

and Br, illustrated in Table V, also confirm a relaxation mechanism similar to that discussed for the HS iron(III) and manganese(III) porphyrins. Estimates³⁶ of $r(\text{Fe}-\text{CH}_2)$ yield $\tau_c \leq 5 \times 10^{-11}$ sec, which is again indicative of $\tau_c \sim T_{1e}$. For these complexes, however, changing X causes major changes in the size and tumbling characteristics of the complex, such that neither τ_r nor the spectral density function for electron spin relaxation is likely to be independent of X. This invalidates use of eq 8. The qualitative trend of decreasing line widths with increasing ZFS parameters, which are available for these complexes from similar far-ir esr work and are reproduced in Table V, clearly reveal that the correlation time is predominantly T_{1e} , which is in turn determined by the ZFS mechanism.

Implications. Our present investigation suggests that for HS porphyrins for which T_{1e} contributes significantly to the correlation time for nuclear relaxation, the nmr spectral resolution can, in principle, be controlled to some extent by the choice of axial ligand. Since D in the axially distorted complexes of interest always increases^{32,37} with decreasing ligand field strength of X, the trend in line width with X will be determined

by the sign of D . Weaker axial ligands will narrow nmr lines if D is positive but will broaden the lines if D is negative. In systems for which no independent esr data on D are available, the trend in line widths with axial ligand could serve to determine the sign of the ZFS parameters.

It may be noted that the present demonstration of a simple relationship between short electron relaxation time (narrow nmr lines) and the magnitude of the ZFS parameter suggests that similarly useful^{3,5,16,17} nmr studies should be applicable to ferrous porphyrins and related complexes. The large ZFS for ferrous phthalocyanine⁴² ($D \sim 64 \text{ cm}^{-1}$), which exhibits the interesting intermediate spin state $S = 1$, indicates that well-resolved proton nmr spectra should be readily obtainable.

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(42) C. G. Barraclough, R. L. Martin, and S. Mitra, *J. Chem. Phys.*, **53**, 1643 (1970).

Spin Density Distribution in Unsymmetrical Sandwich Complexes. II.¹ Electron Spin Resonance Studies of π -Cyclopentadienyl- π -cycloheptatrienechromium(I) and π -Cyclopentadienyl- π -cycloheptatrienylchromium(-I) Radical Anion

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Abstract: Reaction of π -cyclopentadienyl- π -cycloheptatrienylchromium (CpCrTr) with potassium in 1,2-dimethoxyethane yields the relatively stable radical anion CpCrTr \cdot^- which is characterized by its esr spectrum. In the presence of protic impurities, π -cyclopentadienyl- π -cycloheptatrienechromium (CpCrCHT) is formed instead of CpCrTr \cdot^- . However, CpCrCHT \cdot can be converted into CpCrTr \cdot^- on contact with potassium under strictly aprotic conditions. ESR evidence strongly suggests a dominant π -ligand character for the lowest unoccupied MO of CpCrTr which thus correlates with the orbital e_{2u} of bisbenzenechromium. Reduction of π -cyclopentadienyl- π -methylcycloheptatrienylchromium (CpCrMeTr) leads to the unstable radical anion CpCrMeTr \cdot^- which, in contrast to the parent CpCrTr \cdot^- , cleaves off the seven-membered ligand. The latter is identified by esr spectroscopy in the form of the ion triple MeTr $\cdot^{2-}/2\text{K}^+$.

Whereas the radical cations of bisarene-transition metal- π complexes have provided sufficient data to characterize the highest occupied orbital (HOMO) in this class of compounds,² conclusive information on the nature of the lowest unoccupied orbital (LUMO) has not yet been gathered. Reports on the radical anions of bisarene-transition metal- π complexes are scarce,³ in contrast to numerous studies of noncoordi-

nated aromatic radical anions. In a few cases,⁴⁻⁶ negatively charged paramagnetic ions were obtained from ferrocene derivatives bearing strongly electron-attracting substituents, such as benzoyl or nitro groups. However, such radical anions cannot be regarded as suitable model compounds for a study of spin density distribution between the ligands and the central atom, since in these cases the spin population is essentially localized on the substituent groups. It was therefore

(1) Part I: Ch. Elschenbroich and F. Gerson, *J. Organometal. Chem.*, **49**, 445 (1973).

(2) See part I¹ and the references therein.

(3) To our knowledge, there is only one paper in which the formation of such a radical anion is proposed: G. Henrici-Olivé and S. Olivé, *J. Amer. Chem. Soc.*, **92**, 4831 (1970).

(4) Ch. Elschenbroich and M. Cais, *J. Organometal. Chem.*, **18**, 135 (1969).

(5) J. J. McDonnell, G. Capen, and R. Michealson, *Tetrahedron Lett.*, 4251 (1969).

(6) W. C. Danen and C. T. West, *Tetrahedron Lett.*, 219 (1970).

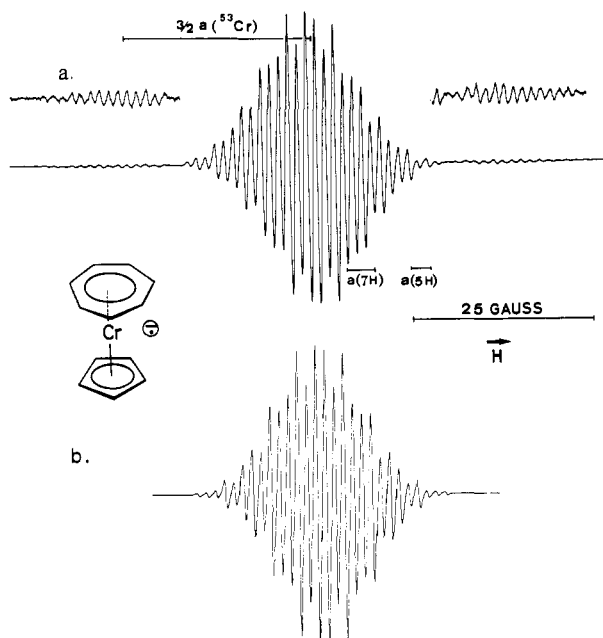


Figure 1. (a) ESR spectrum of $\text{CpCrTr}\cdot^-$: solvent, DME; counterion, K^+ ; temperature, $+20^\circ$. (b) Computer-simulated spectrum: coupling constants, see Table I; line shape, Lorentzian; line width, 0.3 G. The simulation does not account for the ^{53}Cr satellites.

desirable to attempt the preparation of bisarene-metal radical anions, the electronic structure of which is not affected by ring substituents. Since bisbenzenechromium(0) (Bz_2Cr) could not be converted to a stable radical anion,⁷ we turned our attention to the reaction of its isoelectronic, unsymmetrical counterpart, π -cyclopentadienyl- π -cycloheptatrienylchromium(0) (CpCrTr) with strong reducing agents. In the present paper, we wish to report on esr studies of the pertinent radical anion ($\text{CpCrTr}\cdot^-$) and of π -cyclopentadienyl- π -cycloheptatrienylchromium(I) ($\text{CpCrCHT}\cdot$) as an alternate reduction product of CpCrTr .

Experimental Section

π -Cyclopentadienyl- π -cycloheptatrienylchromium (CpCrTr) was synthesized from π -cyclopentadienyl- π -benzenechromium (CpCrBz) according to Fischer and Breitschaft.⁸ π -Cyclopentadienyl- π -cycloheptatrienylchromium (CpCrCHT) was prepared by the method of Fischer and Müller.⁹ π -Cyclopentadienyl- π -methylcycloheptatrienylchromium (CpCrMeTr) was obtained from CpCrBz through a ring expansion reaction.¹⁰

Since the mentioned compounds are air sensitive, they had to be handled under pure nitrogen.

The radical anion $\text{CpCrTr}\cdot^-$ was produced by reaction of the neutral compound with potassium mirror in 1,2-dimethoxyethane (DME) or 2-methyltetrahydrofuran (MTHF). Upon contact with the alkali metal, the solution of CpCrTr immediately turned reddish brown and became paramagnetic. The resulting radical anion $\text{CpCrTr}\cdot^-$ could be stored for several hours even at room temperature. However, its stability was not sufficient to permit the isolation as a radical salt. Special care had to be taken to eliminate traces of protic impurities in the solvent; this was achieved by refluxing over calcium hydride and repeated distillation from potassium mirror.

Air oxidation of CpCrTr yielded the radical cation $\text{CpCrTr}\cdot^+$, as reported previously.^{1,8}

(7) Ch. Elschenbroich, F. Gerson, and J. Heinzer, *Z. Naturforsch. B*, **27**, 312 (1972).

(8) E. O. Fischer and S. Breitschaft, *Chem. Ber.*, **99**, 2905 (1966).

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(10) E. O. Fischer and S. Breitschaft, *Chem. Ber.*, **99**, 2213 (1966).

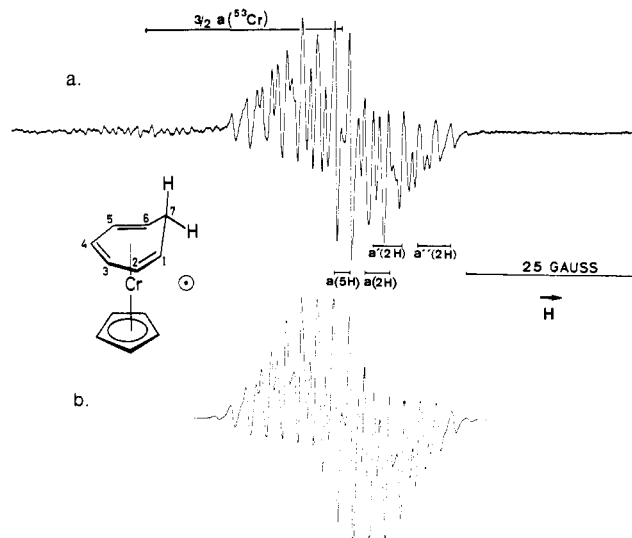


Figure 2. (a) ESR spectrum of $\text{CpCrCHT}\cdot$: solvent, MTHF; temperature, -100° . (b) Computer-simulated spectrum: coupling constants, see Table I; line shape, Lorentzian; line width, 0.7 G. The simulation does not account for the ^{53}Cr satellites.

The methyl derivative CpCrMeTr was treated in the same way as the unsubstituted complex CpCrTr . Reduction of CpCrMeTr in DME led to a greenish-blue solution of a paramagnetic product only after prolonged contact with potassium. In contrast, the behavior of CpCrMeTr on air oxidation closely paralleled that of CpCrTr .

Esr spectra were measured by means of a Varian-E9 spectrometer equipped for magnetic field calibration, Frémy salt being used as the reference.

Results

Reduction of CpCrTr with potassium in a rigorously purified solvent (DME or MTHF) resulted in the esr spectrum shown in Figure 1a. If protic impurities were not completely removed, the reaction first yielded a different spectrum (Figure 2a) which upon further contact of the solution with the alkali metal mirror changed into that of Figure 1a. In order to prove that the intermediate occurrence of the spectrum presented in Figure 2a is linked to the presence of protic impurities, about 1% of water was added to the solvent prior to reduction. Only the spectrum of Figure 2a was observed in this case. The same spectrum could also be obtained by the treatment of the radical cation $\text{CpCrTr}\cdot^+$ with LiAlH_4 in DME or THF solution. However, the resulting esr intensity of $\text{CpCrCHT}\cdot$ was an order of magnitude lower than the initial intensity of $\text{CpCrTr}\cdot^+$.

It is reasonable to assume that the species giving rise to the spectrum of Figure 2a is formed from CpCrTr or $\text{CpCrTr}\cdot^+$ by addition of $\text{H}\cdot$ or H^- , respectively, to the seven-membered ring. This assumption was confirmed by an independent synthesis of the expected product, $\text{CpCrCHT}\cdot$, which displayed a spectrum identical with that of Figure 2a. Furthermore, $\text{CpCrCHT}\cdot$ exhibited the same behavior as the previously mentioned intermediate, since upon reaction with potassium mirror it yielded the spectrum of Figure 1a. Clearly this spectrum must be attributed to the radical anion $\text{CpCrTr}\cdot^-$, in accordance with its esr hyperfine structure (*vide infra*) and chemical behavior (it can be oxidized to the radical cation $\text{CpCrTr}\cdot^+$).

The various interconversions described above are rationalized by Scheme I.

Table I. ESR Data^a for CpCrTr^{·+}, CpCrTr^{·-}, CpCrMeTr^{·+}, CpCrMeTr^{·-}, and CpCrCHT[·]

Radical	$\langle g \rangle$	$g_{ }$	g_{\perp}	$a(\text{H}), \text{G}$			$a(^{53}\text{Cr}), \text{G}$
				Cp	Tr	CHT	
CpCrTr ^{·+} ^b	1.9882	2.0001	1.9797	2.16 (5 H)	3.62 (7 H)		19.0
CpCrTr ^{·-}	2.0036	<i>c</i>	<i>c</i>	2.54 (5 H)	3.81 (7 H)		17.35
CpCrMeTr ^{·+}	1.9879	2.0006	1.9787	2.35 (5 H)	3.81 (6 H) ^d 1.01 (3 H) ^e		19.3
CpCrMeTr ^{·-}	2.0038	<i>f</i>	<i>f</i>	<i>f</i>			18 ± 2
CpCrCHT [·]	1.9886	2.0009	1.9802	2.29 (5 H)		4.95 (2 H): 3,4 ^o 4.45 (2 H): 2,5 ^o 3.68 (2 H): 1,6 ^o	19.7

^a Experimental error: ± 0.0002 for g , ± 0.02 G for $a(\text{H})$, and ± 0.1 G for $a(^{53}\text{Cr})$. ^b Data taken from ref 1. ^c g anisotropy not resolved; $g_{||} - g_{\perp} < 0.001$. ^d Ring protons. ^e Methyl protons. ^f No data available (see text). ^o Position to which the coupling constant is assigned (cf. text and numbering in Figure 2).

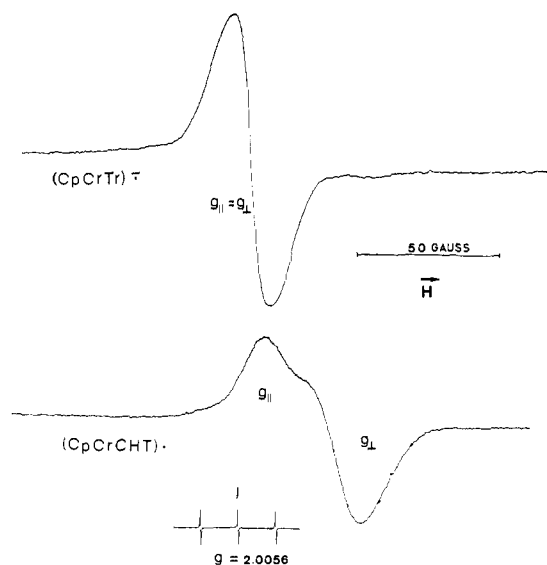
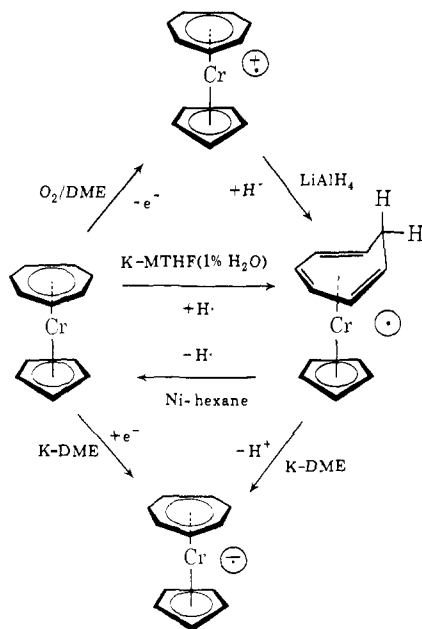


Figure 3. ESR spectra of CpCrTr^{·-} (counterion, K⁺) and CpCrCHT[·] in glassy solution: solvent, MTHF; temperature, -150°. The signals of the Frémy salt (bottom) mark the positions of the spectra in the magnetic field.

Scheme I



The analysis of the hyperfine structure of CpCrTr^{·-} (Figure 1a) in terms of seven and five equivalent protons in the Tr and Cp ligands, respectively, is straight-

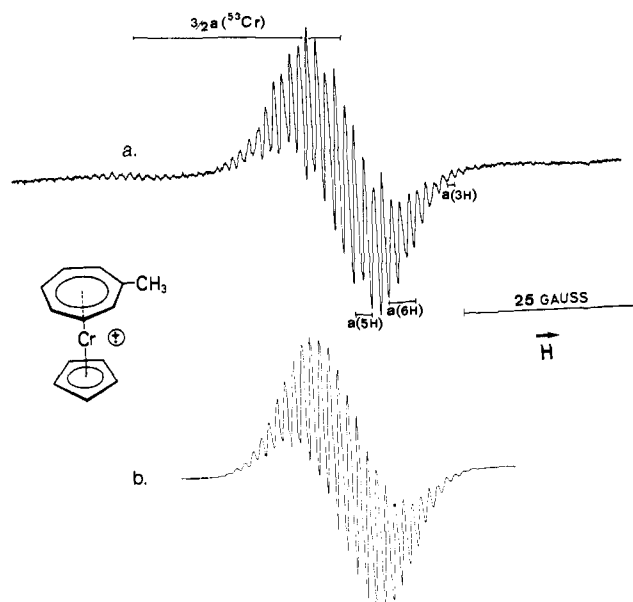


Figure 4. (a) ESR spectrum of CpCrMeTr^{·+}: solvent, *N,N*-dimethylformamide-chloroform (1:1); temperature, -60°. (b) Computer-simulated spectrum: coupling constants, see Table I; line shape, Lorentzian; line width, 0.8 G. The simulation does not account for the ⁵³Cr satellites.

forward. The proton coupling constants $a(\text{H})$ are listed in Table I, along with the isotropic $\langle g \rangle$ value and the splitting $a(^{53}\text{Cr})$ due to ⁵³Cr nuclei in natural abundance (9.54%; $I = 3/2$). The line width, which exhibits only a slight temperature dependence, amounts to 0.3 G both for the main hyperfine components and the ⁵³Cr satellite lines on either side of the spectrum.

The hyperfine structure of CpCrCHT[·] is analyzed in terms of five equivalent protons in the Cp ligand and three pairs of equivalent protons in the CHT ligand. Table I contains the coupling constants $a(\text{H})$ and $a(^{53}\text{Cr})$, as well as the values $\langle g \rangle$, $g_{||}$, and g_{\perp} , the latter two being obtained from glassy solutions.

The assignment of the coupling constants $a(\text{H})$ to 1,6, 2,5, and 3,4 positions in the CHT ligand is based on the geometry of the CrCHT fragment which is assumed to be similar to that of MoCHT in π -cycloheptatrienemolybdenum tricarbonyl.¹¹ In particular, the distances from the metal to the three pairs of 1,6-, 2,5-, and 3,4-carbon π centers in the molybdenum complex (2.45, 2.35, and 2.31 Å, respectively¹¹) are regarded as an adequate substitute for the analogous geometry

(11) J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, **43**, 2188 (1960).

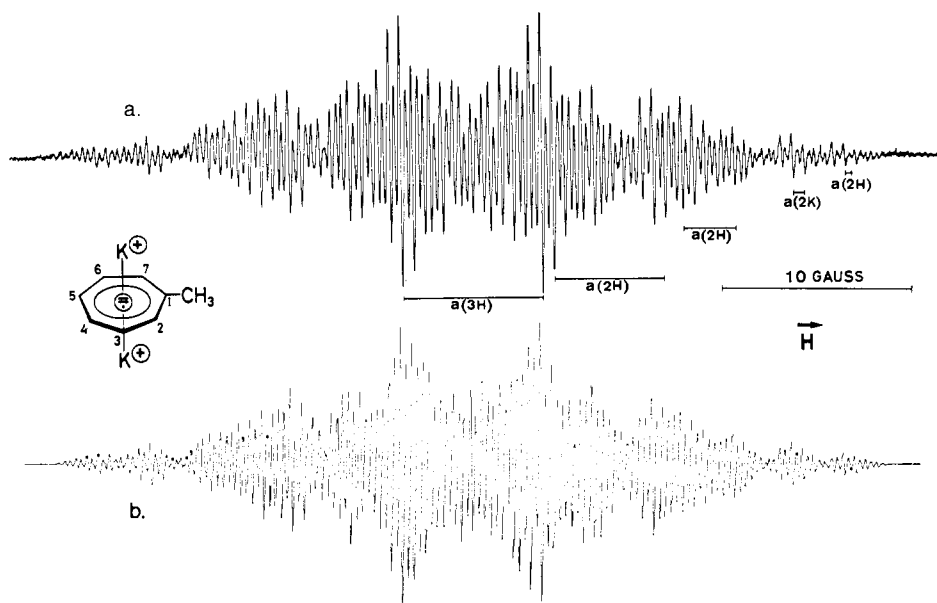


Figure 5. (a) ESR spectrum of $\text{MeTr} \cdot^{2-}$: solvent, DME; counterion, K^+ ; temperature, -80° . (b) Computer-simulated spectrum: coupling constants, see text; line shape, Lorentzian; line width, 0.11 G.

parameters in CpCrCHT . This assumption, along with the generally accepted $3d_z^2(\text{Cr})-\sigma(\text{ligand})$ spin delocalization in the bisarene-chromium d^5 complexes,¹²⁻¹⁴ leads to the expectation that the coupling constants $a(\text{H})$ of the respective ring protons should reflect the metal-carbon distances. In fact, the three $a(\text{H})$ values of 3.68, 4.45, and 4.95 G are approximately proportional to the reciprocal distances given above, and this correlation justifies the assignment made in Table I.

The line width in the spectrum of $\text{CpCrCHT} \cdot$ decreases considerably on lowering the temperature; it is 2.5 and 0.7 G at $+25$ and -100° , respectively. Whereas the ^{53}Cr satellites at the low-field side display the same line widths as the main hyperfine components, the corresponding high-field satellites are broadened beyond recognition, even at -100° .

Figure 3 shows the ESR spectra of $\text{CpCrTr} \cdot^-$ and $\text{CpCrCHT} \cdot$ in glassy MTHF solution. Only in the case of $\text{CpCrCHT} \cdot$ is the g anisotropy sufficiently large to be discernible. Reference to Frémy salt (see the bottom of Figure 3) demonstrates the difference in the g values of $\text{CpCrTr} \cdot^-$ and $\text{CpCrCHT} \cdot$.

As mentioned in the Experimental Section, oxidation and reduction were also performed on the methyl substituted complex CpCrMeTr . (The methyl group was introduced as a probe to test the mechanism of spin transfer in $\text{CpCrTr} \cdot^+$ and $\text{CpCrTr} \cdot^-$.) The spectrum of the radical cation $\text{CpCrMeTr} \cdot^+$ is shown in Figure 4. Its ESR parameters given in Table I closely resemble those of the parent species $\text{CpCrTr} \cdot^+$ described previously.¹ As in the case of the radical cation $\text{Bz}_2\text{Cr} \cdot^+$ and its methyl derivative,¹⁵ the ring proton coupling constants are only slightly affected by the substitution, and the splitting due to the methyl protons is relatively small.

The radical anion $\text{CpCrMeTr} \cdot^-$, which was identified by its $\langle g \rangle$ value and ^{53}Cr satellites (see Table I), could not be generated in sufficient concentration to permit full ESR characterization. Attempts to increase the signal intensity by prolonged contact with potassium in DME led to a well-defined, multiline ESR spectrum reproduced in Figure 5. This spectrum ($\langle g \rangle = 2.0025$; no ^{53}Cr satellites present) must be ascribed to the methyltropylenide radical dianion ($\text{MeTr} \cdot^{2-}$) associated with two counterions K^+ . The coupling constants (in G), 7.28 (3 H, methyl), 5.78 (2 H, positions 3,6), 2.75 (2 H, positions 4,5), 0.33 (2 H, positions 2,7), and 0.57 (2 ^{39}K), are very similar to those reported recently¹⁶ for the ion triple $\text{MeTr} \cdot^{2-}/2\text{K}^+$.

The cleavage of the ligand(methyl)-metal bond in CpCrMeTr on reaction with potassium is of some interest, since no similar complex dissociation could be observed for CpCrTr . The spectrum of the radical anion $\text{CpCrTr} \cdot^-$ was not substantially affected by prolonged contact with the alkali metal mirror, and no evidence for the formation of tropylenide radical dianion was obtained.

Discussion

Chemistry of CpCrTr Reduction. The ready formation of the radical anion from CpCrTr on reaction with potassium contrasts with the reluctance of its symmetric counterpart Bz_2Cr to accept an additional electron.⁷ Whereas the electron affinity of Bz_2Cr is much lower than that of benzene, the reduction potential of CpCrTr lies between those of benzene and biphenyl¹⁷ [$E_{1/2}(\text{benzene}) = -3.2$ to -3.5 V $< E_{1/2}(\text{CpCrTr}) < E_{1/2}(\text{biphenyl}) = -2.7$ V].¹⁸ It is tempting to draw an analogy between the pair of complexes $\text{Bz}_2\text{Cr}/\text{CpCrTr}$ and the two aromatic systems naphthalene/azulene.

(12) R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, **3**, 45 (1969).

(13) R. Prins, *J. Chem. Phys.*, **50**, 4804 (1969).

(14) S. E. Anderson, Jr., and R. S. Drago, *Inorg. Chem.*, **11**, 1564 (1972).

(15) S. E. Anderson and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 4244 (1970); results from NMR contact shift studies.

(16) F. Farr, Y. S. Rim, and N. L. Bauld, *J. Amer. Chem. Soc.*, **93**, 6888 (1971).

(17) This can be inferred from experiments in which CpCrTr is reduced in the presence of either benzene or biphenyl.

(18) The half-wave potentials $E_{1/2}$ refer to the saturated calomel electrode.

This analogy is corroborated by the small dipole moments of both azulene ($\mu \approx 1.0$ D)¹⁹ and CpCrTr ($\mu \approx 0.8$ D),²⁰ which are generally considered to reflect the slight charge separation associated with the tendency of the five- and seven-membered rings to achieve aromatic sextets. The differing electron affinities of Bz₂Cr and CpCrTr could thus be regarded as having a parallel in the reduction potentials of the two aromatic systems [$E_{1/2}$ (naphthalene) = -2.5 V; $E_{1/2}$ (azulene) = -1.6 V],¹⁹ provided the lowest unoccupied orbitals (LUMO) of Bz₂Cr and CpCrTr are of π -ligand type. As will be shown below, the characterization of the LUMO in CpCrTr as a predominantly π -ligand type orbital is supported by esr spectroscopic evidence. In this context it is noteworthy that the methyl derivative CpCrMeTr was found to be reduced with greater difficulty than the parent complex, its electron affinity being even lower than that of benzene. This marked effect of alkyl substitution on the ease of reduction complies with a π ligand rather than with a metal character of the LUMO.

Differing chemical behavior is also exhibited by the radical cations CpCrTr^{·+} and Bz₂Cr^{·+}. Whereas for Bz₂Cr^{·+} reactions with strong reducing agents result in reduction to the diamagnetic parent complex Bz₂Cr and in deprotonation to the neutral radical (BzCr⁺-Ph)[·],⁷ the analogous reactions of CpCrTr^{·+} lead either to the neutral complexes CpCrTr and CpCr-CHT[·] (reagent LiAlH₄) or to the radical anion CpCrTr^{·-} (reagent K). In particular the reaction products (BzCr⁺-Ph)[·] and CpCrCHT[·] of Bz₂Cr^{·+} and CpCrTr^{·+}, respectively, are remarkable, since they demonstrate the preference of π -complexed benzene for proton abstraction and that of similarly bonded tropenyl ligand for hydride addition.

Conversion of CpCrTr into CpCrCHT[·] by K/MTHF in the presence of water (see Scheme I) seems to occur *via* addition of atomic hydrogen (H[·]) which is generated from K and H₂O. An intermediate formation of the radical anion CpCrTr^{·-} and a subsequent protonation to CpCrCHT[·] can be ruled out by the observation that the latter product is not obtained from CpCrTr^{·-} and a proton donor (H₂O, CH₃OH).

The recovery of CpCrTr from CpCrCHT[·] in the presence of Raney nickel catalyst was reported previously³ and is included for completeness in Scheme I. It should be attributed to the higher thermodynamic stability of CpCrTr in which both ligands exhibit cyclic conjugation. Similar arguments may be put forward to account for the ready formation of CpCrTr^{·-} from CpCrCHT with K in DME. This formation cannot proceed by a direct deprotonation (in analogy to the reaction of the free ligand: CHT + PhCH₂-K⁺ → Tr-K⁺ + PhCH₃),²¹ since the complex CpCrCHT was found not to yield the radical anion CpCrTr^{·-} on contact with strong bases such as *n*-BuLi. The conversion of CpCrCHT[·] to CpCrTr^{·-} must therefore proceed in at least two steps: (1) reduction of the neutral complex to the diamagnetic anion CpCrCHT⁻, and (2) loss of hydrogen. Under the experimental conditions (extensive contact with potassium), it is likely that such a

loss occurs along with the uptake of a second electron, the leaving species being a hydride ion.

Spin Distribution in CpCrTr^{·-}. A considerable amount of work has been invested to elucidate the electronic structure of Bz₂Cr.^{12-14,22,23} Whereas the results of these semiempirical calculations describe the highest occupied orbital (HOMO) as one of predominantly metal character (3d_{z²}; a_{1g}), they differ with regard to the lowest unoccupied orbital (LUMO). In some papers,¹²⁻¹⁴ the LUMO is represented as a combination of ligand π MO's (π ; e_{2u}), while other workers predict that the LUMO should be of metal type (4p; a_{2u}'), the a_{2u}' orbital being slightly lower in energy than e_{2u}. Experimental evidence would therefore be desirable to choose between the two theoretical alternatives. In the present paper, the esr data for CpCrTr^{·-} are used as a criterion for the LUMO of CpCrTr which can be correlated with an orbital of Bz₂Cr (*vide infra*).

Comparison of the hyperfine coupling constants a (H) and a (⁵³Cr) given in Table I for the two radical ions CpCrTr^{·+} and CpCrTr^{·-} does not seem to indicate major differences in the character of the HOMO and LUMO of CpCrTr. The similarity in the two sets of data may even suggest a close resemblance of the two orbitals, in analogy to the pairing properties of the MO's in alternant π systems. However, examination of the remaining esr parameters points to substantial differences which are considered in the following.

(1) The isotropic $\langle g \rangle$ value of CpCrTr^{·-} (2.0036) lies well within the range specific for organic π radicals and is distinctly higher than the corresponding value of CpCrTr^{·+} (1.9882) and other isoelectronic chromium complexes with a singly occupied orbital of mainly 3d_{z²} character (d⁵ complexes). Furthermore the g anisotropy of CpCrTr^{·-} is negligible ($g_{\parallel} - g_{\perp} < 0.001$), in accordance with the magnetic properties of π radicals and in contrast to those of the chromium d⁵ complexes.

(2) The line width in the spectrum of CpCrTr^{·-} at +20° (0.3 G) is considerably smaller than that observed for CpCrTr^{·+} (2.0 G) and the isoelectronic species CpCrCHT[·] and Bz₂Cr^{·+} (2.5 G). On the other hand, this line width compares favorably with that found for the tropenyl radical (Tr[·])²⁴ in which the odd electron occupies an antibonding MO e₂ of the tropenyl π system. Moreover, the line width in the spectrum of CpCrTr^{·-} does not markedly depend on temperature, whereas considerable narrowing of the hyperfine components is exhibited by the spectra of CpCrTr^{·+} and its isoelectronic species.

(3) No pronounced line broadening is displayed by the high-field ⁵³Cr satellites of CpCrTr^{·-}, such broadening being characteristic of CpCrTr^{·+} and its isoelectronic analogs.^{1,12}

The differences quoted under (1) to (3) point to the absence of a substantial spin-orbit coupling in the radical anion CpCrTr^{·-}, since such coupling would result in a large deviation of $\langle g \rangle$ from the free electron value, a considerable g anisotropy, a relatively short and temperature-sensitive relaxation time T_{1e} , and a marked ⁵³Cr hyperfine anisotropy. A major participation of a metal AO, either of 3d or 4p type, can therefore be

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excluded for the LUMO of CpCrTr, and a *dominant contribution of the ligand π MO's must be favored*. This conclusion implies that the similarity in the absolute values of the coupling constants $a(\text{H})$ and $a(^{53}\text{Cr})$ for CpCrTr \cdot^+ and CpCrTr \cdot^- should be regarded as accidental.

The LUMO of CpCrTr is considered to be a combination of the antibonding MO's e_2 of the cyclopentadienyl (Cp) and tropenyl (Tr) π systems. The relative magnitudes of the proton coupling constants $a(\text{H})$ indicate that Tr is the major ($2/3$) and Cp the minor ($1/3$) contributor to this combination, in accordance with the relative energies of the component MO's (the orbitals e_2 of Tr lie considerably lower than the corresponding orbitals of Cp). Since the MO's e_2 of Cp and Tr display the same nodal properties as the benzene antibonding e_{2u} orbitals, a π -type LUMO of CpCrTr (represented by a combination of ligand e_2 MO's) should correlate with the above mentioned e_{2u} orbital of Bz $_2$ Cr. It is therefore tempting to assume that the characterization of the LUMO in CpCrTr as a dominantly π -ligand orbital is also valid for Bz $_2$ Cr.

The single occupancy of an orbital with a dominant π -ligand character demands that the coupling constant $a(\text{H})$ of a ring proton bound to a carbon π center μ should essentially arise from π (ligand)- σ (ligand) spin polarization and be opposite in sign to the carbon π -spin population ρ_{μ^π} . Since the high symmetry of Cp and Tr requires positive values ρ_{μ^π} at all ligand π centers, the coupling constants $a(\text{H})$ of the ring protons in CpCrTr \cdot^- should be negative, in contrast to the corresponding cation CpCrTr \cdot^+ and the isoelectronic species CpCrBz \cdot and Bz $_2$ Cr \cdot^+ . For these d^3 complexes, the sign of the coupling constants $a(\text{H})$ was determined to be positive by ^1H nmr studies on solid samples,^{1,12} in accordance with the postulated $3d(\text{metal})$ - σ (ligand) spin delocalization as the major mechanism responsible for the spin transfer onto ring protons. Analogous ^1H nmr investigations of CpCrTr \cdot^- which could have provided an experimental confirmation for the negative sign of the coupling constants $a(\text{H})$ have been unsuccessful so far, because of difficulties in preparing solid samples of K $^+$ CpCrTr \cdot^- . An alternative procedure was therefore attempted which can in principle offer

information about the character of the ligand spin population *via* esr studies of the effect of methyl substitution on the proton hyperfine structure. As stated in the Results, the instability of the pertinent radical anion CpCrMeTr \cdot^- prevented a detailed esr analysis which would have provided data for an application of this procedure.

As for the coupling constants $a(^{53}\text{Cr})$ of the central metal atom in CpCrTr \cdot^- , the absence of a substantial spin-orbit coupling renders improbable a significant contribution of a chromium d or p AO to the singly occupied orbital. The observation of a considerable value $a(^{53}\text{Cr})$ must therefore be ascribed to π (ligand)-ns(metal) spin polarization. The sign of $a(^{53}\text{Cr})$ cannot be readily predicted, because the effective spin density at the ^{53}Cr nucleus may result from ns contributions of either sign.²⁵ Nor can this sign be determined experimentally, as done in the case of CpCrTr \cdot^- , CpCrBz \cdot , and Bz $_2$ Cr \cdot^+ by studies of the ^{53}Cr hyperfine anisotropy, since such an anisotropy is missing for CpCrTr \cdot^- .

Conclusion

A general characterization of the LUMO's in bis-arene-chromium complexes as π -ligand type orbitals would provide a basis for interpreting the resistance of these compounds to form radical anions. The energies of the LUMO's having such a π -ligand character should follow the same sequence as the corresponding orbitals of the respective free π ligands. However, since the coordination of a neutral π system to chromium is accompanied by a net metal \rightarrow ligand charge transfer,²⁶ the energy of the LUMO is *raised* upon complex formation: *i.e.*, the electron affinity *decreases*. In order to achieve a reduction of the π complex to its radical anion, such decrease must be compensated either by strongly electron-attracting substituents or by hydrocarbon ligands with an inherently higher electron affinity.

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