solvent (dioxane, for example) would produce good glasses. It would seem wise to compare several possible solvents when the resolution of a particular spectrum is in question.

The perpendicular branch of the esr spectrum of the 2:1 complex is markedly different in the present study than that of Co(pc) in the presence of various amines.[3] The only spectrum of a 2:1 adduct which was similar to those observed by Assour[3] was that of the quinuclidine adduct. This may indicate that this six-coordinate complex (and possibly also those of Co(pc)[3]) is distorted from octahedral symmetry, possibly causing one amine–cobalt bond to be longer than the other, or pushing the cobalt ion out of the plane of the porphyrin ring as it probably is in the five-coordinate complexes.[23a,b,e,g] Such distortions have been observed in metal porphyrins; for example, see ref 23f for an interesting report on the crystal structure of the low-spin Fe(III) complex FeTPP(imidazole)$_2^+$Cl$^-$, which shows distinctly different bond lengths for the two imidazole N–Fe bonds, and a slight displacement of Fe from the plane of the porphyrin nitrogens.

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Electron Delocalization and Bonding in Some Paramagnetic Bisarene Complexes. I. Nuclear Magnetic Resonance Contact Shift Studies

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Abstract: The nuclear magnetic resonance contact shifts have been observed for a large number of paramagnetic bisbenzene and methyl-substituted bisbenzene complexes of first row transition metals. Electron delocalization was rationalized consistently on the basis of competing direct σ and indirect π delocalization mechanisms, the π mechanism becoming dominant in traversing the transition series from left to right. Pseudocontact shifts were estimated for D_{6h} and C_{2v} symmetries, and found to be negligible in all cases studied except possibly for the bishexamethylbenzeneiron(I) cation. The anomalous upfield methyl resonance shifts for Cr(I) and V(0) methyl-substituted complexes have been explained in terms of a strong polarization of the filled, predominantly metal e_{2g} MO's by the unpaired spin in the a_{1g} MO. Contrary to proposals which place the highest energy electrons in ring antibonding orbitals, in the complexes reported here as in most of the metallocenes, the highest energy electrons are placed in molecular orbitals which are largely metal ion and whose energy ordering is precisely that predicted by ligand-field theory: $d_{x^2-y^2}, d_{xy} < d_{z^2} \ll d_{xy}, d_{yz}$.

The recent nmr contact shift studies of the metallocenes by Rettig and Drago,[2,3] which recognized the importance of the σ orbitals of the ligand in delocalization of spin density, prompted our investigation of the contact shifts of a large number of paramagnetic bisarene complexes. Preliminary results for Cr(C$_6$H$_6$)$_2^+$ and V(C$_6$H$_6$)$_2$ have been reported.[4] The dominance of σ delocalization has been demonstrated for these species and a detailed analysis of the value of ψ^2 at the ring protons has shown that a "direct interaction" between the metal orbitals and the hydrogen 1s orbital, recently postulated by several workers,[5,6] makes only a small contribution to this extensive σ delocalization. Subsequent qualitative work by Prins[7] has reached essentially the same conclusions as Rettig and Drago[3] concerning delocalization in the metallocenes.

The nature of electron delocalization in the analogous benzene complexes, while having been the subject of several epr,[8–13] nmr,[6] and theoretical[7,13,14] studies, has

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been elusive owing to the widespread interpretation of these species primarily as "π complexes" and the neglect of the possible role of σ orbitals (it is recognized that σ and π separability is only approximate; σ is conveniently used to specify in-plane ring orbitals). At the same time, the above workers mention the probable role of σ orbitals, without, however, investigating it further. Recent extended Hückel calculations by different workers for various metallocenes,[3,15,16] bisbenzenechromium cation,[4,14] and benzenechromium tricarbonyl[17] have all supported the quantitative importance of the in-plane ring orbitals in bonding in these systems.

The contact shifts observed by Karimov, *et al.*,[6] for bisbenzenechromium and bistoluenechromium cations pose an interesting problem, as recently pointed out by Prins.[7] While large downfield shifts are observed for the ring protons, analogous to vanadocene and chromocene and characteristic of σ delocalization, the methyl resonance is shifted *upfield* in the substituted species, which is not characteristic of either σ or π delocalization mechanisms[2,3,7] in the metallocenes. Since the pseudocontact effect must be small at the protons owing to the very small anisotropy observed in the g tensor,[14] obviously some other mechanism is operative which places net β spin on the methyl protons in these d^5 systems. Several substituted and unsubstituted d^5 complexes were therefore investigated in our attempt to elucidate the nature of electron delocalization and arrive at a consistent interpretation of all experimental data. In a subsequent article, we shall show that molecular orbital calculations for various bisbenzene complexes give a good account of experimental coupling constants in terms of competing σ and π delocalization mechanisms. Consistent with our earlier work on the metallocenes, π delocalization increases across the transition series in the bisarene complexes until it finally dominates σ delocalization effects, which are still quite large. In this regard, we disagree with Fritz, Keller, and Schwarzhans[18] recently proposed qualitative theory to account for experimentally observed differences between the biscyclopentadienyl and bisbenzene complexes.

Experimental Section

A. Preparation of Compounds. The preparation of the bisarene complexes described below required, in general, inert atmosphere techniques, particularly the use of Schlenk tubes. Herzog, *et al.*,[19] have discussed the use of this equipment and the various manipulations of samples in an inert atmosphere. Commercial HP oil-pumped compressed nitrogen was used as the inert gas in all cases and was dried prior to use by passing it through a 30-in. column of Aquasorb, supplied by Mallinckrodt Chemical Co. No difficulty was experienced with oxygen contamination of the commercial nitrogen. If present, its effects were not great enough to cause any noticeable oxidation of samples.

Prior to use all solvents were deoxygenated by bubbling nitrogen through them for at least 1 hr. Rubber serum caps were used to seal the containers. Small quantities of nmr solvents were degassed by the freeze–thaw technique. Aldrich mesitylene was further purified by extraction with concentrated H_2SO_4 followed by washing with H_2O, drying, and redistillation.

Air- and moisture-sensitive materials were handled in a polyethylene I^2R glove bag connected to a nitrogen supply. Sensitive materials were exposed to the atmosphere in the bag for a minimal amount of time. Materials that were merely water sensitive were handled in a continuous flow drybox. The dew point within the drybox was generally less than $-60°$.

The reagent aluminum halides used required purification before use. Aluminum chloride was easily sublimed under high vacuum at a temperature of about 150°, giving an almost pure white, waxy product. Aluminum bromide was easily sublimed or distilled to give pure white crystalline material. The bromide was generally used immediately after sublimation because of its reactivity. Carbon and hydrogen were analyzed by conventional methods. In several cases, the samples were too sensitive to obtain satisfactory analyses. Larger amounts of these latter materials were analyzed for the metal only, to minimize the error.

1. Solutions Containing $M(arene)^{2+}$ Cations. Since $M(arene)^{2+}$ species (where arene = benzene and toluene) generally cannot be isolated as stable salts, it was decided to prepare solutions containing these species where M = V and Co by the method of Calderazzo,[20] who demonstrated the existence of $V(MES)_2^+$ (MES = 1,3,5-trimethylbenzene) species in the reaction by precipitating an extremely unstable $V(MES)_2I$. The solutions of $Co(C_6H_6)_2^+$ and $Co(C_6H_5CH_3)_2^+$ were prepared from $CoBr_2$, Al powder (equimolar with $CoBr_2$), a threefold excess of $AlBr_3$, and excess benzene or toluene, respectively. The reactants were heated in a sealed tube at 120° for 24 hr. During this time, the $CoBr_2$ was observed to react and the reaction mixtures turned a deep yellow-brown. Upon cooling a large amount of yellow material precipitated. The sealed tubes were opened in a nitrogen filled glove bag, transferred to a Schlenk tube, and the solutions were filtered under nitrogen. The characterization of these species will be discussed in detail presently.

2. Bistoluenechromium(I) Iodide. The procedure described in *Inorganic Syntheses*[21] was followed, using toluene and $AlBr_3$ in place of benzene and $AlCl_3$, respectively. This crude product (containing Cr_2O_3) was purified by dissolving it in a minimum of deoxygenated CH_2Cl_2, filtering off the green Cr_2O_3, and precipitating a fine, yellow, air-sensitive powder.

Anal. Calcd for $CrC_{14}H_{16}I$: Cr, 14.32; C, 46.29; H, 4.44. Found: Cr, 14.14; C, 46.50; H, 4.51.

3. Bishexamethylbenzenechromium(I) Iodide. Anhydrous $CrCl_3$ (3.06 g, 0.0194 mol), 0.9 g of Al powder, 8.01 g of $AlCl_3$, and 7.01 g of hexamethylbenzene were placed in a 50-ml round-bottom flask fitted with a stopcock. The flask was evacuated and the reactants were melted together at 140° for 18 hr. The red-brown melt was pulverized under nitrogen, and the iodide was prepared after dithionite reduction, the cation being formed by air oxidation of the neutral $Cr(HMBZ)_2$ in benzene. The air- and light-sensitive iodide was reprecipitated from CH_2Cl_2 with ether to give a yellow-orange air-sensitive powder which was dried under vacuum. The preparation of this compound was reported first by Fischer, who unfortunately gave few details.

Anal. Calcd for $CrC_{24}H_{36}I$: Cr, 10.33; C, 57.25; H, 7.21. Found: Cr, 10.41; C, 57.24; H, 7.32.

4. Bisbenzenevanadium(0). The procedure of Fischer and Reckziegel[22] was followed exactly, using a threefold excess of $AlCl_3$. The red-brown product was sublimed twice at 150° under high vacuum to effect purification. The pyrophoric, crystalline, deep red solid was too air-sensitive to obtain C and H analyses; however, larger samples could be analyzed for vanadium. Properties agreed with those previously reported by these workers.

Anal. Calcd for $VC_{12}H_{12}$: V, 24.60. Found: V, 24.33.

5. Bishexamethylbenzenevanadium(0). The product was obtained by melting together reactants as in the preparation of the chromium analog and working up according to the procedure of Fischer and Reckziegel.[22] The extremely air-sensitive, red-brown product was purified by recrystallization. The preparation of this compound is only alluded to in the literature.[23] No details or properties were given.

Anal. Calcd for $VC_{24}H_{36}$: C, 13.57. Found: V, 13.3.

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6. Bishexamethylbenzeneiron(II) Hexafluorophosphate and Hexachloroplatinate. $Fe(HMBZ)_2(PF_6)_2$ was synthesized by melting together, as previously described, stoichiometric quantities of $FeBr_2$, $C_6(CH_3)_6$, and $AlBr_3$ at 90° for 6 hr. Both Zeiss[24] and Fischer[25] have prepared these compounds without elaborating on their properties. The infrared spectrum of $Fe(HMBZ)_2(PF_6)_2$ exhibits the following absorption frequencies (in cm^{-1}): 3000 (vw), 2945 (w), 1625 (w), 1448 (m), 1400 (s), 1301 (m), 1265 (vw), 1078 (m), 1022 (m), 1004 (m), 850 (vs), 743 (w), 563 (s), 488 (w), 475 (sh), 444 (w), 404 (w), and 377 (w). $Fe(HMBZ)_2PtCl_6$ shows bands at 3040 (w), 2990 (w), 2915 (m), 1625 (w), 1442 (m), 1392 (s), 1302 (m), 1265 (vw), 1078 (m), 1018 (sh), 1000 (m), 488 (w), 378 (w), and 322 (s).

Anal. Calcd for $FeC_{24}H_{36}P_2F_{12}$: Fe, 8.33; C, 43.00; H, 5.41. Found: Fe, 8.13; C, 42.33; H, 5.55. Calcd for $FeC_{24}H_{36}PtCl_6$: Fe, 7.09; C, 36.57; H, 4.60. Found: Fe, 6.84; C, 34.87; H, 4.34.

7. Bismesityleneiron(II) Hexafluorophosphate. Following the earlier preparation of Fischer and Böttcher,[26] this compound was prepared by allowing anhydrous $FeBr_2$, $AlCl_3$, and mesitylene to react under nitrogen at 90° for 4 hr.

Anal. Calcd for $FeC_{18}H_{24}P_2F_{12}$: Fe, 9.53; C, 36.88; H, 4.13. Found: Fe, 8.95; C, 37.30; H, 4.22.

8. Bishexamethylbenzeneiron(I) Hexafluorophosphate. $Fe(HMBZ)_2PF_6$ was prepared by a modification of Fischer and Rohrscheid's preparation of this compound,[25] using solid $Fe(HMBZ)_2(PF_6)_2$ obtained above instead of the cation solution during the dithionite reduction step. Their procedure led to contamination of the product with insoluble aluminum hydroxide. $Fe(HMBZ)_2(PF_6)_2$ (2.2 g, 0.0030 mol) was placed in a Schlenk tube which was evacuated and filled with nitrogen. A reducing solution (50 ml) was prepared under nitrogen using 5.0 g of sodium dithionite buffered with 5.0 g of sodium acetate. This solution was then added to the iron salt in a countercurrent of nitrogen, which immediately gave a deep purple suspension. After stirring for several minutes the product was filtered, washed with four portions of deoxygenated water, and dried under vacuum for several hours. The dry product was then washed with several portions of ether to remove hexamethylbenzene impurities. The yield was essentially quantitative. $Fe(HMBZ)_2PF_6$ is essentially insoluble in water, methanol, and ethanol; slightly soluble in acetone and chloroform; and very soluble in nitromethane, trimethyl phosphate, sulfolane, DMSO, pyridine, acetonitrile, and dichloromethane. Decomposition occurs within a short period of time in all solvents. Solutions in dichloromethane were found to be stable indefinitely if kept at Dry Ice temperatures. The infrared spectrum agreed with that reported by Fischer and Rohrscheid.[25]

Anal. Calcd for $FeC_{24}H_{36}PF_6$: Fe, 10.63; C, 54.87; H, 6.91. Found: Fe, 10.45; C, 54.77; H, 6.79.

9. Bismesityleneiron(I) Hexafluorophosphate. The preparation was carried out as for $Fe(HMBZ)_2PF_6$ using $Fe(MES)_2(PF_6)_2$ as the starting material and taking care to exclude air from the system. The dithionite reducing solution was added quickly to the orange reactant causing it to turn deep purple. The mixture was stirred manually under N_2 for a few seconds, the reducing solution immediately removed under vacuum, and the product washed repeatedly with water, followed by acetone and ether, and finally dried under vacuum. The blackish purple material was purified by extracting the product with about 25 ml of deoxygenated CH_2Cl_2 at −78° and filtering the extract into 300 ml of anhydrous deoxygenated ether, causing a deep blue precipitate to form. The ether and CH_2Cl_2 were evaporated under high vacuum leaving a blue air-sensitive powder. This compound had not been prepared previously.

Anal. Calcd for $FeC_{18}H_{24}PF_6$: C, 49.00; H, 5.48. Found: C, 46.57; H, 5.69.

10. Bishexamethylbenzenecobalt(I) Hexafluorophosphate. The preparative procedure described by Fischer and Lindner[27] was followed for these complexes, melting together stoichiometric amounts of anhydrous $CoCl_2$, $C_6(CH_3)_6$, and Al powder with a fivefold excess of freshly sublimed $AlCl_3$ and heating the mixture at 120° for 2 hr. The product was air stable and very soluble in both acetone and dichloromethane. Decomposition was observed within a few minutes with acetone and within 15 min with CH_2Cl_2. Solutions in CH_2Cl_2 were stable indefinitely if kept in a Dry Ice bath. The infrared spectrum of $Co(HMBZ)_2PF_6$ agreed with that reported by Fischer and Lindner.[27]

Anal. Calcd for $CoC_{24}H_{36}PF_6$: Co, 11.15; C, 54.55; H, 6.87. Found: Co, 10.92; C, 54.34; H, 6.79.

11. Bishexamethylbenzenecobalt(II) Hexachloroplatinate. The preparation above for the Co(I) complex was repeated without the Al powder in the melt step. Precipitation of the *cold* hydrolysis solution with 3.0 g of H_2PtCl_6 in about 25 ml of water gave a yellow-brown hydrophobic substance which was dried under vacuum, digested with several portions of ether, and finally vacuum dried. This compound was identical with that reported by Fischer and Lindner,[27] exhibiting an identical infrared spectrum. The substance was insoluble in all solvents except for DMSO and DMF, where decomposition was nearly instantaneous.

Anal. Calcd for $CoC_{24}H_{36}PtCl_6$: Co, 7.45; C, 36.32; H, 4.58. Found: Co, 7.18; C, 35.65; H, 4.59.

12. Bishexamethylbenzenenickel(II) Hexachloroplatinate. The preparative procedure described for this complex by Lindner and Fischer[28] was followed exactly to give a brownish yellow product which contained a slight excess of $PtCl_6^{2-}$. $Ni(HMBZ)_2PtCl_6$ is insoluble in practically all solvents.

Anal. Calcd for $NiC_{24}H_{36}PtCl_6$: Ni, 7.42; C, 36.44; H, 4.59. Found: Ni, 6.68; C, 33.99; H, 4.66.

B. Apparatus and Techniques. 1. Nmr Spectra. Nuclear magnetic resonance data were obtained using Varian DP-60, HA-100, or Jeolco C-60H spectrometers. Signals were usually recorded on the DP-60 employing the wide-line phase detector which gives a derivative presentation of the spectrum. We found this technique useful in increasing the signal-to-noise ratio when recording extremely broad signals. Calibration of the spectrum was accomplished with an external rf oscillator. Contact shifts were measured from the free ligand reference, which, in many cases, was also the solvent. In most instances, the shifts were so large that this procedure caused errors much less than the hysteresis effects of sweeping the field. The latter effects were averaged out by recording several spectra (sweeping upfield and downfield) and averaging the results. Spectra generally were run at a fairly high power level, but at a modulation amplitude low enough to avoid distortion of the line shape. Any modulation amplitude less than half the observed line width is satisfactory. Spectra were recorded on the DP-60 without spinning the sample. Temperature measurements were made on the DP-60 or Jeolco C-60H with a calibrated copper–constantan thermocouple or with a commercial thermistor; the accuracy of these measurements was estimated to be ±1.0°.

Wide-line spectra were recorded on the DP-60 using the Model V-4280 precession scanning unit, generally at a rate of 0.9700–2.586 G/min. Shifts were measured relative to an external diamagnetic material (benzene or water). The variable temperature probe has a lower limit of around −95°.

2. Visible and Near-Infrared Spectra. All visible and near-infrared spectra were recorded on a Cary spectrometer, Model 14RI. The solvent usually was run as a reference blank. Mull spectra were run in Nujol against a reference of Nujol on filter paper.

3. Infrared Spectra. All spectra were run on a Model 521 Perkin-Elmer grating spectrometer. Since Nujol, Fluorolube, and KBr spectra were found to be identical, spectra generally were run in KBr pellets without decomposition occurring. In all cases where stability permitted, ir spectra agreed with results reported in the literature.

4. Epr Spectra. The spectrum of $V(C_6H_6)_2$ was recorded in 1:1 methylcyclohexane–toluene solution at both room temperature and at 77°K (glass) on the Varian V-4502 epr.

Results and Discussion

The goal of this investigation is to obtain a consistent picture of electron delocalization in the bisarene complexes of the first row transition metals, and to further understand molecular structure and bonding in these species. While theoretical models of bonding have been proposed, very little experimental work has been done to validate these theories. We therefore will critically examine several ideas which have been proposed to explain delocalization and bonding, and then

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present evidence from a variety of experimental studies which will support what we feel to be a more consistent model.

General Aspects of Bonding in the Bisarene Complexes. Our discussion and interpretation of this experimental investigation will utilize a MO approach. While calculations of this type have been of an approximate, semiempirical nature, they have provided considerable insight into and general agreement regarding the ordering of the filled energy levels relative to one another. Figure 1 presents a molecular orbital diagram for bisbenzenecobalt(I) cation which is isoelectronic with nickelocene. The filled orbitals in the semiempirical calculation of Fischer[29] for $V(C_6H_6)_2$ and the SCF calculation of Shustorovich and Dyatkina for $Cr(C_6H_6)_2^+$ [30] are in substantial agreement with this scheme. As previously reported,[3,15] on the basis of extended Hückel calculations (EHC), the *relative* ordering of molecular orbitals remains constant for the neutral molecule series from vanadocene to nickelocene. Three electrons in vanadocene occupy e_{2g} and a_{1g} molecular orbitals $(\ldots e_{2g}{}^2a_{1g}{}^1)$ which are mainly $d_{x^2-y^2}$, $d_{xy}(e_{2g})$, and $d_{z^2}(a_{1g})$. The additional electrons required as we proceed to nickelocene spin pair in these orbitals and then are added to $e_{1g}{}^*$ (largely d_{xz}, d_{yz}) in cobaltocene and nickelocene. The configuration is that predicted by ligand-field theory but there is extensive mixing of the ligand orbitals in these molecular orbitals. This study eliminated the possibility of proposed configurations which contained unpaired electrons in largely ligand, antibonding molecular orbitals. The same results are obtained for the bisbenzene complexes which for a given metal atom contain two more electrons than the biscyclopentadienyl complexes. The highest energy electrons are added to molecular orbitals which are largely metal in the order $e_{2g} < a_{1g} \ll e_{1g}{}^*$. Again there is confusion regarding the electron configuration of many bisarene complexes. The epr of $Fe(HMBZ)_2^+$ was interpreted by Brintzinger, *et al.*,[13] as suggesting the electron occupies the $e_{2u}{}^*$ level. We shall show that this is incorrect and that the configuration most probably is $(e_{2g})^4(a_{1g})^2(e_{1g}{}^*)^1$ as predicted from a ligand-field approach. In our discussion of these complexes, we have eliminated from consideration the relative energies and orderings of empty molecular orbitals. There is considerable uncertainty in the ability of our MO calculation to give valid information about virtual orbitals. Since EHC are carried out with all valence orbitals including the 2s, $2p_x$, and $2p_y$ in-plane carbon orbitals and the 1s orbitals of the ring protons, this gives rise to many more molecular orbitals than are shown in Figure 1. We have indicated only the highest energy filled molecular orbitals. The ring σ orbitals transform under the symmetry group D_{6h} to give the same irreducible representations as the π ring orbitals. This implies that the "σ" framework molecular orbitals are substantially mixed with the "π" framework orbitals, and that in fact it is impossible to conceive of their *physical* separation. Conceptually, however, it is convenient to distinguish between the in-plane (p_x,p_y) ring orbitals comprising σ MO's and out-of-plane ring orbitals (p_z) comprising π MO's, and we shall take this liberty in this discussion.

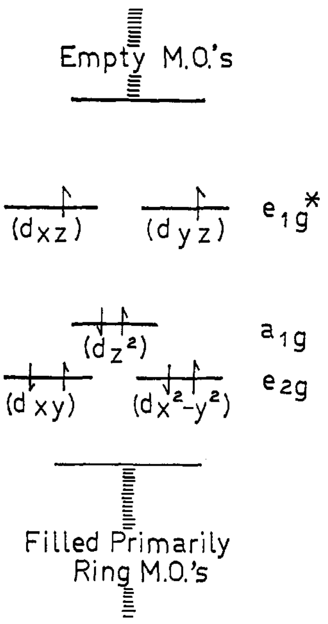

Figure 1. An approximate partial molecular orbital diagram for bisbenzenecobalt(I) cation.

An important clue to the electronic configuration of the bisarene complexes is the magnetic moment which leads directly to the number of unpaired electrons. The departure from the "spin-only" value of μ_{eff} also gives important information about the electronic ground state. Magnetic moment data for a large number of these benzene and substituted benzene complexes are tabulated in Table I. Both Schustorovich and Dyatkina[31] and Robertson and McConnell[32] have

Table I. Magnetic Moments of Bisarene Complexes

Compound	No. of unpaired electrons	μ_{eff}, exptl	μ_{eff}, spin-only	Ref
$V(BZ)_2$[a]	1	1.68 ± 0.08	1.73	*e, f*
$V^I(MES)_2AlCl_4$[b]	2	2.80 ± 0.17	2.83	*e*
$Cr(BZ)_2$	0	0	0	*f, g*
$Cr(TOL)_2$[c]	0	0	0	*g*
$Cr(MES)_2$	0	0	0	*g*
$Cr(HMBZ)$[d]	0	0	0	*g*
$Cr^I(BZ)_2AlCl_4$	1	1.77	1.73	*g*
$Fe^{II}(MES)_2I_2$	0	0	2.83	*e*
$Fe^I(HMBZ)_2PF_6$	1	1.89	1.73	25
$Fe^0(HMBZ)_2$	2	3.08	2.83	25
$Co^{II}(HMBZ)_2PtCl_6$	1	1.73 ± 0.05	1.73	27
$Co^I(HMBz)_2PF_6$	2	2.95 ± 0.08	2.83	27
$Co^0(HMBZ)_2$	1	1.86	1.73	*h*
$Ni^{II}(HMBZ)_2(AlCl_4)_2$	2	3.00 ± 0.09	2.83	28

[a] BZ = benzene. [b] MES = mesitylene = 1,3,5-trimethylbenzene. [c] TOL = toluene. [d] HMBZ = hexamethylbenzene. [e] E. O. Fischer, G. Joos, and W. Meer, *Z. Naturforsch. B*, **13,** 456 (1958). [f] E. O. Fischer and H. P. Kögler, *Chem. Ber.*, **90,** 250 (1957). [g] E. O. Fischer and J. Piesbergen, *Z. Naturforsch. B*, **11,** 758 (1956). [h] E. O. Fischer and H. H. Lindner, *J. Organometal. Chem.*, **2,** 222 (1964).

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(32) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.*, **64,** 70 (1960).

Table II. Electronic Configurations of Various Bisarene and Metallocene Complexes

Compound	No. of d electrons	Probable configuration	Probable ground state	Ref
$V(cp)_2$	3	$\ldots(e_{2g})^2(a_{1g})^1$	$^4A_{1g}$	2
$Cr(cp)_2$	4	$\ldots(e_{2g})^3(a_{1g})^1$	$^3E_{2g}$	2
$V(BZ)_2^+$	4	$\ldots(e_{2g})^3(a_{1g})^1$	$^3E_{2g}$	This work, *a*
		or		
		$\ldots(a_{1g})^2(e_{2g})^2$	$^3A_{1g}$	
$Cr(BZ)_2^+$	5	$\ldots(e_{2g})^4(a_{1g})^1$	$^2A_{1g}$	32, *b*
$Fe(cp)_2^+$	5	$\ldots(a_{1g})^2(e_{1g})^3$	$^2E_{2g}$	2, *c*
$V(BZ)_2$	5	$\ldots(e_{2g})^4(a_{1g})^1$	$^2A_{1g}$	12, *d*
$Cr(BZ)_2$	6	$\ldots(e_{2g})^4(a_{1g})^2$	$^1A_{1g}$	e, *f*
$Fe(cp)_2$	6	$\ldots(e_g)^4(a_{1g})^2$	$^1A_{1g}$	2
$Fe(HMBZ)_2^{2+}$	6	$\ldots(e_{2g})^4(a_{1g})^2$	$^1A_{1g}$	*d*
$Co(cp)_2$	7	$\ldots(e_{2g})^4(a_{1g})^2(e_{1g}^*)^1$	$^2E_{1g}$	2
$Co(HMBZ)_2^{2+}$	7	$\ldots(e_{2g})^4(a_{1g})^2(e_{2g}^*)^1$	$^2E_{1g}$	This work
		or		
		$\ldots(e_{2g})^4(a_{1g})^2(e_{2u}^*)^1$	$^2E_{2u}$	
$Fe(HMBZ)_2^+$	7	$\ldots(e_{2g})^4(a_{1g})^2(e_{2u}^*)^1$	$^2E_{2u}$	13
		or		
		$\ldots(e_{2g})^4(a_{1g})^2(e_{1g}^*)^1$	$^2E_{1g}$	This work
$Ni(cp)_2$	8	$\ldots(e_{2g})^4(a_{1g})^2(e_{1g}^*)^2$	$^3A_{1g}$	*g*
$Co(HMBZ)_2^+$	8	$\ldots(e_{2g})^4(a_{1g})^2(e_{1g}^*)^2$	$^3A_{1g}$	This work
$Ni(HMBZ)_2^{2+}$	8	$\ldots(e_{2g})^4(a_{1g})^2(e_{1g}^*)^2$	$^3A_{1g}$	This work

[a] E. M. Shustorovich and M. E. Dyatkina, *Russ. J. Inorg. Chem.*, **6**, 249 (1961). [b] See also ref 14. [c] D. R. Scott and R. S. Becker, *J. Phys. Chem.*, **69**, 3207 (1965). [d] See foonote *e* of Table I. [e] See footnote *f* of Table I. [f] See footnote *g* of Table I. [g] R. Prins, J. D. W. Van Woorst, and E. J. Schinkel, *Chem. Phys. Lett.*, **1**, 54 (1967).

Table III. Solution Nmr Contact Shifts[a] and Hyperfine Coupling Constants for Various Bisarene Complexes

Complex	$\Delta\nu_H$[b] (line width)	$\Delta\nu_{CH_3}$ (line width)	A_H, G[c]	A_{CH_3}, G
$V(C_6H_6)_2^+$	−13,990 (1850)		1.13	
$V(C_6H_5CH_3)_2^+$	−16,740 (4960)	−8400 (1630)	1.34	0.824
$V(C_6H_3(CH_3)_3)_2^+$	−16,410 (2903)	−3860 (410)	1.23	0.306
$Co(C_6H_6)_2^+$	+3,540 (190)		−0.276	
$Co(C_6H_5CH_3)_2^+$	+3,350 (500)	−2660 (73)	−0.294	0.211
	+4,100 (500)		−0.334	
$Co(HMBZ)_2PF_6$		−3695 (65)		0.308
$Fe(HMBZ)_2PF_6$[d]		−259 (60)		0.0646

[a] Temperature = 298° K. [b] $\Delta\nu$'s and line widths are in Hz at 60 MHz. Shifts for very broad lines are accurate to ±3%; otherwise the uncertainty is ≤1%. [c] A's are in G. The values were calculated from the least-squares slope of the $\Delta\nu_{obsd}$ *vs.* $1/T$ plots using eq 2, and values of g_{av} were derived from the μ_{eff}'s given in Table I from the formula $g_{av} = \mu_{eff}/\sqrt{S(S+1)}$. [d] $g_{av} = (g_x + g_y + g_z)/3$. g values were obtained from ref 13.

discussed electronic configuration for these sandwich molecules, in general, by consideration of departure from spin-only moments and of orbital contributions to observed moments. A Jahn–Teller distortion is, of course, predicted for molecules with degenerate ground states. Table II summarizes the reported electronic configurations of the bisarene complexes and, where more than one possible configuration are listed, our contact shift studies have resolved this uncertainty (*vide infra*).

Theory and Treatment of the Solution Contact Shift Data. Under conditions of rapid electron relaxation (which will be justified presently), when the Curie law is obeyed, the nuclear magnetic resonance contact shift $\Delta\nu$ (in Hz) is given by the familiar expression

$$\frac{\Delta\nu}{\nu_0} = \frac{-Ag_{av}\beta_e S(S+1)}{g_N\beta_N(3kT)} \qquad (1)$$

The symbols in (1) are defined in the literature.[3] Since the coupling constant A in (1) is in ergs but is conveniently expressed in gauss, the following equation was derived to convert the contact shift $\Delta\nu$ in Hz to A (gauss)

$$A = \frac{-(2.265 \times 10^{-6})T\Delta\nu}{g_{av}^2 S(S+1)} \qquad (2)$$

assuming a probe frequency of 60 × 10⁶ Hz. Since this equation requires that the system under investigation obey the Curie law, the observed contact shift data were plotted *vs.* $1/T$ in all cases to ensure linearity and extrapolation through $\Delta\nu = 0$ for $1/T = 0$.

In Table III, the contact shifts $\Delta\nu$ are reported for all species studied in solution, along with the hyperfine coupling constants A in gauss units. These shifts are reported relative to the solvents, benzene and toluene, respectively, for the bisbenzene and bistoluene complexes. The large magnitude of the shifts and the experimental error in measuring them were always greater than the error of not reporting these shifts relative to resonances in diamagnetic complexes. The contact shifts for $Co(HMBZ)_2PF_6$ and $Fe(HMBZ)_2PF_6$ were measured in CD_2Cl_2 as solvent, and were calculated with respect to the methyl resonance in diamagnetic $Fe(HMBZ)_2(PF_6)_2$, since the shifts were on the order of only several hundred hertz. A typical spectrum, that of bistoluenecobalt(I) cation, is illustrated in Figure 2. The temperature dependence of the contact shifts has been determined for $V(C_6H_6)_2^+$, $V(C_6H_5CH_3)_2^+$, V[C$_6$H$_3$-

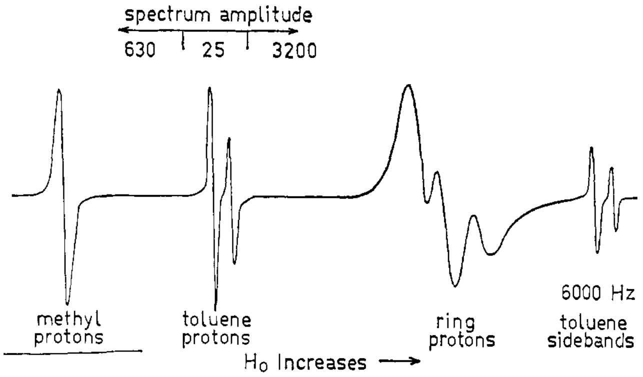

Figure 2. Nmr spectrum of bistoluenecobalt(I) cation in toluene at 298°K.

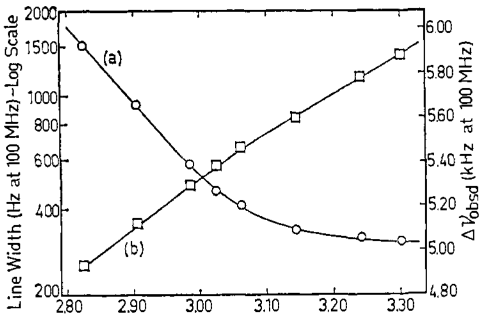

Figure 3. (a) Temperature dependence of log (line width) for ring protons of $Co(C_6H_6)_2^+$ in benzene; (b) temperature dependence of observed ring proton contact shift of $Co(C_6H_6)_2^+$.

$(CH_3)_3]_2^+$, and $Co(C_6H_5CH_3)_2^+$ in the ligand as solvent. $Co(HMBZ)_2PF_6$ and $Fe(HMBZ)_2PF_6$ were studied in CD_2Cl_2. In all cases, each species studied gave straight-line plots and, with the exception of the three vanadium cations, extrapolated to $\Delta\nu_{obsd} = 0$ as $1/T \rightarrow 0$, within experimental error. Nonzero intercepts have been found for a large number of systems and will be discussed in a future publication from this laboratory.[33]

Nature of the Species in Solution. Any discussion of the nmr contact shifts in solution is predicated on knowing the nature of the species in solution. The species observed in the solid state is not necessarily the same in solution. Rearrangements, dissociation, exchange phenomena, and solvation effects may alter the observed contact shifts in such a way that any interpretation on the basis of a supposed species actually is meaningless. All too often in contact shift studies, this problem is overlooked. Strong evidence is available to establish with certainty the existence of all these species in solution. The arguments are identical in all cases.

(1) Confidence in the existence of $V(MES)_2^+$ is based on the work of Calderazzo,[20] who studied this cation in solution. He unequivocally demonstrated the existence of this species in the Friedel–Crafts reaction mixture by precipitating $V(MES)_2I$ with lithium iodide in THF. Our contact shift experiments were done directly on this reaction mixture. The strongest evidence for a *single* species corresponding to $V(MES)_2^+$ is the linearity of the $\Delta\nu_{obsd}$ *vs.* $1/T$ plot. This also holds true at higher temperatures where decomposition might be expected. Plots of $\Delta\nu_{obsd}$ *vs.* $1/T$ were also linear for $V(C_6H_6)_2^+$ and $V(C_6H_5CH_3)_2^+$, prepared using the same procedure as for $V(MES)_2^+$. While the large nonzero intercepts of these plots (non-Curie behavior) may perhaps indicate certain interactions in solution, we feel that the coupling constants, A, determined from the slope of these plots are accurate to within 10%, which will not affect our interpretation of the observed shifts.

(2) Line widths (Table IV) are also consistent with the presence of a single species in solution. Plots of line width *vs.* $1/T$ are linear within experimental error for the vanadium complexes (a slight curvature is detected at very high temperature, about 100°), characteristic of the situation in which exchange is *not* occurring with the solvent or excess ligand.[34] It is this linearity over a rather large temperature range which gives us a degree of confidence in the coupling constants for these vanadium cations in spite of their anomalous non-Curie behavior described above. In Figure 3, the contact shift and the line width behavior of $Co(C_6H_6)_2^+$ is illustrated as a function of $1/T$. The line width (Figure 3a) is again linear with respect to $1/T$ near room temperature, with drastic changes indicative of exchange commencing at higher (~60°) temperature. Decomposition can be ruled out since this effect is reversible; the low-temperature spectrum is reproducible upon cooling the sample. This effect is reflected in the plot of $\Delta\nu_{obsd}$ *vs.* $1/T$ for this same species (Figure 3b), the break in Curie behavior occurring in the same temperature region as exchange begins. The low-temperature region of this plot extrapolates to $\Delta\nu_{obsd} = 0$ as $1/T \rightarrow 0$. $Co(C_6H_5CH_3)_2^+$ shows analogous behavior with a single broad resonance being observed at high temperature (880 Hz wide), broadening commencing rapidly at around 60°. From the behavior of these two cobalt species, we may conclude that they are considerably less stable than the corresponding vanadium species. However, in spite of this obvious exchange at higher temperatures, the contact shifts follow exact Curie law behavior at temperatures below 60°, and we feel safe in interpreting our contact shift data on the basis of a *single* species in solution.

Table IV. Line Width[a] Data for the Bisarenevanadium(I) Cation as a Function of Temperature

		$V(C_6H_5CH_3)_2^+$		$V(MES)_2^+$	
T, °K	$V(C_6H_6)_2^+$	Ring	Methyl	Ring	Methyl
263			2020	3324	465
298	1850	4958	1630	2903	410
319	2200				
337	2020	4000	1280	2730	355
365	2090	3900	1100	2675	347
395		3310	1050	2650	320

[a] Line width is in Hz at 60 MHz. It was measured as the difference between the maximum and minimum points of the derivative spectrum. The experimental error for the very broad lines is ±10%.

(3) In all cases the observed contact shifts themselves are consistent with the presence of the expected single species in solution. The *relative intensities* of signals, *i.e.*, for methyl and ring proton resonances, are ex-

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(33) W. D. Perry and R. S. Drago, manuscript in preparation.

(34) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, 2, 349 (1967).

actly those expected for the proposed complexes in all cases. Furthermore, the solution shifts of $Co(HMBZ)_2PF_6$ and $Fe(HMBZ)_2PF_6$ are identical with the wide-line shifts observed for the respective solids, within experimental error—a strong case that the species in solution is identical with that in the solid.

(4) In the case of $Co(HMBZ)_2PF_6$, infrared spectra of the solid and solution (in CH_2Cl_2) are essentially identical and the bands agree with those reported by Fischer and Lindner.[27] The solution optical spectrum of $Co(HMBZ)_2PF_6$ in CH_2Cl_2 is reported in Table V. Unfortunately, the charge-transfer band is very intense in the visible portion of the spectrum and makes observation of the low-energy bands impossible to observe in the mull.

Table V. Solution Spectral Data for $Co(HMBZ)_2PF_6$

Energy, cm^{-1}	ϵ_{max}
11,910[a]	16.3
13,610[a]	23.9
20,500 (sh)[b]	186
24,100 (sh)	1.23×10^3
26,650 (sh)	1.99×10^3
30,300	4.87×10^3
32,600 (sh)	3.80×10^3
39,200	3.00×10^3

[a] Concentration = 0.0536 *M*, 10-mm cell. [b] Concentration = 4.462×10^{-4} *M*, 2-mm cells.

Interpretation of Solution Contact Shift Data. a. Bisarenevanadium(I) Cations. $V(C_6H_5CH_3)_2^+$ is predicted on the basis of MO calculations to have an electronic configuration of $\ldots(e_{2g})^3(a_{1g})^1$, leading to the degenerate ground state $^3E_{2g}$ (see Figure 1 and Table I). $V(C_6H_6)_2^+$ exhibits a huge downfield shift reminiscent of the shifts observed in vanadocene and chromocene. Upon substitution of a methyl group, a less intense additional downfield peak appears for $V(C_6H_5CH_3)_2^+$, the ring proton resonance being essentially unshifted (see Table III). The fact that the methyl peak also appears downfield in $V(MES)_2^+$ and $V(TOL)_2^+$, but not as far as the ring protons, is indicative that delocalization is occurring *via* a σ mechanism. Dominance of a π mechanism, on the other hand, would lead to an upfield shift of a substituted methyl group, which is not observed.

The situation is analogous to the case of the isoelectronic $Cr(C_5H_5)_2$, except no apparent splitting of the ring protons is observed for $V(C_6H_5CH_3)_2^+$ compared to $Cr(C_5H_4CH_3)_2$. Apparently, the nonequivalence of the ring protons (either on the basis of symmetry or a possible Jahn–Teller distortion[18]) is hidden because of the extremely broad resonance line. Overlapping resonances with a line width of about 2500 Hz would be completely unresolved since the observed line width for the ring protons is ~4900 Hz at 298°K. It is interesting to note that this line width is twice as large as that for the ring protons of either the benzene or symmetrical mesitylene species where no splitting is predicted. This lends additional support to the possibility that the ring proton resonance is indeed split but unresolved in the toluene complex. Unfortunately, experimental data bearing on the actual ground state of $V(C_6H_6)_2^+$ are scarce. The magnetic moment observed for $V(MES)_2AlCl_4$ of 2.80 BM (see Table I) is within experimental error of 2.83, the spin-only value, providing no support for the $^3E_{2g}$ ground state where some orbital contribution to μ_{eff} would be expected. While in opposition to theoretical predictions, an orbital configuration of $\ldots(a_{1g})^2(e_{2g})^2$ would lead to a $^3A_{1g}$ ground state which also would exhibit a near spin-only magnetic moment and favorable nmr relaxation time. As will be seen in a future publication, the spin density calculation conclusively supports the $^3E_{2g}$ ground state.

b. Bisarenecobalt(I) Cations. The spectrum of $Co(C_6H_6)_2^+$ exhibits a large upfield shift of +3535 Hz with a relatively narrow line width of ~300 Hz at 298°. Upon substitution of methyl groups to form the $Co(C_6H_5CH_3)_2^+$ derivative, an additional, equally large downfield shift of −2650 Hz is observed (see Table III). This situation is completely analogous to the isoelectronic case of nickelocene except the shifts are one-fifth the magnitude of the nickelocene shifts. It is clear from the direction and magnitude of the methyl shift that delocalization is dominated by a π mechanism. It is also significant that upon methyl substitution, the nmr resonance of the ring protons *splits* and *broadens*. This upfield multiplet has an intensity ratio of 4:1, which implies that the *ortho* and *meta* resonances occur together, while the *para* proton resonance is by itself farther upfield (see Figure 2). This is reminiscent of the epr behavior observed by Solodovnikov[35] for toluene negative anion. In this latter case, equivalent spin densities (and coupling constants) were observed for the *ortho* and *meta* ring protons and a different (but smaller in this case) spin density (coupling constant) for the *para* position.

The broadening of the ring proton resonances is easily understood upon substitution because of the longer correlation time. The dipolar broadening of the resonance line is increased because of less effective averaging of this effect due to slower tumbling. We will further consider relaxation processes presently.

The narrow line width and near spin-only value of the magnetic moment (2.95 BM based on $Co(HMBZ)_2PF_6$) is consistent with an orbital configuration of $\ldots(a_{1g})^2(e_{1g}^*)^1(e_{1g}^*)^1$ to give a $^3A_{1g}$ ground state. This is in full agreement with predictions based on the analogous isoelectronic nickelocene species.[3] It is also immediately obvious why the observed coupling constants of these Co(I) bisarene complexes are only about one-fourth of the coupling constants reported for isoelectronic nickelocene. In both instances, the unpaired electrons are in e_{1g}^* orbitals so that the mechanisms of delocalization should be similar. However, the *charge* on the $Co(C_6H_6)_2^+$ species, leading to a contracted radial distribution of electron density as well as delocalization over a *larger* ring system, would predict a smaller observed coupling constant than for nickelocene.

c. Bishexamethylbenzeneiron(I) Cation. The methyl proton resonance for the $Fe(HMBZ)_2^+$ species is shifted downfield by 259 Hz from the diamagnetic reference position compared to the 3600-Hz downfield shift observed for the $Co(HMBZ)_2^+$ species (see Table III). Such a small shift could conceivably have its origin in a variety of effects, including the pseudocontact shift which we will examine shortly. Apparently very little net spin is delocalized directly onto the methyl

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[35] S. P. Solodovnikov, *Zh. Strukt. Khim.*, 2, 282 (1961).

group protons, since both σ and π mechanisms are expected to lead to downfield shifts for a methyl group attached to an aromatic ligand. The observation of a *single* relatively sharp resonance ($\sim$60 Hz) at room temperature is consistent with a dynamic Jahn–Teller distortion which seriously broadens the low-temperature epr signal. At any rate, the static distortion observed at 25°K by Brintzinger[13] is not detected in the nmr spectrum at 298°K.

The methyl proton coupling constant of 0.0601 for $Fe(HMBZ)_2^+$ is compared to a value of 0.206 found for $Co(HMBZ)_2^+$. This decrease by a factor of about 3 is entirely reasonable for a species containing one less electron, assuming a similar orbital ordering for the iron and cobalt complexes. Similar decreases in the methyl coupling constant are found in analogous circumstances going from $V(C_5H_4CH_3)_2$ to $Cr(C_5H_4CH_3)_2$ or $Ni(C_5H_4CH_3)_2$ to $Co(C_5H_4CH_3)_2$, for example, where we have the same molecular orbital ordering and a one-electron difference in orbital occupations. Removing an electron from $Co(HMBZ)_2^+$ would give a configuration. . .$(a_{1g})^2(e_{1g}^*)^1$ or an $^2E_{1g}$ ground state for the isoelectronic $Co(HMBZ)_2^{2+}$, which disagrees with Brintzinger's proposal of the electron being in an essentially ligand e_{2u}^* orbital which gives rise to a $^2E_{2u}$ ground state.

The main difference in these two ground states, both of which in principle are susceptible to Jahn–Teller distortions, is that an electron in an e_{1g}^* orbital is mainly associated with the metal, while an electron in an e_{2u}^* orbital is largely on the ligand. Indeed, Brintzinger has claimed the e_{2u}^* orbital is the *only* degenerate level in the orbital scheme where metal spin–orbit coupling cannot bring about resistance to a Jahn–Teller distortion. Nicholson and Longuet-Higgins,[36] whose theoretical work on calculation of a Jahn–Teller distortion for neutral $Co(HMBZ)_2$ bears on this question, admit that electrons located more on the metal atom than the ring would not be expected to cause large Jahn–Teller distortions within the rings. However, a $^2E_{1g}$ ground state can mix configurationally with excited states such as the A_{1u}, A_{2u}, and E_{2u} excited states by E_{1u} vibrational distortions, on which basis these authors predict a high probability of Jahn–Teller distortion in $Co(HMBZ)_2$. Returning to $Fe(HMBZ)_2^+$, the distortion observed by Brintzinger induces very little anisotropy into the observed g values, making an $^2E_{1g}$ ground state (and the small Jahn–Teller distortion) reasonable. An $^2E_{2u}$ ground state in which the electron is mainly located on the ligand would surely give a large static distortion which conceivably could persist even at higher temperatures. The most convincing argument against an $^2E_{2u}$ ground state is that huge contact shifts would be expected and, obviously, this is not observed.

Nmr Line Widths and Electron Relaxation Processes. It is apparent from a comparison of line width data for the bisarene complexes (see Table III) with those for the metallocenes and 1,1′-dimethylmetallocenes[2] that very little difference exists for analogous, isoelectronic species. Since the zero-field splitting parameter D is not available for bisarenevanadium(I) and bisarenecobalt(I) species ($S = 1$), we will assume similar values of T_1 based on this close similarity of line widths to vanadocene and nickelocene, respectively. Using reported estimates,[2] T_1 (bisbenzenevanadium(I) cation) $\sim 3.7 \times 10^{-11}$ sec and T_1 (bisbenzenecobalt(I) cation) $\sim 6 \times 10^{-12}$ sec. Transferability of these numbers also assumes the similar values of τ_r (2×10^{-10} sec), the tumbling time. We feel this conclusion is certainly justified in light of similar structure and nmr solvents in which the line widths were measured.

It is evident that the similarity in line widths, bond distances, and coupling constants will lead to essentially the same conclusions: electron relaxation times in $V(C_6H_6)_2^+$ and $Co(C_6H_6)_2^+$ are quite short and the dominant nuclear relaxation process is dipolar. These reasonable estimates of $1/T_1$ will suffice for a consideration of the pseudocontact interaction.

Evaluation of Pseudocontact Shifts. Using the estimates of τ_r and T_1 in the preceding section, we have $T_1 \ll \tau_r$ in all cases, a conclusion which is supported by the experimental line widths for the substituted and unsubstituted bisarene complexes studied. Substitution has considerably more effect on the line width, however, in these complexes than in the corresponding metallocenes, implying that $1/\tau_c$ is not dominated by $1/T_1$ to the same extent in the bisarene complexes. Equation 3, where τ_c is the correlation time for dipolar broadening, implies that T_1 may be more on the same order of magnitude as τ_r than in the metallocenes, where T_1 appeared to swamp τ_r, even though the latter

$$\tau_c^{-1} = \tau_r^{-1} + T_1^{-1} \tag{3}$$

surely increases upon substitution. We referred to this earlier in a consideration of the line widths of $Co(C_6H_5CH_3)_2^+$.

Evaluation of the pseudocontact shift in axial symmetry is dependent upon the relative magnitudes of τ_r, T_1, and the anisotropy $(g_\parallel - g_\perp)$. Equations 8 and 10 in Jesson's paper[37] are the relevant cases for $T_1 \ll \tau_r$.

Calculating this shift for $Cr(C_6H_6)_2^+$ using the values of $g_\perp$ and $g_\parallel$ reported by Prins and Reinders[14] of 1.9785 and 2.0023, respectively, a Cr–H distance of 2.942 Å, and a geometric factor $(3 \cos^2 \theta - 1)/r^3 = -0.0173$ Å^{-3} based on this distance, we obtain $\Delta\nu = +6$ Hz using eq 8 and $\Delta\nu = +13$ Hz using eq 10 for the ring protons, which is entirely negligible. For species where $S = 1$ these results become, respectively, $\Delta\nu = +16$ and $+34$ Hz. While these values are strongly dependent on the very small anistropy $(g_\parallel - g_\perp = 0.0238)$, small anistropy is expected in $V(C_6H_6)_2$ and $Co(C_6H_6)_2^+$ because of A_{1g} ground states. The epr spectrum of $V(C_6H_6)_2$ in 1:1 methylcyclohexane–toluene glass at 77°K shows $|g_\parallel - g_\perp| < 0.02$, similar to $Cr(C_6H_6)_2^+$ as expected. $V(C_6H_6)_2^+$ with a $^3E_{2g}$ ground state presumably could have considerable anistropy, which of course is unknown. Reasoning from the isoelectronic $Cr(C_5H_5)_2$ also with a ground state $^3E_{2g}$, a pseudocontact shift of ±600 Hz is estimated[2,3] if the anisotropy $|g_\parallel - g_\perp|$ does not exceed 1.8. This shift is entirely negligible compared to the huge shifts (13,000 Hz) observed for the $V(C_6H_6)_2^+$ species.

Evaluation of the pseudocontact shifts for methyl substitution is more difficult since the value of $(3 \cos^2 \theta - 1)/r^3$ must be averaged over all rotations of the methyl group. Also, one is less sure of the relationship be-

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(36) B. J. Nicholson and H. C. Longuet-Higgins, *J. Mol. Phys.*, 9, 461 (1965).

(37) J. P. Jesson, *J. Chem. Phys.*, 47, 579 (1967).

tween τ_r, T_1, and $|g_\parallel - g_\perp|$ in going to a substituted complex. We have therefore used Jesson's[43] eq 8–11 to estimate the pseudocontact shifts for $S = {}^1/_2$ and $S = 1$ systems (see Table VI). The g values were taken from the values found by Brintzinger[13] for Fe(HMBZ)$_2^+$ so that $g_z = g_\parallel$ and $g_\perp = {}^1/_2(g_x + g_y)$. The geometric factor was found to be -0.0108 Å^{-3}, averaging over rotational increments of 1°. It is evident from Table VI that the calculated pseudocontact shifts are very small for all possible limiting cases, using what we consider to be the *extreme* anisotropies (which are yet quite small) measured for a complex which presumably undergoes distortion. Jesson's eq 8, which is probably a reasonable limiting case (as shown in the previous section), gives a maximum shift of ~+71 Hz and ~+189 Hz for $S = {}^1/_2$ and $S = 1$ cases, respectively, which are quite small contributions to the total shifts observed for all systems except for Fe(HMBZ)$_2^+$, ($S = {}^1/_2$), where it is still less than 30% of the total observed shift at 298° K (259 Hz).

Table VI. Pseudocontact Shifts for Axial[a] Systems at 298°K

Eq	$S = {}^1/_2$	$S = 1$
8	70.8[b]	188.7
9	56.2	149.9
10	49.2	131.4
11	34.9	93.1

[a] $(3 \cos^2 \theta - 1)/r^3 = -0.0108$ Å^{-3}. [b] Shifts are given in Hz at 60 MHz.

The possibility of distortions in Fe(HMBZ)$_2^+$ giving pseudocontact shifts larger than we would predict assuming axial symmetry was investigated using derived equations[38,39] for systems of C_{2v} symmetry (rings oblique to each other). An additional geometric factor, $\sin^2 \theta \cos 2\Omega/r^3$, where Ω is an angle of rotation about the C_{2v} axis, is included. There are two limiting cases, (a) $T_1 \gg \tau_r$,[38] and (b) $T_1 \ll \tau_r$.[39] In all cases for distortions from 5 to 35° away from axial symmetry, the absolute value of the pseudocontact shifts is *less* than that of the shifts calculated assuming axial symmetry. We may conclude that the pseudocontact shift is entirely negligible in the systems studied except possibly in the case of Fe(HMBZ)$_2^+$, where it may account for up to 30% of the total shift.

Table VII. Wide-Line Nmr Results for Bisarene Complexes[d]

Complex	No. of d electrons	ΔH_{pp},[a] G	Second moment[b]	ΔH, G Ring	ΔH, G Methyl	A, G Ring	A, G Methyl
Cr(HMBZ)$_2$I	5	1.92 ± 0.07	0.919		+0.545 ± 0.05		−0.531
		(2.24 ± 0.07)	1.25		+0.956 ± 0.05		−0.537
Cr(TOL)$_2$I	5			−3.56	+0.65	+3.46	−0.46
V(C$_6$H$_6$)$_2$	5	2.82	1.98	−4.10 ± 0.04		+3.99	
Ni(C$_5$H$_5$)$_2$	8	3.06 ± 0.05	2.34				
		(3.26 ± 0.01)	2.66				
Fe(MES)$_2$PF$_6$	7	4.65	5.40				
		(10.85)	28.3				
V(HMBZ)$_2$	5	1.99 ± 0.07	0.987		+369 ± 0.05		−0.360
		(2.13 ± 0.07)	1.13				
Fe(HMBZ)$_2$(PF$_6$)$_2$	6	1.66 ± 0.04	0.693		(Diamagnetic)		
		(1.91)	0.912				
Fe(HMBZ)$_2$PF$_6$	7	1.74 ± 0.01	0.752		+0.002[c]		0.000
		(1.85)	0.856				
Ni(HMBZ)$_2$PtCl$_6$	8	1.74 ± 0.02	0.757		−2.83 ± 0.10		+0.898
Co(HMBZ)$_2$PF$_6$	8	1.81 ± 0.03	0.816		−0.671 ± 0.01		+0.222
		(2.04)	1.04				
Co(HMBZ)$_2$PtCl$_6$	7	1.59	0.629		−0.185 ± 0.01		+0.178
		(1.99)	0.993				

[a] Measured at 298°K; value at 203°K in parentheses. External reference was benzene or H$_2$O. [b] The second moment was calculated assuming gaussian line shape from expression $(\Delta H)^2 = {}^1/_4(\Delta H_{pp})^2$. [c] Shift was slightly upfield from the diamagnetic reference. [d] Measured at 60 MHz.

Results of Contact Shift Experiments in the Solid State. The observed contact shifts and calculated coupling constants (using eq 2) are reported in Table VII for a large number of paramagnetic complexes. With the exception of Fe(HMBZ)$_2$PF$_6$, Fe(MES)$_2$PF$_6$, and Co(HMBZ)$_2$PF$_6$, we were unable to observe solution shifts for these complexes either for relaxation or solubility–stability reasons, so the wide-line nmr technique proved quite useful. Within experimental error, the shifts for Co(HMBZ)$_2$PF$_6$ and Fe(HMBZ)$_2$PF$_6$ are *identical* for solution and solid state. We expect solid and solution contact shifts to be equal in all cases.

The huge shifts to lower field for Ni(HMBZ)$_6$PtCl$_6$ compared to the isoelectronic d^8 system, Co(HMBZ)$_2$PF$_6$, are not unexpected in view of the greater nuclear charge and anticipated greater Lewis acidity of nickel(II) compared to cobalt(I). The effect of oxidation state is not nearly as pronounced comparing the Co(HMBZ)$_2$PF$_6$ coupling constant with that for Co(HMBZ)$_2$PtCl$_6$. Since Co(I) has one more unpaired electron than Co(II), the greater electron repulsions in cobalt(I) are evidently such that the increased delocalization gives rise to nearly equal coupling constants for the two species. The Co(HMBZ)$_2$PtCl$_6$ coupling constant is larger than that for Fe(HMBZ)$_2$PF$_6$ because of the difference in oxidation state for the isoelectronic configurations. The downfield shifts of the methyl protons in these complexes are consistent with a π delocalization mechanism as discussed earlier.

V(C$_6$H$_6$)$_2$, d^5, exhibited a very intense signal and a large downfield shift of −4.1 G. This gives a coupling

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(38) G. N. La Mar, W. DeW. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, 41, 2126 (1964).

(39) G. N. La Mar, *ibid.*, 43, 1085 (1965).

constant of +3.99 G, which is in excellent agreement with the epr coupling constant of 4.0 ± 0.1 G measured by Hausser.[11] A σ mechanism, where delocalization occurs *via* unpaired spin in the a_{1g} orbital comprised of mainly metal d_{z^2} orbital, is consistent with the large downfield shift observed. Theoretical calculations for both $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2$ predict the values of these coupling constants quite well[4] and agree with this interpretation of extensive σ delocalization. Prins[7] has subsequently corroborated this conclusion for $Cr(C_6H_6)_2^+$.

This brings us to a real problem. A σ delocalization mechanism which leads to the large downfield shift for $V(C_6H_6)_2$ and $Cr(C_6H_6)_2^+$ implies that a substituent methyl group would show an attenuated shift still in the downfield direction. This is in dramatic contrast to what is actually observed. Our coupling constants for $Cr(C_6H_5CH_3)_2^+$ agree with those reported by Karimov, *et al.*,[6] who also report an *upfield* shift for the attached methyl group, but were unable to explain it satisfactorily. Our work has indicated that this upfield methyl shift also occurs in $V(C_6H_5CH_3)_2$, but overlapping resonances prevent accurate assessment of this effect. $V(HMBZ)_2$ and $Cr(HMBZ)_2I$ were synthesized to resolve this problem more clearly. Table VII shows that again the methyl groups are clearly shifted upfield to give coupling constants of −0.36 and −0.53 G for these respective species. Coupling constants of this order of magnitude are comparable to shifts of up to several kHz, so the effect is not small. Geometric distortion is unreasonable for these d^5 symmetrically substituted species which are unquestionably of the same D_{6h} symmetry as the unsubstituted species.

A negative coupling constant observed for these methyl protons requires that net spin *opposed* to the external field be delocalized onto these hydrogens. Any delocalization mechanism invoked must also delocalize spin aligned with the field onto the ring hydrogens, reasoning from the partially substituted species. This problem can be solved by invoking the polarization mechanism proposed by Levy and Orgel,[40] which would polarize electrons in any of the strong bonding, mainly ring, orbitals leaving net β spin in the carbon $2p_z$ orbitals and on the methyl protons, giving rise to the upfield methyl shift and a downfield shift for the ring protons. It appears unreasonable to expect large shifts from this mechanism compared to polarization of the largely metal e_{2g} set. This e_{2g} set has a large d_{xy}, $d_{x^2-y^2}$ contribution and lies *above* the mainly ligand e_{1g} set in all cases. Now the extent of polarization is inversely proportional to the energy separation between the orbital containing the unpaired electron, summed over all filled and unfilled molecular orbitals, as shown by McLachlan.[41] Our molecular orbital calculations show that, on the average, the filled e_{2g} and e_{1g} levels for $Cr(C_6H_6)_2^+$ lie respectively ~1.3 and ~2.5 eV below the a_{1g} molecular orbital. These numbers are respectively ~2.2 and ~3.2 eV for $V(C_6H_6)_2$. The $d_{x^2-y^2}$ coefficients in the e_{2g} molecular orbital for both species are about 0.65, showing the strong metal orbital contribution. This would lead us to expect that in terms of contribution to the total polarization, the absolute magnitude from the e_{2g} molecular orbitals should be greater than from the e_{1g} molecular orbitals. This conclusion must be qualified since all filled and unfilled molecular orbitals are involved in this summation process, and polarization from the remaining molecular orbitals could be larger than either of these contributions. Since the sign of the polarization is dependent solely upon the summation of products of atomic orbital coefficients, which may be either positive or negative, there is no rigorous way to ascertain the sign of the effect without actually doing the calculation. However, we feel we may be able to predict signs by judicious choice of an important contributing molecular orbital, such as the e_{2g} molecular orbital. Polarization of electrons on the same center should be more effective than polarization involving two centers. Since the unpaired electron in our case is in an a_{1g} molecular orbital of predominantly d_{z^2} character, and since d_{xy} and $d_{x^2-y^2}$ are the only other valence orbitals occupied on the metal, polarization of e_{2g} electrons should undoubtedly make an important contribution to the total polarization. Polarization of e_{2g} will place net spin of the opposite sign of that on the metal onto the ring carbon atoms. Our MO calculations show that π contributions to the proton coupling dominate in the e_{2g} orbital, so β spin is predicted at the methyl hydrogens in accordance with experiment. It is reasonable to assume that the total polarization will follow the same trend as that for spin delocalization in the e_{2g} orbital.

The example of $Fe(C_5H_4CH_3)_2^+$ will suffice to show that we have assessed the effect of β spin in the e_{2g} orbitals correctly in delocalization of spin onto the methyl hydrogens. Fritz, Keller, and Schwarzhans[42] have reported a detailed analysis of substituted ferricinium cations, where the unpaired electron undoubtedly occupies an e_{2g} orbital (see Table II). They report an observed *upfield* methyl contact shift of +680 Hz. Using the value of the methyl group geometric factor which they calculated (-7.63×10^{21} cm^{-3}) and the values of $g_{\parallel} = 4.36$ and $g_{\perp} = 1.30$ recently determined for $Fe(C_5H_5)_2^+$ by Prins and Reinders,[43] the pseudocontact contribution is estimated to be +890 Hz, assuming $T_{1e} \ll \tau_r$.[2] Correcting the observed shift by this term gives a net of ~ −200 Hz which is due to Fermi contact interaction. Since this value arises from an α spin in the e_{2g} orbital, it is easily concluded that a β spin in this level would give rise to a net *upfield* shift of ~+200 Hz.

The question remains: why is this polarization effect so much more important for the methyl group than for the ring hydrogens? In accordance with our molecular orbital calculations on $Cr(C_6H_6)_2^+$, $V(C_6H_6)_2$, and $Cr(C_6H_5CH_3)(C_6H_6)^+$ to be published subsequently, evaluation of contributions to the coupling constants shows dominance of σ delocalization leading to the large downfield resonance shifts observed for the ring protons. However, β spin on the ring carbon atom required to produce the upfield methyl shift for substituted species also would lead to a *downfield* shift of the ring proton resonance. A competition is clearly seen at the methyl protons since σ delocalization would shift the methyl proton resonance downfield. Since this downfield

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(40) D. A. Levy and L. E. Orgel, *Mol. Phys.*, 3, 583 (1960).

(41) A. D. McLachlan, *ibid.*, 3, 233 (1960).

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(43) R. Prins and F. J. Reinders, *J. Amer. Chem. Soc.*, 91, 4929 (1969).

shift attenuates with distance, and the methyl protons are actually shifted upfield, polarization effects dominate at these methyl protons.

Assuming these competing mechanisms, we can account for both the dominance of σ delocalization at the ring protons, as well as the dominance of spin polarization leading to β spin on the methyl hydrogens. Using a similar analysis to that employed by Prins,[7] let X = the contribution (G) to the *ring* proton coupling constant A_H from σ delocalization, and Y = the contribution (G) from spin polarization. Using the result from studies of aromatic radicals, in which spin polarization produces methyl proton coupling constants approximately equal to A_H but with opposite sign, let $-Y$ be the spin polarization contribution to A_{CH_3} (at the methyl proton). Assuming a 20% attenuation of spin density in going from ring to methyl protons, $0.2X$ is the σ contribution to A_{CH_3}. Using Karimov's[6] experimental values for A_H, the following simultaneous equations may be written.

$$+4.0 = X + Y$$

$$-0.75 = 0.2X - Y$$

Solving, we obtain $X = +2.71$ G and $Y = +1.29$ G, which shows that both spin polarization and σ delocalization make large positive contributions to the ring coupling constants, although σ delocalization dominates. The σ delocalization contribution to A_{CH_3}, however, is smaller than the larger negative contribution from spin polarization. The larger σ contribution to A_H is in good accord with our MO calculation on $Cr(C_6H_5CH_3)(C_6H_6)^+$, which predicts a value corresponding to an X of $+2.84$ G.

The polarization proposed here obviously will be more effective for $Cr(C_6H_6)_2^+$ than for $V(C_6H_6)_2$ based on the smaller a_{1g}–e_{2g} separation in the former. This is reflected in the methyl coupling constants for the respective substituted species, -0.53 and -0.36 G for $Cr(HMBZ)_2^+$ and $V(HMBZ)_2$. A strong competition between the σ delocalization, giving rise to the large downfield shifts for the ring hydrogens, and the polarization mechanism which transfers β spin to the methyl hydrogens may also be reflected in the relative methyl coupling constants for these species: the greater σ effect for the vanadium case, "shifting" the methyl resonance less upfield than the chromium case, where A_H is less and presumably this opposing σ delocalization mechanism is somewhat less.

This proposal of competing σ delocalization and polarization of paired e_{2g} electrons (and other filled levels) by the unpaired a_{1g} electron is completely consistent with the earlier work from this laboratory[2,3] on substituted vanadocene and chromocene. In these molecules the e_{2g} level has two and one unpaired spins, respectively. In the e_{2g} level of vanadocene, there is no β spin present. Slight polarization is possible in chromocene since one electron with β spin is now present in the e_{2g} level, but it is expected to be insufficient to overcome the α spin of the unpaired electron in the e_{2g} set. Comparing the A_{CH_3} coupling constants for $V(C_5H_4CH_3)_2$ and $Cr(C_5H_4CH_3)_2$, 0.32 and 0.14 G, respectively, it is significant that the value for the latter is *less* than for the vanadium species (where no polarization of e_{2g} electron is possible) in spite of the fact that the ring coupling constants (0.91 and 1.2 G, respectively) show the *opposite* trend. This smaller A_{CH_3} value for the chromium case could also be a manifestation of the polarization of the e_{2g} electrons. While an overall "σ" delocalization is observed, this polarization effect competes in the chromocene case, putting a component of β spin on the methyl group which, when added to the dominant σ effect, produces a smaller downfield shift than expected from the MO calculation.[3]

It is also easy to see why these effects are not important in nickelocene. In this case, the antibonding e_{1g}^* level is occupied by two unpaired electrons which are delocalized directly on the ligand. The strong component of α spin completely dominates the observed shift.[3] The e_{1g}^* level is separated from the much lower filled metal orbitals by 3–5 eV and, consequently, spin polarization or configuration interaction with them should be smaller. Summarizing, the relatively large magnitude of the *upfield* methyl shift in substituted vanadium and chromium bisarene complexes is predicated on the effectiveness of this polarization of *metal* electrons when the e_{2g} level is completely *filled.* It is therefore possible to delocalize net β spin in the e_{2g} orbitals which can be delocalized onto the methyl group, producing a sizable upfield resonance shift.

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