possible characterization by Mössbauer measurements in frozen solutions (provided of course that it does not rearrange to the solid-state molecular structure). Unfortunately, reported attempts[89] to obtain the Mössbauer spectrum in frozen solutions have so far been unsuccessful because of the low solubility of the compound in inert solvents.

Acknowledgments. The use of the CDC 1604 and 3600 computers at the University of Wisconsin was made available through partial support of NSF and WARF through the University Research Committee; the use of the CDC 1604 and IBM 360 computers at the ORNL Computing Center was supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

One of us (L. F. D.) wishes to acknowledge the late Professor Robert E. Rundle for his invaluable lessons as a teacher and researcher and his stimulation and encouragement in the preliminary stage of this particular work.

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Electron Delocalization in Paramagnetic Metallocenes. I. Nuclear Magnetic Resonance Contact Shifts[1,2]

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Abstract: The 1,1′-dimethylcyclopentadienyls of V, Cr, Co, and Ni were prepared, and the nmr contact shifts were determined at 60 MHz in toluene. Analysis of electron relaxation times and nmr line widths suggests that the dominant nuclear relaxation mechanism is dipolar. The temperature dependencies of the contact shifts were examined, and it was shown that the Curie law is obeyed in each case. It was shown that the pseudocontact (dipolar) shift should be negligible in all cases except perhaps at the methyl group in 1,1′-dimethylchromocene. Comparison of the methyl contact shifts and the ring contact shifts leads to the conclusion that the unpaired electron density in vanadium and chromium metallocenes is not in ring π orbitals (out of plane) as previously supposed. Instead the magnitudes and signs of the chromium and vanadium shifts strongly suggest that the unpaired spins are delocalized in σ (in-plane) cyclopentadienyl orbitals. Delocalization in π-type orbitals is found to predominate in cobalt and nickel metallocenes.

It is now widely recognized that the study of nuclear resonance in paramagnetic complexes can yield detailed information concerning metal–ligand bonding and electron delocalization. This appeared to be an excellent technique to apply to a study of the electronic structure of the metallocenes, an area that has been the subject of much controversy over the years. In this paper we discuss the proton nmr contact shifts for the unsubstituted and 1,1′-dimethyl-substituted metallocenes of the first transition series. We consider first the experimental results and then propose a unified electron delocalization scheme.

McConnell and Holm first observed proton resonance for paramagnetic, solid nickelocene.[3] Later, the same workers reported nuclear resonance shifts for solid manganocene, cobaltocene, vanadocene, and chromocene.[4] Fritz, Keller, and Schwarzhans[5,6] reported nmr data for all the paramagnetic unsubstituted metallocenes in solution. These workers have also observed nmr for substituted ferricenium cations.[7]

The extremely large nmr shift observed for solid nickelocene by McConnell and Holm[3] was the first example of what are now generally known as nmr contact shifts. Such shifts are observed only in paramagnetic molecules, and arise by virtue of the Fermi contact unpaired electron spin–nuclear spin hyperfine coupling, according to eq 1,[8] where A is the hyperfine

$$A = \frac{8\pi}{6S} g_e\beta_e g_N\beta_N|\psi(0)|^2 \qquad (1)$$

coupling constant, in ergs. g_e and g_N are electron and nuclear g values, respectively; β_e and β_N are Bohr and nuclear magnetons, respectively; and $\psi(0)$ is the molecular wave function evaluated at the nuclear position.

The contact shifts of the metallocenes pose an interesting problem, in that the vanadocene and chromocene proton shifts are negative, while those of manganocene, cobaltocene, and nickelocene are positive. And in fact, all of these shifts are quite large. In 1960, Levy

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[1] Abstracted from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; NSF Predoctoral Fellow, 1963–1967.

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and Orgel[9] attempted to account for the metallocene contact shifts on the basis of a combined spin polarization–electron delocalization model. This model was later reiterated by Fritz, Keller, and Schwarzhans.[6,7]

In a preliminary communication of this work[10] we reported nmr results for the 1,1′-dimethylmetallocenes, and it was shown that the Levy–Orgel model could not account for the methyl contact shifts. We now present a complete account of our work and will show that metal-to-ligand electron delocalization in σ orbitals makes an important contribution to the nmr contact shifts.

Experimental Section

A. **Apparatus and Techniques.** Nuclear magnetic resonance spectra were obtained using either a Varian A-60A or a Varian DP-60 nmr spectrometer. Chemical shift measurements on the DP-60 were made using the side-band technique. Occasionally, certain resonances could not be recorded on the chart paper but could be observed on the oscilloscope. In such instances chemical shifts were measured directly from the oscilloscope trace, again using the side-band technique. Temperature measurements on the DP-60 were made using a calibrated copper–constantan thermocouple. Temperature measurements on the A-60A were made with a commercial thermistor–thermometer (YSI Model 42 SC). Solvents were degassed using the freeze–thaw technique.

Water sensitive materials were handled in a continuous flow drybox (Vacuum Atmospheres Corp., Model HE43-2). The dry air source was a Trinity Heat-Les dryer. Normally the water content of the air was found to be about 10 ppm, as determined by measurement of the dew point. Oxygen-sensitive materials were handled in an I^{2}R glove bag connected to an argon tank and were exposed to the atmosphere in the bag for only a few seconds, usually just long enough to transfer to an nmr tube.

B. **Preparation of Compounds. 1. Cyclopentadiene.** Crude dicyclopentadiene (Eastman) was dried over Linde 4A molecular sieve pellets and then cracked by distillation, bp 42–43°. The distillate was condensed in a Dry Ice trap at $-78°$ and was stored at that temperature until use. No significant dimerization was noted after 3 days at $-78°$.

2. **Monomethylcyclopentadiene.** The crude dimer of monomethylcyclopentadiene was dried for several hours over Linde 3A molecular sieve pellets. The material was then slowly distilled through a 40-cm Vigreux column, and the fraction boiling at 71.5–74° was then immediately redistilled in the same apparatus. A fraction, bp 72.8–73.2°, was collected at $-78°$ over a period of 90 min and stored at that temperature until use.

3. **Vanadium Trichloride.** Vanadium trichloride was used as received from Alfa Inorganics. *Anal.* Calcd for VCl_3: V, 32.34. Found: V, 32.11, 32.18. This material is very hygroscopic and was handled in the drybox.

4. **Nickelocene, $Ni(C_5H_5)_2$.** Nickelocene was obtained commercially from Alfa Inorganics. As received, the material was quite impure. After sublimation at 0.1 mm and 100°, nicely formed blue needles were produced which were then handled in the inert atmosphere bag. *Anal.* Calcd for $NiC_{10}H_{10}$: C, 63.6; H, 5.34. Found: C, 63.9; H, 5.63.

5. **Vanadocene, $V(C_5H_5)_2$.** Vanadocene was prepared by a modified literature method[11] using NaH instead of Na for preparation of NaC_5H_5.

6. **Sodium Monomethylcyclopentadienide, NaC_6H_7.** Mallinckrodt Reagent tetrahydrofuran (THF) was purified by slowly passing through a column of Linde 5A molecular sieve pellets. The first few hundred milliliters was rejected, and about 800 ml of THF purified in this way gives a negative test for peroxides and shows no discernible H_2 evolution on contact with NaH.

The mineral oil was removed from Metal Hydrides 59% NaH dispersion. THF (50 ml, purified as described above) was then added, the flask was fitted with N_2 inlet and outlet and a pressure-equalized dropping funnel containing 46.10 g of monomeric monomethylcyclopentadiene (0.575 mole). The monomethylcyclopentadiene was added dropwise with good stirring over a period of 70 min. The reaction is vigorous, but very little heat is evolved. At the conclusion of the diene addition, the reaction mixture was a very light brown. The mixture was stirred for an additional 2 hr and was then allowed to stand protected from oxygen until use. A very small amount of solid settled out on standing.

7. All of the **1,1′-dimethylmetallocenes** were prepared using NaC_6H_7 obtained by the procedure outlined above. The synthetic procedure was patterned after that of Reynolds and Wilkinson.[12]

8. **1,1′-Dimethylnickelocene, $Ni(C_6H_7)_2$.** A flask fitted with a mechanical stirrer, reflux condenser, and pressure-equalized dropping funnel was charged with 5.88 g of Ni powder, and 100 ml of 1,2-dimethoxyethane (purified by passing through a 25 cm × 1 cm column of Linde 5A molecular sieve pellets during a 20-min period). To this mixture was added with stirring 5.5 ml of neat Br_2. The Br_2 addition took about 10 min. The reaction mixture was refluxed for 5.5 hr, at the end of which time a large amount of pale orange precipitate had appeared. The solvent was partially removed leaving a solid slightly damp with dimethoxyethane. The solvated $NiBr_2$[13] was treated with 100 ml of THF, giving a green solution and a yellow solid. The mixture was transferred to a 500-ml, three-necked flask, and 0.2 mole of NaH in 250 ml of THF was added by means of an inert atmosphere transfer tube. Very little heat was evolved initially, and the mixture was refluxed for 2.5 hr. The solvent was removed leaving a semisolid green mass. The mass was extracted for 45 min with 300 ml of deoxygenated hexane. The mixture was filtered under argon using a Schlenk tube, followed by stripping the hexane from the filtrate. This treatment left approximately 15 ml of semisolid green oil. The oil was vacuum distilled at approximately 0.2 mm. A 10-ml middle fraction, bp 52.5–53°, was collected and analyzed. *Anal.* Calcd for $NiC_{12}H_{14}$: C, 66.5; H, 6.50. Found: C, 66.49; H, 6.64.

Dimethylnickelocene is a green solid at room temperature. The material instantly oxidizes on contact with atmospheric oxygen. The melting point is just above room temperature.

9. **1,1′-Dimethylvanadocene, $V(C_6H_7)_2$.** A 300-ml, three-necked flask fitted with a mechanical stirrer, argon inlet, and argon outlet was charged with 0.21 mole of NaC_6H_7 in 175 ml of THF. The solution was cooled to 0°, and 11.05 g of VCl_3 (0.070 mole) was quickly added and the mixture was then put under gentle reflux. After 15 min, the solution was purple with NaCl floating about. After an additional 2 hr of reflux, the solvent was removed, leaving a purple sludge which was stirred overnight with 250 ml of deoxygenated hexane. The brownish purple hexane extract was filtered in the Schlenk tube. After removal of the hexane, 20–25 ml of a purplish oily sludge was obtained. The material was vacuum distilled, giving only 4 ml of volatile product. A 2-ml middle fraction, bp 54–57° (0.2–0.3 mm), was analyzed. *Anal.* Calcd for $V(C_6H_7)_2$: C, 68.9; H, 6.70. Found: C, 69.0; H, 6.66.

Caution! The liquid $V(C_6H_7)_2$ ignites violently on exposure to the air. The product is a purple oil at room temperature.

10. **1,1′-Dimethylchromocene, $Cr(C_6H_7)_2$.** The flask assembly described above was charged with 0.21 mole of NaC_6H_7 in 175 ml of THF. With good stirring, 11.05 g of anhydrous $CrCl_3$ (0.07 mole) was quickly added to the NaC_6H_7 solution. The solution immediately began to darken and warm. After 5 min the reaction mixture had warmed itself to 50–60° and had begun to turn red. After 45 min, the reaction was put under gentle reflux, and the reflux was continued for 90 min. The brownish solution was cooled and the solvent was removed. The brownish residue was treated with 250 ml of deoxygenated hexane, followed by filtration of the hexane extract with the Schlenk tube and removal of the solvent. This treatment left about 15 ml of a reddish brown oil. The oil was vacuum distilled from a 120° oil bath. A late fraction (2 ml, bp 65–66° at 0.45 mm) was taken for analysis. About 7 ml was collected altogether. *Anal.* Calcd for $CrC_{12}H_{14}$: C, 68.55; H, 6.71. Found: C, 68.43; H, 6.79.

Caution! 1,1′-Dimethylchromocene ignites spontaneously in the air. This material was obtained as red-orange platelets, which crystallized quite readily in the distilling condenser and the receiving flasks. The melting point is just above room temperature.

11. **1,1′-Dimethylcobaltocene, $Co(C_6H_7)_2$.** A three-necked flask was charged with 7.75 g of anhydrous $CoCl_2$ (0.06 mole) in the dry bag. A THF solution of NaC_6H_7 (0.12 mole) was then cautiously

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Table I. Magnetic Moments of $M(C_5H_5)_2$

Metal ion	μ_{eff} (exptl)	S	μ_{eff} (spin only)	Ref
Ti[a]	0	0	0	14
V	3.84 ± 0.04	$^3/_2$	3.87	15
Cr	3.20 ± 0.16	1	2.83	16
Mn	5.71 ± 0.29	$^5/_2$	5.91	17
Fe	0	0	0	16
Co	1.76 ± 0.07	$^1/_2$	1.73	16
Ni	2.86 ± 0.11	1	2.83	16

[a] $Ti(C_5H_5)_2$ is now believed to be a dimer.[18]

added to the solid $CoCl_2$. The addition was exothermic and was done with periodic cooling. The reaction mixture was then refluxed under N_2 for 2 hr quickly turning brown. The reaction mixture was cooled, the solvent removed, and the residue extracted overnight with 250 ml of deoxygenated hexane. The hexane extract was filtered using the Schlenk tube. Removal of the solvent left a brown, oily sludge which was vacuum distilled from a 120° oil bath, using a 15-cm, wrapped Vigreux column. A middle fraction (2 ml, bp 56–57.5° at 0.37 mm) was collected for analysis. About 4 ml was collected over-all. *Anal.* Calcd for $CoC_{12}H_{14}$: C, 66.35; H, 6.49. Found: C, 66.38; H, 6.34. The middle fraction crystallized to a brownish purple, extremely air-sensitive solid.

Results and Discussion

The objective of this work is to find a consistent explanation for the nuclear magnetic resonance contact shifts of the paramagnetic metallocenes. In what follows, the pertinent experimental data will be presented and analyzed in terms of the delocalization model proposed by Levy and Orgel[9] in 1960. It will be shown that this model is inadequate in several respects. A new explanation of the mechanisms of electron delocalization in the metallocenes will be given, and it will be shown that the model is consistent with the known experimental facts.

A. Magnetic Properties. The measured magnetic moments of the metallocenes are given in Table I.[14–18] The magnetic moments are generally consistent with the d-orbital arrangement (d_{yz}, $d_{x^2-y^2}$) < d_{z^2} < (d_{xz}, d_{yz}) (see Figure 1). The ordering of the lower levels may vary from compound to compound. In principle, one should be able to observe esr spectra for $V(C_5H_5)_2$, $Mn(C_5H_5)_2$, $Co(C_5H_5)_2$, and $Ni(C_5H_5)_2$. However, resonances have been observed only for vanadocene,[19] manganocene,[20] and cobaltocene.[21] General discussions of the expected magnetic resonance properties of the metallocenes have been given by Robertson and McConnell[22] and by Nussbaum and Voitländer.[21,23]

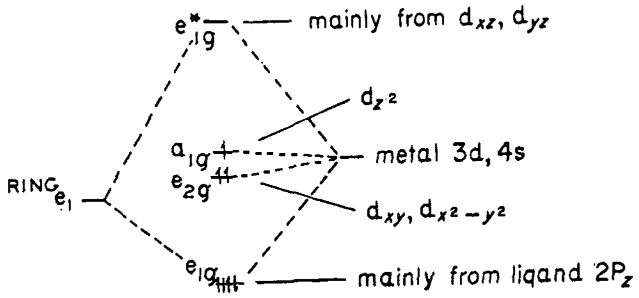

Figure 1. Partial, approximate MO diagram for $M(C_5H_5)_2$. Electrons assigned as for vanadocene.

Prins, Biloen, and van Voorst[19] found that vanadocene gives a well-resolved eight-line esr spectrum in a glass at 77°K. The vanadocene parameters obtained from the esr spectrum are $g_\parallel = 2.002$, $g_\perp = 1.99$, $|D| = 2.3\ cm^{-1}$, $|A| = 37 \times 10^{-4}\ cm^{-1}$, and $|B| = 21.5 \times 10^{-4}\ cm^{-1}$. Nussbaum and Voitländer[23] were unsuccessful in their attempts to observe electron resonance for chromocene and nickelocene. Experiments were conducted at both X and Q bands, at room temperature, 77°K, and 4°K, in dilute single crystals, and in powders. The lack of success was attributed to probable large zero-field splittings. Indeed, for nickelocene, zero-field splittings of 35–45 cm^{-1} were predicted on the basis of a ligand field model. Using the same model, $g_\parallel$ was predicted to be 2.00, while $g_\perp$ was expected to lie in the range 2.27–2.35. Very recently, these predictions have been supported by experimental measurements of the bulk magnetic susceptibility of nickelocene over a wide range of temperature.[24] The results of the susceptibility measurements for nickelocene are $g_\parallel = 2.0023$, $g_\perp = 2.06$, and $D = 25.6\ cm^{-1}$.

Voitländer and Schimitschek[20] investigated the electron spin resonance of manganocene. It was found that the g values are nearly isotropic, the extreme values being 1.99 and 2.01. The resonance was rather broad and no hyperfine structure was observed.

Nussbaum and Voitländer[21] recorded the very broad resonance of cobaltocene doped into a ferrocene single crystal at 4°K. The eight-line cobalt hyperfine structure was observed for some orientations of the single crystal. Owing to uncertainties in orienting the crystal, the esr parameters could not be definitely assigned. It is known that the g values and hyperfine terms have near axial symmetry and that $g_1 = 1.67$ and $g_2 = 1.74$; A is either 274 or 469 Mc, and B is either 274 or 384 Mc.

B. The Ground-State Electronic Configurations of the Metallocenes. 1. Ferrocene. Shustorovich and Dyatkina,[25] on the basis of SCF-MO calculations, predict that the highest filled levels for ferrocene are $(a'_{1g})^2(e_{2g})^4$, which are mainly d_{z^2} and $d_{x^2-y^2}$, d_{xy}, respectively. This ground-state configuration is consistent with the magnitude and sign of the electric field gradient at iron. Collins[26] determined that the sign of the field

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Table II. Nmr Results and Derived Quantities for Metallocenes and 1,1-Dimethylmetallocenes[e]

	$\Delta\nu^{\text{ring}\,c}$ (line width) Proton A	$\Delta\nu^{\text{ring}\,c}$ (line width) Proton B	$\Delta\nu^{CH_3}$ (line width)	$\Delta H_{1/2}^{\text{ring}\,d}/\Delta H_{1/2}^{CH_3}$	A/h^{ring}, Mcps Proton A	A/h^{ring}, Mcps Proton B	A^{ring}, G[f] Proton A	A^{ring}, G[f] Proton B	A/h^{CH_3}, Mcps	A^{CH_3}, Gauss[f]
$V(C_5H_5)_2$[a]	−18,500 (2,250)				2.33		0.832			
$V(C_6H_7)_2$	−20,190 (2,680)		−7,195 (402)	6.6	2.54		0.908		0.906	0.323
$Cr(C_5H_5)_2$[a]	−18,850 (1,300)				3.92		1.23			
$Cr(C_6H_7)_2$	−18,630 (1,250)	−21,890 (1,370)	−2,160 (230)	5.7	3.87	4.55	1.22	1.43	0.449	0.141
$Fe(C_5H_5)_2^+$[b]	−1,490 (750)				0.692		0.183			
$Fe(C_6H_7)_2^+$[b]	−1,800 (1,700)		+660 (. . .)		0.835		0.221		−0.307	−0.081
$Co(C_5H_5)_2$[a]	−3,230 (185)				−2.39		−1.01			
$Co(C_6H_7)_2$	−2,917 (234)	−4,305 (279)	−687 (55)	4.7	−2.15	−3.18	−0.904	−1.34	0.508	0.214
$Ni(C_5H_5)_2$[a]	+15,300 (550)				−3.53		−1.24			
$Ni(C_6H_7)_2$	+15,190 (529)		−11,900 (182)	2.9	−3.51		−1.23		2.75	0.96

[a] $\Delta\nu$ and line width from ref 6. [b] $\Delta\nu$ and line width from ref 5. [c] $\Delta\nu$'s in cps relative to dimethylferrocene (ring protons at −237 cps and methyl protons at −117 cps, relative to TMS). [d] Line width = $\Delta H_{1/2}$ (measured at half-maximum intensity). [e] At 60 Mc, 298 °K. [f] A (gauss) = $2.0023A(\text{Mcps})/2.80g_{\text{av}}$.

gradient at iron is positive by observing the Mössbauer spectrum in a magnetic field, which indicates that d_{xy}, $d_{x^2-y^2}$, and d_{z^2} (or the weakly bonding molecular orbitals derived therefrom) are each occupied in the ground state. The relative energies are not determined by this method. Further, Schraml and Voitländer[27] found that the wave functions of Shustorovich and Dyatkina[25] can be used to calculate the field gradient with good precision.

2. **Vanadocene.** The nearly isotropic g values for vanadocene, as well as the comparatively high temperature (77 °K) at which electron spin resonance is observed, leaves little doubt that the ground state is nondegenerate.[19] The electron configuration $(e_{2g})^2(a'_{1g})^1$ or $(a'_{1g})^1(e_{2g})^2$ (*i.e.*, ${}^4A_{2g}$) seems certain here. The former choice was suggested by Shustorovich and Dyatkina,[28] and, as will be seen in a future article, the former configuration is confirmed by our own MO calculations.

3. **Chromocene.** Little is known directly about chromocene. As can be seen from Table I, the magnetic moment is considerably greater than the spin-only value, implying an orbitally degenerate ground state. This fact is consistent with the failure of Nussbaum and Voitländer[21] to observe esr signals for chromocene even under the most ideal conditions, implying either a very short electron relaxation time or a large zero-field splitting. Shustorovich and Dyatkina[29] did a complete SCF calculation for chromocene, the predicted ground state being $(e_{2g})^3(a'_{1g})^1$. The a'_{1g} level was predicted to lie 0.4 eV above the e_{2g}. In summary, everything that is known about chromocene suggests the ground state $(e_{2g})^3(a'_{1g})^1$ or ${}^3E_{2g}$.

4. **Cobaltocene.** Shustorovich and Dyatkina[30] sugested that the ground state of cobaltocene is $(a'_{1g})^2(e_{2g})^4(a^*_{1g})^1$ on the basis of their ferrocene calculations. Thus, the extra cobaltocene electron is placed in the first empty ferrocene orbital (a^*_{1g}) which is composed almost entirely of the 4s orbital. Using a similar approach, Dahl and Ballhausen[31] favored an $(a'_{1g})^2(e_{2g})^4(e_{2u})^1$ ground state for cobaltocene. The electron spin resonance results for cobaltocene rule out both possibilities.[21] An unpaired spin in the cobalt 4s orbital is expected to give rise to cobalt hyperfine coupling as large as 4800 Mcps, while the observed hyperfine coupling is only 300–400 Mcps. An electron in the nonbonding e_{2u} orbital of the ligands, which by symmetry does not interact with the cobalt at all, should show only a vanishingly small cobalt hyperfine structure due mainly to second-order exchange polarization effects. The ground state $(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$ was deduced from the esr results,[21] and as will be seen, this ground state is predicted by our own cobaltocene calculations. The most reasonable ground-state configuration for cobaltocene is thus ${}^2E_{1g}$, $(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$.

5. **Nickelocene.** Dahl and Ballhausen, extending their ferrocene molecular orbital diagram as for cobaltocene, suggested an $(a'_{1g})^2(e_{2g})^4(e_{2u})^2$ ground state for nickelocene.[31] It is now known that this prediction is untenable. The extremely large zero-field splitting found by Prins and van Voorst[24] suggests strongly that the two unpaired spins are localized mainly on the metal, since only a very small zero-field splitting is ever observed for triplet organic molecules. It will be recalled that the e_{2u} ligand orbitals are nonbonding and would, if doubly occupied, be expected to give rise to very small zero-field splitting. The suggested ground states were[24] $(a'_{1g})^2(e_{2g})^4(e^*_{1u})^2$ or $(a'_{1g})^2(e_{2g})^4(e^*_{1g})^2$. The former finds the unpaired spins mainly in the nickel $4p_x$ and $4p_y$ orbitals, while the latter involves the d_{xz} and d_{yz}. Our own results for nickelocene suggest $(e_{2g})^4(a'_{1g})^2(e^*_{1g})^2$ or ${}^3A_{2g}$.

C. Nuclear Magnetic Resonance Contact Shifts.

1. Nmr Results for the 1,1′-Dimethylmetallocenes. The nmr spectra of the dimethylmetallocenes in toluene at 298 °K are presented in Figures 2 and 3. The contact shifts, $\Delta\nu$, and the hyperfine coupling constants for all the molecules of interest will be found in Table II. The

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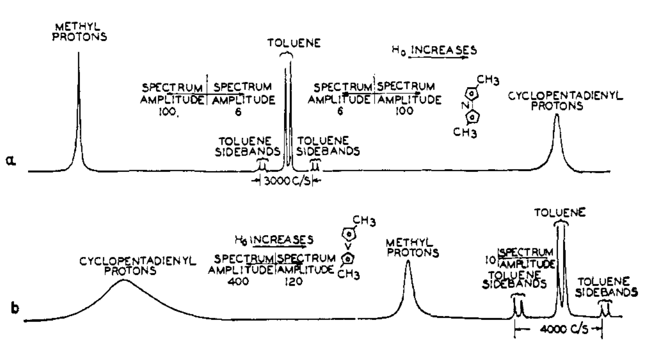

Figure 2. Nmr spectrum in toluene at 298°K of (a) dimethylnickelocene and (b) dimethylvanadocene.

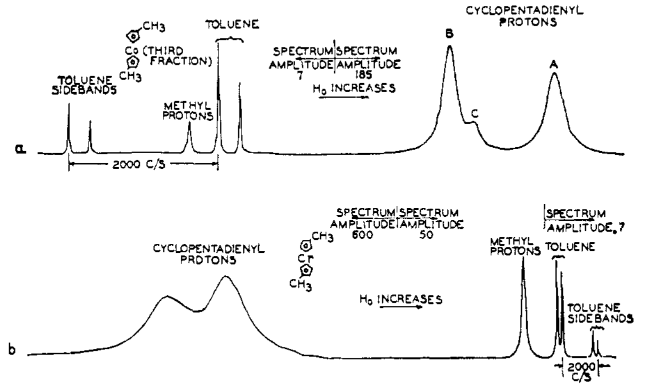

Figure 3. Nmr spectrum in toluene at 298°K of (a) dimethylcobaltocene and (b) dimethylchromocene.

contact shifts are stated relative to diamagnetic dimethylferrocene, where the cyclopentadienyl and methyl protons are found at −237 and −117 cps relative to TMS, respectively. The dependence of the contact shifts on temperature is shown in Figures 4–7. Note that in Figures 4–7 the contact shifts are measured relative to toluene or to TMS, while the results in Table II are referenced to diamagnetic dimethylferrocene. These results will now be considered in turn.

(a) 1,1′-Dimethylvanadocene. The nmr spectrum of dimethylvanadocene is shown in Figure 2b. The peaks were assigned by making reference to the published work for vanadocene[5,6] and by integration (the spectrum was recorded at low power and was spread out considerably on the chart paper; the peaks were then cut out and weighed). The intensity ratio found was approximately 1:1. There appears to be a slight shoulder on the upfield side of the cyclopentadienyl peak, possibly reflecting the nonequivalence of the ring protons. Spectra recorded at various stages of air oxidation showed that the chemical shifts for the nonoxidized dimethylvanadocene are not significantly affected by the presence of oxidation products. After strongly oxidizing the sample, weak new peaks were observed several thousand cycles/per second downfield. Hence, possible contamination of the sample with traces of O_2 should not affect our conclusions.

(b) 1,1′-Dimethylchromocene. The nmr spectrum is presented in Figure 3b. Integration (as above) showed that the cyclopentadienyl protons are split into a 1:1 doublet, and that the intensity ratio of the doublet to the methyl singlet is 3.8/3, which compares favorably to the theoretical 4/3. Moderate intentional oxidation had no noticeable effect on the chemical shifts. New signals were not observed on moderate oxidation. The temperature dependence of the methyl proton shift is given in Figure 4. The expected linear $1/T$ dependence is fairly accurately realized, though one can discover a slight curvature in the data. It was possible to obtain spectra for the cyclopentadienyl protons at only two temperatures, 24 and −11°. At −11°, the doublet resonances are at −21,200 and −25,100 cps. For each cyclopentadienyl proton, it was found that eq 2 holds accurately, where $\Delta\nu_1$ is the contact shift at

$$\Delta\nu_1 T_1 = \Delta\nu_2 T_2 \qquad (2)$$

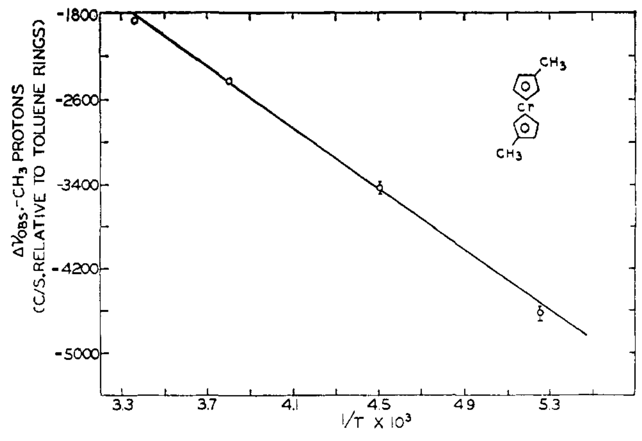

Figure 4. Temperature dependence of the methyl contact shift of dimethylchromocene in toluene.

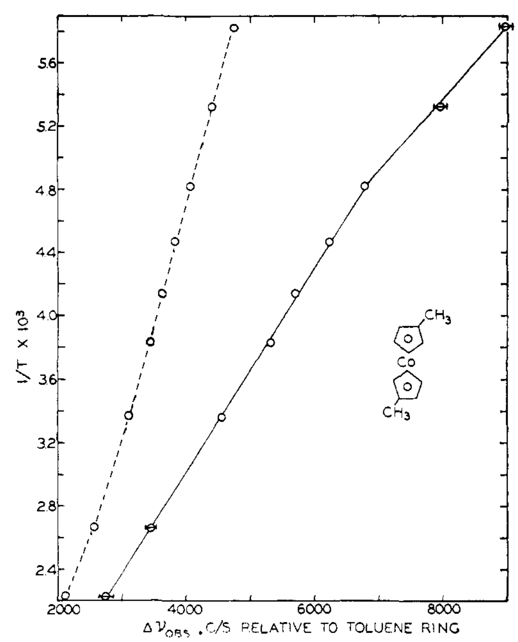

Figure 5. Temperature dependencies of the two types of ring protons (labeled A and B in Figure 3a) of dimethylcobaltocene. The dotted line refers to type-B protons, and the solid line to type A protons.

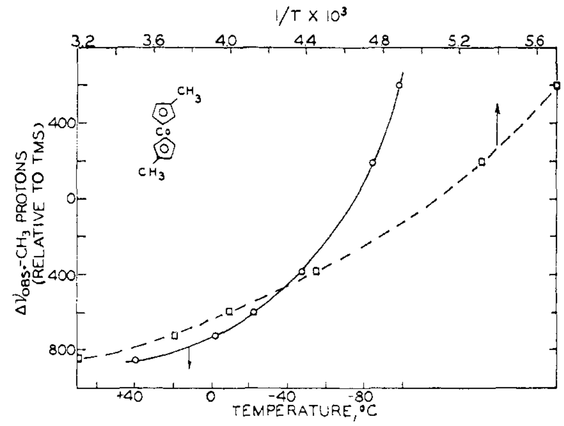

Figure 6. *T* and 1/*T* dependence of the methyl contact shift of dimethylcobaltocene in THF.

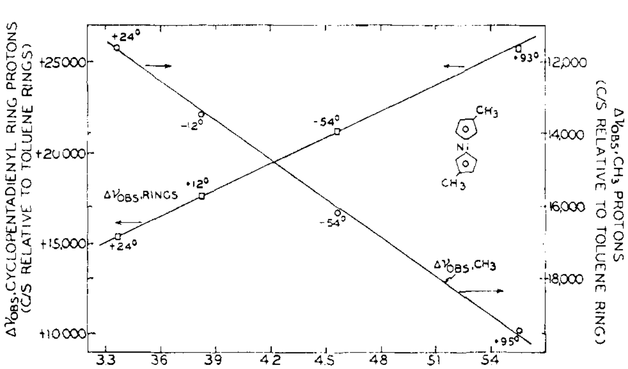

Figure 7. Temperature dependence of the nmr contact shifts for dimethylnickelocene in toluene.

T_1 = 297 °K and $\Delta\nu_2$ is the contact shift at T_2 = 262 °K. Equation 2 must hold if the expected Curie law temperature dependence is obeyed. Thus both the methyl contact shifts and the ring proton shifts closely conform to Curie law behavior. Limited data were obtained for the ring proton shifts because of solubility–line width difficulties.

(c) 1,1′-Dimethylcobaltocene. The nmr spectrum of dimethylcobaltocene is presented in Figure 3a. The main features of the spectrum are (1) the slightly shifted downfield methyl peak, assigned on the basis of its intensity and line width; (2) the strong doublet, A and B, several thousand cycles per second upfield, assigned to the two nonequivalent ring protons by comparison with the contact shift observed for cobaltocene, and on the basis of intensity measurements; (3) a smaller peak C which is an impurity, as will be shown. On partial oxidation of the nmr sample of dimethylcobaltocene, it was observed that peak C (Figure 3a) was essentially unaffected, while peaks A and B decreased markedly in amplitude. Meanwhile, a new peak appears on oxidation at about −290 cps relative to TMS. This peak is presumably due to diamagnetic $Co(C_6H_7)_2^+$. Thus, we believe that peak C is due to the presence of the possible impurities cobaltocene or monomethylcobaltocene. This is consistent with the location of C at +2975 cps relative to TMS, and with the fact that the substance responsible for peak C is less easily oxidized than is dimethylcobaltocene. The cobaltocene resonance is reported to be +2990 cps relative to TMS.[6] The temperature dependence of the contact shifts for peaks A, B, and the methyl group are shown in Figures 5 and 6. Figure 5 shows that the ring proton A has a Curie law temperature dependence until about −60°, at which temperature the line deviates. Notice that the linear portion of the curve spans a range of more than 240°. Figure 5, for the type-B ring protons, is again linear over most of the range, the deviation here being at *high* temperature rather than at low temperature as for the A protons. Figure 6 indicates the extreme temperature dependence of the methyl contact shift for dimethylcobaltocene. At about −50°, the temperature curve turns sharply upward, and the contact shift changes sign from negative to positive. The data in Figure 6 were obtained in THF solution, and similar behavior was observed in toluene. These anomalously temperature-dependent shifts will be discussed in more detail in a later paper. It is noted here that the ring proton shifts of dimethylcobaltocene imply that the Curie law is obeyed over a wide range of temperature. It was observed that the dimethylcobaltocene contact shifts exhibit no measurable concentration dependence in toluene at room temperature.

(d) 1,1′-Dimethylnickelocene. The nmr spectrum of dimethylnickelocene is presented in Figure 2a. The intensity ratio of the upfield peak to the downfield peak was found to be 3.93/3, in good agreement with the expected 4/3. This result, together with the shift observed for nickelocene,[6] leads to a clear assignment: the upfield peak, which shows no fine structure, is assigned to the ring protons, and the downfield peak to the methyl protons. Figure 7 shows the Curie law behavior of both the methyl and the ring contact shifts. Moderate oxidation had no effect on the location of the dimethylnickelocene resonances. New peaks were not noticed on moderate oxidation.

2. Electron Relaxation and Nmr Line Widths. We now consider the electron relaxation times, T_1, and the nuclear resonance line widths, $\Delta H_{1/2}$. McGarvey[32] gives the relation between the zero-field splitting and the electron relaxation time. This relation is indicated in (3)

$$\frac{1}{T_1} = \frac{32\pi^2}{5}\left(\frac{D^2}{h^2}\right)\left[\frac{\tau_r}{1 + \omega_s^2\tau_r^2} + \frac{\tau_r}{1 + 4\omega_s^2\tau_r^2}\right] \tag{3}$$

where T_1 is the electron relaxation time, in seconds; D is the zero-field splitting, in ergs; h is Planck's constant, in erg sec; τ_r is the rotational tumbling time of the complex, given approximately by the Debye equation (eq 4); ω_s is the Larmor frequency for the electron at the applied field strength, in radians/sec. At 14,092 G, $\omega_s = 2.48 \times 10^{11}$ radians/sec.

The approximate τ_r is obtained with eq 4,[33] where

$$\tau_r = 4\pi\eta r^3/3kT \tag{4}$$

η is the viscosity of the solution, in poise; r is the mean effective radius of the complex, approximated as a sphere, in cm; k and T have their usual significance.

La Mar[33] considered the various possible contri-

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[32] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

[33] G. N. La Mar, *J. Am. Chem. Soc.*, **87**, 3567 (1965).

butions to T_1 in certain nickel and cobalt complexes which have very short T_1's and therefore well-resolved nuclear resonance spectra. It was concluded that, for zero-field splittings of the order of a few reciprocal centimeters, coupling of the zero-field splitting to the molecular tumbling probably dominates the relaxation. Such a mechanism could apply only to complexes where $S \geq 1$, and therefore may be important for vanadocene, chromocene, and nickelocene. Since the values of D are known experimentally for vanadocene ($|D| = 2.3\ \text{cm}^{-1}$ [19]) and for nickelocene ($|D| = 25.6\ \text{cm}^{-1}$ [24]), it is possible to estimate T_1.

Using eq 4 with η for toluene at 25° equal to 5.58×10^{-3} P[34] and estimating an effective radius $r = 7 \times 10^{-8}$ cm for a metallocene, τ_r becomes about 2×10^{-10} sec. Equation 3 gives $1/T_1 = 2.7 \times 10^{10}\ \text{sec}^{-1}$, with $\tau_r = 2 \times 10^{-10}$ sec and $|D| = 2.3\ \text{cm}^{-1}$ for vanadocene. Similarly, $1/T_1$ for nickelocene is $3.4 \times 10^{12}\ \text{sec}^{-1}$. Hence T_1(vanadocene) $\sim 3.7 \times 10^{-11}$ sec and T_1(nickelocene) $\sim 3 \times 10^{-13}$ sec.

The nuclear resonance line width can be related to the above parameters by means of eq 5, as was done by La Mar[33]

$$\Delta H_{1/2} = K_1\left[4\tau_c + \frac{3\tau_c}{1 + \omega_I^2\tau_c^2} + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2}\right] + K_2\left[T_1 + \frac{T_1}{1 + \omega_s^2 T_1^2}\right] \quad (5)$$

with

$$K_1 = S(S + 1)\gamma_I^2 g^2 \beta^2 / 15r^6$$

$$K_2 = \frac{1}{3}S(S + 1)(A/h)^2$$

where r is the distance of the nucleus from the metal ion; τ_c is defined by $\tau_c^{-1} = \tau_r^{-1} + T_1^{-1}$, and τ_c is the correlation time for dipolar broadening; A/h is the hyperfine coupling constant, in cps; and the other symbols are familiar or have been defined previously (see below for the calculation of A/h).

In the present instance we have

$$\tau_c^{-1} = (2 \times 10^{-10})^{-1} + (3.7 \times 10^{-11})^{-1} \cong 3 \times 10^{10}\ \text{sec}^{-1}$$

and taking $r = 3.044 \times 10^{-8}$ cm, $S = {}^3/_2$, and A/h from Table II, the following result is obtained for vanadocene.

$$\Delta H_{1/2} \cong 1800 \text{ cps (dipolar)} + 250 \text{ cps (contact)} \cong 2050 \text{ cps}$$

Here we have indicated that the first term in (5) gives rise to dipolar (through space) broadening of the resonance, while the second term, which includes the hyperfine coupling constant explicitly, gives rise to contact broadening of the nuclear resonance. An analogous calculation for nickelocene leads to

$$\Delta H_{1/2} \cong 25 \text{ cps (dipolar)} + 5 \text{ cps (contact)}$$

The vanadocene result compares favorably with the experimental line width of 2250 cps, and the indication is that the broadening is mainly dipolar in origin. On the other hand, the nickelocene result is in rather poor agreement with the experimental line width of 550 cps. The expectation that the calculated result for nickelocene would indicate a considerably narrower line width than vanadocene is, however, upheld. It is perhaps not surprising that the nickelocene result is poor, since the calculation is very sensitive to the value of T_1. For $T_1 = 6 \times 10^{-12}$ sec, one obtains for nickelocene

$$\Delta H_{1/2} \cong 500 \text{ cps (dipolar)} + 80 \text{ cps (contact)} \cong 580 \text{ cps}$$

which is in good agreement with the experimental result of 550 cps.

It seems fairly clear that the electron relaxation times in both vanadocene and nickelocene are quite short, and that the dominant nuclear relaxation is dipolar. One expects therefore that eq 6 will hold approximately for the methyl-substituted metallocenes

$$\Delta H_{1/2}(\text{ring})/\Delta H_{1/2}(\text{methyl}) = r^6(\text{methyl})/r^6(\text{ring}) \quad (6)$$

From the coordinates calculated for the molecular orbital calculations, we estimate $r^6(\text{methyl}) = 2.95 \times 10^{-45}\ \text{cm}^6$, and $r^6(\text{ring}) = 7.9 \times 10^{-46}\ \text{cm}^6$. This leads to

$$\Delta H_{1/2}(\text{ring})/\Delta H_{1/2}(\text{methyl}) \cong 3$$

This result compares favorably with the range of values in Table II. The ratio is of course very sensitive to the distances, which are raised to the sixth power, and which are not known accurately in any event. If the line widths of the dimethylmetallocenes were determined solely by the second (contact) term in (5), then the ratio of ring proton to methyl line widths should vary as the square of the hyperfine coupling constants. Using the data in Table II, the following approximate ring/methyl line-width ratios are obtained for contact broadening: V, ~8; Cr, ~88; Co, ~28; Ni, 1.6. Thus, contribution to the line width by the contact part would lead to a net ring/methyl ratio greater than ~3 for V, Cr, and Co, and less than 3 for Ni. The fact that this is what is observed experimentally suggests that both contributions are important, with the dipolar term being dominant in each case, except possibly for vanadocene.

The dominant relaxation mechanism in chromocene is not known. There probably is a significant zero-field splitting in chromocene ($S = 1$), and this would lead to short relaxation times, according to eq 3. A second relaxation mechanism may also be important with chromocene: interaction of the ground state with low-lying excited states. Both the near-degeneracy of the a_{1g} and e_{2g} molecular orbitals and the expected Jahn–Teller splitting of the $^3E_{2g}$ state could lead to excited states very close in energy to the ground state. The effects of these low-lying levels on electron relaxation have been worked out by Van Vleck.[35]

Cobaltocene ($S = {}^1/_2$) cannot undergo relaxation *via* zero-field splitting, but is expected to undergo a Jahn–Teller distortion to relieve the $^2E_{1g}$ ground-state degeneracy, giving rise to low-lying excited states. As with chromocene, this can lead to efficient relaxation.

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(34) "Handbook of Chemistry and Physics," 42nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 2202.

(35) J. H. Van Vleck, *Phys. Rev.*, 57, 426 (1940).

The very narrow line width of the nuclear resonance for cobaltocene and the appearance of an esr signal only at 4°K both suggest very short T_1's for cobaltocene.

Since the dipolar nuclear relaxation is strongly dominant in chromocene and cobaltocene (see above), only the first (dipolar) term in eq 5 is used to estimate $1/T_1$. The results are $1/T_1$ (est) $< 5 \times 10^{-11}$ sec for chromocene and $1/T_1$ (est) $< 2 \times 10^{-11}$ sec for cobaltocene.

This section is concluded with a consideration of the relative magnitudes of the tumbling time (τ_r) and the electron relaxation time. The molecular rotation frequency, $1/\tau_r$, was found to be approximately 5×10^9 cps for the metallocenes and would be somewhat smaller for a substituted metallocene. And the values of T_1 were all estimated to be of the order 10^{-11} sec or less. One then has $T_1 < \tau_r$ in all cases. The conclusion that $T_1 < \tau_r$ in all cases is supported by the experimental line widths of the substituted and unsubstituted neutral metallocenes. Table II indicates that substitution has little effect on the line width of the ring protons. This implies that τ_c^{-1} is dominated by T_1^{-1} and not by τ_r^{-1}, since τ_r should increase significantly on substitution. Changes in τ_r^{-1} are therefore swamped by the much larger T_1^{-1}. Dimethylferricenium appears to be an exception.

3. Calculation of the Hyperfine Coupling Constants. Jesson[36] has discussed the relation between the nmr contact shift and the hyperfine coupling constants. Various cases are recognized, depending on the relative magnitudes of τ_r, $|g_\parallel - g_\perp|\beta H/\hbar$, and T_1.

In the limit of small anisotropy, with $g_{av} = (g_\parallel + 2g_\perp)/3$, and with $T_1 < \tau_r$ (see above), we have

$$\Delta\nu = -g_{av}\beta_e S(S+1)\nu A/g_N\beta_N(3kT) \qquad (7)$$

where $\Delta\nu$ is the contact shift (the difference in chemical shift between the paramagnetic complex and the diamagnetic reference). ν is the spectrometer frequency (60 MHz), S is the total spin, and A is the hyperfine coupling constant, in ergs. g_{av}, β_e, g_N, and β_N have been previously defined.

Equation 7 can be converted to (for proton resonance)

$$(A/h)\ (\text{MHz}) = \frac{(9.43 \times 10^{-4})\Delta\nu\ (\text{Hz})}{g_{av}S(S+1)}\left(\frac{T}{298}\right) \qquad (8)$$

for convenience in calculation. The results are listed in Table II. The g_{av} values were obtained either from the esr results (vanadocene, $g_{av} = 2.00$; cobaltocene, $g_{av} = 1.7$) or from the bulk susceptibility results in Table I (chromocene, $g_{av} = 2.27$; ferricenium ion, $g_{av} = 2.7$; nickelocene, $g_{av} = 2.04$). The use of eq 8 implies that the complex obeys the Curie law, which we have shown experimentally for dimethylvanadocene, dimethylchromocene, dimethylcobaltocene, and dimethylnickelocene. There is little doubt that the $^4A_{2g}$ ground state of vanadocene does obey the Curie law.

D. Interpretation of the Hyperfine Coupling Constants. 1. Pseudocontact Shifts. We now examine what part the through-space dipolar electron–proton coupling might play in the observed resonance shifts. In order to calculate the pseudocontact shift, one needs estimates of τ_r, $|g_\parallel - g_\perp|\beta H/\hbar$, and T_1, which have already been discussed. For the two relevant cases, Jesson[36] gives

(a) for $1/\tau_r \ll |g_\parallel - g_\perp|\beta H/\hbar;\ T_1 \ll \tau_r$

$$\frac{\Delta\nu}{\nu} = K(g_\parallel + g_\perp)(g_\parallel - g_\perp)/3 \qquad (9)$$

(b) for $1/\tau_1 \gg |g_\parallel - g_\perp|\beta H/\hbar;\ T_1 \ll \tau_r$

$$\frac{\Delta\nu}{\nu} = K(3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)/15 \qquad (10)$$

with

$$K = \frac{-\beta^2 S(S+1)}{3kT}\left(\frac{3\cos^2\chi - 1}{r^3}\right) \qquad (11)$$

For a cobaltocene ring proton, $r = 2.91 \times 10^{-8}$ cm and $\chi \approx 53°$. For cobaltocene, where $|g_\parallel - g_\perp| \sim 0.07$,[21] one gets $|\Delta\nu| \cong 8$ cps (from eq 9) and $|\Delta\nu| \cong 5$ cps (from eq 10) for the ring protons. The geometric factor $(3\cos^2\chi - 1)/r^3$ is difficult to calculate for a methyl group attached to a cyclopentadienyl ring, since the entire term must be averaged over all the rotations of the methyl group. Such an average was apparently carried out by Fritz, Keller, and Schwarzhans[7] in their study of the dimethylferricenium ion. We estimate from their results that the geometric factor for a methyl group is approximately four times as large as that for the ring proton, and with opposite sign. Pseudocontact shifts of 15–25 cps would therefore be expected at the methyl protons of dimethylcobaltocene.

Using the relatively large anisotropy observed in the di(π-(1)2,3-dicarbollyl)iron(III) and related species by Maki and Berry,[37] where $g_\parallel \sim 3.6$ and $g_\perp \sim 1.8$, a pseudocontact shift of approximately -300 cps is calculated at the ring proton of ferricenium ion. Under these conditions, an attached methyl group should have a pseudocontact shift of approximately $+1200$ cps. Fritz, Keller, and Schwarzhans[7] concluded that, for an R group attached to ferricenium ion, the geometric factors are all nearly equal and of the same sign for each different set of protons in the R group. For *n*-propyl attached to the ring, the experimentally observed shifts are α-CH$_2$, $+1110$ cps; β-CH$_2$, $+420$ cps; γ-CH$_3$, $\sim$0 cps. Hence it appears that the pseudocontact shift is not important even in ferricenium cation, where a fairly large anisotropy might reasonably have been expected.[37]

It is concluded that, for vanadocene, cobaltocene, nickelocene, and the dimethyl analogs, the pseudocontact contribution to the observed shift is completely negligible. This conclusion follows from the experimentally determined small anisotropies, which have been discussed. The magnitude of the anisotropy in chromocene is unknown. However, pseudocontact shifts of the order -600 cps are expected if the anisotropy does not exceed $(g_\parallel - g_\perp) = 1.8$. Such a shift is small in comparison with the observed shift for chromocene, and it is concluded that the contact shift strongly dominates the pseudocontact shift (if any) in chromocene. A comparatively large pseudocontact shift may be expected at the methyl group of dimethylchromocene. For $g_\parallel - g_\perp = 2$ and $S = 1$, one would

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

(37) A. H. Maki and T. E. Berry, *J. Am. Chem. Soc.*, 87, 4337 (1965).

expect a pseudocontact shift of perhaps +3500 cps at the methyl hydrogens. This point will be considered in more detail below.

Fritz, Keller, and Schwarzhans[6] concluded that the similarity of the metallocene contact shifts in solution and in the solid state implies a small or zero pseudocontact contribution. It is not correct to draw such a conclusion, however, since in the present case it has been shown that $1/\tau_r < |g_{\parallel} - g|\beta H/\hbar$ and $T_1 < \tau_r$ are nearly satisfied. Under these conditions, the pseudocontact shift is the same in the solid state and in solution.[36]

That small pseudocontact shifts are expected for the metallocenes is due mainly to the $(3 \cos^3 \chi - 1)$ term. At $\chi = 55°$, $3 \cos^2 \chi = 1$, and $(3 \cos^2 \chi - 1)$ vanishes. Hence for $\chi = 53°$, as was shown to apply here, this term is rather small. On the other hand, the r^{-3} term is relatively large, since 3 Å is a fairly short metal–proton distance.

2. The Levy–Orgel Model for Electron Delocalization in the Metallocenes. In 1960, Levy and Orgel attempted to interpret the nmr contact shifts of the metallocenes. At that time the only experimental results available were for the solid metallocenes of V, Cr, Mn, Co, and Ni.[3,4] It was considered that the unpaired spin delocalization involves orbitals which are of π symmetry, and that the unpaired π electron density in the cyclopentadienyl molecular orbitals polarizes the C–H σ bond such that spin density of sign opposite that in the π system is induced in the hydrogen 1s orbital. The π–σ polarization effect was first discussed by McConnell and coworkers[38–40] in connection with the proton hyperfine interactions observed in aromatic free radicals. For the trigonal aromatic C–H fragment, eq 12 was deduced for the description of the proton hyperfine interaction

$$A_{\mathrm{H}} = Q_{\mathrm{H}}\rho_{\mathrm{c}} \qquad (12)$$

where A_{H} is the hyperfine splitting, in gauss, due to the proton; Q_{H} is an empirical constant; and ρ_{c} is the unpaired electron density in the carbon p_z orbital. For the benzene radical ion, $A_{\mathrm{H}} = -3.75$ G, $\rho_{\mathrm{c}} = {}^1/_6$ for each carbon, and therefore $Q_{\mathrm{H}} = -22.5$ G.

It is immediately apparent that delocalization of π electrons in the metallocenes (e_{2g} for V and Cr, e_{1g}^* for Co and Ni) would lead to negative spin density on the protons, and positive contact shifts in every case. This, of course is not observed, and prompted Levy and Orgel to examine the metallocene contact shifts in more detail.

Levy and Orgel discussed the delocalization on the basis of Figure 1, which is a crude partial molecular orbital picture of the bonding, but which does reflect the proper ground state as successive electrons are added. Figure 1 implies the following electron distributions: vanadocene, $(e_{2g})^2(a_{1g})^1$; chromocene, $(e_{2g})^3(a_{1g})^1$; cobaltocene, $(e_{2g})^4(a_{1g})^2(e_{1g}^*)^1$; nickelocene, $(e_{2g})^4(a_{1g})^2(e_{1g}^*)^2$. These ground-state electron distributions are consistent with those which were established above on the basis of the best experimental evidence.

Levy and Orgel proposed that the weakly bonding, unpaired e_{2g} and a_{1g} electrons in vanadocene and chromocene *polarize* the paired electron density in the ring e_{1g} orbitals. This polarization would be such that net unpaired spin density parallel to that on the metal would appear in the e_{1g} orbital near the metal ion, leaving a net *negative* spin density near the cyclopentadienyl carbon atom. This negative spin density would then lead to the appearance of positive spin density in the hydrogen 1s orbital, according to eq 12. The resultant positive spin density at hydrogen would lead to the observed downfield contact shifts for vanadocene and chromocene. Levy and Orgel argued that *delocalization* of *positive* spin density in the a_{1g} and e_{2g} molecular orbitals (from d_{z^2}, d_{xy}, $d_{x^2-y^2}$) is a minor process compared to the *polarization* of the e_{1g} orbitals by a_{1g} and e_{2g} electrons, leading to negative spin density in e_{1g}. It was supposed that the "weakly bonding" character of a_{1g} and e_{2g} justifies the small part assigned delocalization of positive spin density.

Levy and Orgel considered that the delocalization of positive spin density predominates in cobaltocene and nickelocene, for here the unpaired electron density is in the strongly mixed e_{1g}^* orbital, which comes from d_{xz} and d_{yz}. This delocalization effect then leads to positive contact shifts, consistent with the experimental results.

While the theory proposed by Levy and Orgel does give an account of the *direction* of the contact shifts, it does not seem to give a consistent explanation of the relative *magnitudes* of the shifts. Hence Levy and Orgel calculated that the unpaired spin density in the carbon $2p_z$ orbital in chromocene is twice that in vanadocene. But clearly there is one less unpaired spin in chromocene, so we should expect to find *less* spin density at carbon in chromocene, if the theory is to be accepted. A second difficulty with the theory is more serious. We may accept, for the moment, the hypothesis that the polarization effect is much stronger than e_{1g} or a_{1g} delocalization, but can we expect a second-order polarization effect (*e.g.*, as proposed in chromocene) to be more important than direct delocalization of e_{1g}^* electrons (*e.g.*, as in nickelocene)? This would seem to be required for the Levy and Orgel model, since the "polarization-induced" hyperfine coupling constants are as large or larger in absolute magnitude than the "delocalization" coupling constants. Hence, for the two $S = 1$ cases, chromocene and nickelocene, the coupling constants are +1.40 and −1.26 G, respectively.

These inconsistencies led us to inquire into how large a coupling constant might be expected for the Levy–Orgel "Consecutive Polarization" model. Colpa and de Boer have discussed spin polarization and delocalization effects in the $\cdot$C–C–H fragment,[41] and their conclusions are of interest in the present connection. The problem is formally similar to that of the V–C–H or Cr–C–H fragments.

Consider the $\cdot C_1$–C_2–H fragment: for the process involving (1) polarization of the C_1–C_2 bond by the unpaired spin and (2) consecutive polarization of the C_2–H bond by the C_1–C_2 bond, a hyperfine coupling constant of +0.65 G was calculated.[41] For the process involving *direct* polarization of the C_2–H bond by the

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[38] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[39] H. M. McConnell, *ibid.*, **24**, 764 (1956).

[40] H. M. McConnell and D. B. Chesnut, *ibid.*, **27**, 984 (1957).

[41] J. P. Colpa and E. de Boer, *Mol. Phys.*, 7, 333 (1963–1964).

unpaired p_z electron on C_1, a coupling constant of -1.76 G was obtained. The net electron–proton coupling constant calculated theoretically is therefore -1.1 G and is the sum of a consecutive and a direct polarization. Notice that *negative* spin density is expected, at hydrogen, on the basis of spin-polarization arguments.

These magnitudes of the spin-polarization coupling constants are strongly dependent on the two-center, two-electron exchange integrals involved. Hence, we would reasonably expect that polarization effects would be much larger in C–C bonds than in M–C bonds, since, in the latter case, the exchange interactions are diminished, even as the magnitudes of the overlap integrals are diminished. One therefore concludes that consecutive M–C–H polarization should occur with a coupling constant considerably smaller than $+0.65$ G, which is appropriate for C–C–H fragments. The fact that the vanadocene and chromocene couplng constants are greater than those observed in carbon frameworks further supports our idea that polarization is not a dominant factor in the metallocenes. Moreover, as Colpa and de Boer have shown, when the *direct* polarization of the C_2–H bond is considered, the conclusion is that the net process of direct and consecutive polarization leads to *negative* spin density on the hydrogen. One might expect that a full treatment of d-electron-ligand polarization would in fact predict negative spin density in the hydrogen 1s orbital, not positive spin density as supposed by Levy and Orgel. Even so, one would not expect such effects to dominate the coupling constants. It is seen, therefore, that when the theory is examined critically, difficulties emerge.

In order to clarify the problem of delocalization in the metallocenes, we determined that an experimental test of the Levy–Orgel hypothesis should be carried out. It is well known that methyl groups attached to aromatic radicals show hyperfine splittings of the same order of magnitude as the in-plane aromatic protons. It is also known that the methyl group–electron coupling can be crudely described by an equation similar to eq 12, with the proportionality term, Q_{CH_3}, being in this case a positive quantity, rather than negative.[41–45] Hence the unpaired spin density is of the same sign in the aromatic system (or a $2p_z$ orbital) and on the CH_3 hydrogens. The CH_3–electron coupling has been treated theoretically by several workers.[41–44] It is concluded that unpaired spin density in the carbon $2p_z$ orbital is directly delocalized onto the methyl hydrogens, with no change in sign. This effect arises by virtue of the fact that the methyl hydrogens are not orthogonal to the p_z orbital, and that suitable linear combinations of the 1s orbitals give rise to a bonding p_z CH_3 molecular orbital. McLachlan,[42] using such a molecular orbital approach, estimated $Q_{CH_3} \approx 28$ G. Colpa and de Boer[41] and Chesnut[43] concur in the estimation of Q_{CH_3}. The experimental values for Q_{CH_3} lie in the range 20–35 G, with $\sim$30 G being common.[41,42]

Since the experimental value of Q_H for cyclopentadiene is -29.9 G,[46] and the expected Q_{CH_3} is $\sim+30$ G, the Levy–Orgel hypothesis would imply that the 1,1′-dimethylmetallocenes should show methyl contact shifts with sign opposite the ring proton shifts, and approximately the same magnitude. In order to experimentally test the theory, we therefore decided to prepare the 1,1′-dimethylmetallocenes and record their nmr spectra.

Table II indicates the complete failure of the polarization model in accounting for the methyl shifts in dimethylvanadocene and dimethylchromocene. Indeed, the methyl groups are found fully 25,000–30,000 cps downfield from where one might have expected to find the resonances. Thus, the methyl coupling constants have both the wrong magnitude and the wrong sign, according to the Levy–Orgel model. Dimethylnickelocene does have $A_H = -1.25$ G and $A_{CH_3} = +0.98$ G, and is therefore in accord with the expectations based upon delocalization of e_{1g} electrons into the ring π system. The anomalously low A_{CH_3} for dimethylcobaltocene can be understood on the same basis, as will be discussed in more detail in a subsequent paper in which our model for delocalization is treated with a molecular orbital calculation.

We have found that the Levy–Orgel spin polarization model fails in four areas: (1) the *relative* magnitudes of the vanadocene and chromocene shifts cannot be explained; (2) the *relative* magnitudes of the chromocene and nickelocene shifts are not easy to understand; (3) the *absolute* magnitude and sign of the effect may have been improperly assessed; (4) predictions of the magnitudes and signs of methyl group contact shifts are not borne out by the experimental facts. We therefore, seek to understand these contact shifts on a different basis.

The fact that in both vanadocene and chromocene the methyl group shows a much smaller positive hyperfine coupling constant than the ring protons suggests strongly that the unpaired spin density is in fact in an orbital of σ symmetry rather than π symmetry. Electron delocalization in ligand σ orbitals is expected to lead to positive coupling constants (positive spin density on the protons) and to strong attenuation of the magnitude of the coupling constant as the number of bonds between the metal and the proton increases. Electron delocalization in orbitals of σ symmetry has been observed for nickel complexes of pyridine,[47,48] for nickel complexes of aliphatic amines,[49] and in aliphatic side chains attached to nickel aminotroponeiminate complexes.[50] In every case the observed positive spin density attenuates strongly as the number of bonds increases, which seems reasonable if one considers σ electron density to be "localized."

In order to estimate the possible influence of σ bonding in the metal dicyclopentadienyls, we have carried out extended Hückel molecular orbital calculations for vanadocene, methylvanadocene, cobaltocene, methylcobaltocene, nickelocene, and methylnickelocene. The results of these calculations and conclusions drawn therefrom will be discussed in a subsequent paper.

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