyperfine structure has been observed previously for the related sandwich complex ($\eta^{12}$-[2.2.2](1,2,4)-cyclophane)chromium(·+): $a_1(4\ ^1H_{Ar}) = 3.2$ G and $a_2(4\ ^1H_{Ar}) = 5.3$ G (Zenneck, U. Ph.D. Thesis, University of Marburg, 1980. Elschenbroich, Ch.; Hopf, H.; Zenneck, U., unpublished results).

(24) ¹H NMR assignment for **5** in CCl₄: Tori, K.; Anono, K.; Hata, Y.; Muneyuki, R.; Tsuji, T.; Tanida, H. *Tetrahedron Lett.* **1966**, 9.

$4^{\cdot +}$ ($\theta \cong 18°$)

$a_1(4\,^1H_{Ar}) = 3.13\ G$
$a_2(4\,^1H_{Ar}) = 4.50\ G$
$a(^{53}Cr) = 17.32\ G$
$\langle g \rangle = 1.9886$
$g_{\parallel} = 1.9971$
$g_{\perp} = 1.9862$

$6^{\cdot +}$ ($\theta = 0°$)

$a(8\,^1H_{Ar}) = 3.6\ G$
$a(^{53}Cr) = 18.1\ G$
$\langle g \rangle = 1.9867$
$g_{\parallel} = 2.0023$
$g_{\perp} = 1.9785$

covering the region closer to the central metal—about –30° 300 pm in Figure 3—will be our prime objective. Ultimate goal is the construction of a diagram of "iso coordination shift lines" mapping the periphery of bis($\eta^6$-benzene)-chromium. Such a diagram would be invaluable in the stereochemical analysis of new derivatives of parent complex 1 by means of $^1$H NMR.

## Experimental Section

**General Comments.** Unless stated otherwise, operations were carried out under an inert atmosphere employing solvents which were thoroughly dried and deoxygenated.

In order to achieve high resolution, we performed $^1$H NMR measurements (Bruker, WH-400) in sealed tubes which were provided with a potassium mirror at their upper end. In this way, complex radical cations adventitiously present and leading to line broadening via electron self-exchange[25] could be eliminated. The NMR spectra were obtained at ambient temperature from solutions in $C_6D_6$ whereby the solvent served as the standard. Chemical shifts reported are on the $\delta$ scale; the coupling constants are apparent rather than calculated with absolute values listed in hertz.

**ESR spectra** (Varian E 12, X-band) were measured for solutions of the respective radical cation in methanol. These samples were prepared by air oxidation of the neutral diamagnetic precursor during a 10-min period and successive degassing of the solutions by a sequence of freeze–pump–thaw cycles. *g* factors were determined by means of a dual-sample cavity, perylene($\cdot +$) ($g = 2.00258$) served as the standard. The *cyclovoltammogram* of 4 was recorded at room temperature against a SCE with electrochemical equipment from AMEL, employing a glassy carbon working electrode, ($n$-Bu)$_4$NClO$_4$ as the supporting salt, and dimethoxyethane as the solvent. At a scan rate of 0.1 V s$^{-1}$ only one reversible wave was observed. The starting materials benzonorbornene (5)[26] and 5,12:6,11-dimethano-

5,5a,6,11,11a,12-hexahydro-$\eta^{12}$-tetracene (3)[8] were obtained as described previously.

**(5,12:6,11-Dimethano-5,5a,6,11,11a,12-hexahydro-$\eta^{12}$-tetracene)chromium (4).** In a 4-L evacuated (10$^{-3}$ mbar) reactor which was cooled with liquid nitrogen, 300 mg (5.76 mmol) of chromium and 5 g (19.3 mmol) of 3 were evaporated from a resistively heated conically shaped tungsten spiral and a heated furnace, respectively. During the 3-h cocondensation period, a pale brown matrix formed. Before being warmed to room temperature, the cocondensate was kept at –77 °C for 2 h whereby a color change to dark brown was observed. After having reached room temperature, the product was suspended in tetrahydrofuran and the chromium slurry was removed via filtration through a 2-cm layer of silica gel. The solvent was stripped off and the residue subjected to high vacuum fractional sublimation. A temperature gradient of 85–62 °C had to be created at a length of 20 cm along the sublimation tube in order to effectively separate ligand 3 from complex 4. From the lower zone about 20 mg (1% based on chromium evaporated) of 4 is obtained as brown microcrystalline material, mp (sealed tube, N$_2$) 195 °C (ligand, ref 8). FD-MS (cocondensate before fractional sublimation): $m/e$ (relative intensities) 568 (30.1, (3)$_2$Cr$^+$), 524 (27.1), 523 (11.9), 522 (11.6), 310 (100). EI-MS (4, sublimate): $m/e$ 310 (8.6, M$^+$), 258 (36.1, 3$^+$), 143 (12.8), 142 (15.0), 141 (16.7), 130 (13.8), 129 (20.7), 128 (17.9), 117 (45.6), 116 (100), 115 (23.8), 52 (5.2). Anal. Calcd for C$_{20}$H$_{18}$Cr: C, 77.41; H, 5.81. Found: C, 78.50; H, 6.18. $^{13}$C NMR (100.6 MHz, C$_6$D$_6$): complex 4, 71.4 (C-1), 73.2 (C-2), 105.1 (C-4a), 40.6 (C-5), 65.7 (C-5a), 57.3 (C-13), C-4a,13, assignment via spin echo, C-5,5a, assignment based on intensity ratio, C-1,2, inverted assignment possible; ligand 3, 143.1 (C-4a, $^1J_{CH}$ = 105.1 Hz), 125.8 (C-1, $^1J_{CH}$ = 155.5 Hz), 123.8 (C-2, $^1J_{CH}$ = 155.5 Hz), 59.1 (C-13, $^1J_{CH}$ = 130.4 Hz), 47.0 (C-5, $^1J_{CH}$ = 40.6 Hz), 46.1 (C-5a, $^1J_{CH}$ = 65.7 Hz), C-5,5a, inverted assignment possible.

**Bis($\eta^6$-benzonorbornene)chromium, ($\eta^6$-5)$_2$Cr (Mixture of Isomers).** The wall of a 4-L reactor was covered with a solid layer of ~30 mL of tetrahydrofuran, then chromium (~0.5 g, 9.6 mmol), and benzonorbornene (5 g, 34.6 mmol) were cocondensed at –196 °C (10$^{-3}$ mbar), the ligand being introduced from an external heated reservoir. After the mixture was warmed to room temperature and filtered through a 3-cm layer of silica gel, a burgundy red solution was obtained. Solvent and excessive ligand were removed under high vacuum at room temperature during 3 h. The residual oil was distilled in a sublimation tube at 100 °C (10$^{-3}$ mbar) whereby the product solidified to an amorphous reddish brown material (yield 35 mg, 1% based on chromium evaporated). EI-MS (70 eV): $m/e$ (relative intensities) 340 (16.1, M$^+$) 196 (100, M$^+$ – 5), 52 (53.9, Cr). $^1$H NMR: see text. Anal. Calcd for C$_{22}$H$_{24}$Cr: C, 77.62; H, 7.11. Found: C, 76.96; H, 7.23.

(25) Elschenbroich, Ch.; Zenneck, U. *J. Organomet. Chem.* **1978**, *160*, 125.
(26) Wittig, G.; Knauss, E. *Chem. Ber.* **1958**, *91*, 895.