

## Nuclear Magnetic Resonance Contact Shifts of Substituted Paramagnetic Metallocenes

By MICHAEL F. RETTIG and RUSSELL S. DRAGO

(Department of Chemistry, University of Illinois, Urbana, Illinois, 61801)

SUBSEQUENT to the initial reports<sup>1,2</sup> and discussion<sup>3</sup> of the n.m.r. contact shift results for the paramagnetic metallocenes of the first transition series, almost no new pertinent experimental data have appeared. This Communication reports results which cannot be accounted for on the basis of the simple model previously postulated.<sup>3</sup> That treatment<sup>3</sup> of the metallocene contact shifts assumed that the unpaired spin density resides in metallocene  $\pi$ -orbitals, and that the cyclopentadienyl protons interact with the  $\pi$  spin density by the atomic exchange coupling mechanism.<sup>4</sup> The coupling constant,  $A$ , for such a  $\pi$ - $\sigma$  coupling is related to the unpaired spin density,  $\rho$ , in the  $\pi$ -orbital of the aromatic carbon by the equation  $A = Q\rho$ , where  $Q$  is a proportionality constant equal to approximately  $-22.5$  gauss for an aromatic C-H fragment. It has been shown<sup>5</sup> that an equation of exactly the same form describes the hyperconjugative coupling of a methyl group

with the  $\pi$ -orbital of an aromatic carbon, but in this case  $Q$  is *positive*, with values near 25 gauss usually being observed.

Clearly, if the postulated mechanisms<sup>3,4</sup> dominate the metallocene contact shifts, then the methyl contact shifts of the 1,1'-dimethylmetallocenes should be numerically about the same magnitude as the ring proton contact shifts, but should occur with opposite sign.

The compounds described here were prepared analytically pure as extremely air-sensitive, low-melting solids, using a modification of the procedure reported for the preparation of dimethylnickelocene.<sup>6</sup> The n.m.r. spectra were obtained in thoroughly degassed toluene at 28°, using a Varian DP-60 spectrometer. The n.m.r. results are presented in the Table.

In every case studied so far the methyl resonance is shifted downfield. Only for 1,1'-dimethylnickelocene does the result approximate to that

TABLE  
N.m.r. contact shifts of dimethylmetallocenes

	$\nu_{\text{ring}}^a$	$\nu_{\text{methyl}}$
V(C <sub>6</sub> H <sub>7</sub> ) <sub>2</sub>	$-2.000 \times 10^4$ (2680)	$-6.895 \times 10^3$ (402)
Cr(C <sub>6</sub> H <sub>7</sub> ) <sub>2</sub>	$-1.844 \times 10^4$ (1250) <sup>b</sup> $-2.170 \times 10^4$ (1370)	$-1.860 \times 10^3$ (230)
Co(C <sub>6</sub> H <sub>7</sub> ) <sub>2</sub>	$+3.107 \times 10^3$ (234) <sup>b</sup> $+4.495 \times 10^3$ (279)	$-3.87 \times 10^2$ (55)
Ni(C <sub>6</sub> H <sub>7</sub> ) <sub>2</sub>	$+1.538 \times 10^4$ (529)	$-1.160 \times 10^4$ (182) <sup>c</sup>

<sup>a</sup> Shifts relative to aromatic protons of toluene, in c./sec.; numbers in parentheses are linewidths in c./sec.; spectra were assigned by comparison with the spectra of the unsubstituted metallocenes and by integration.

<sup>b</sup> Ring protons resolved into equal intensity doublet.

<sup>c</sup> This result is in sharp disagreement with a recent report (H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch.*, 1966, **21b**, 809): [ $\nu_{\text{ring}} = +1.54$

$\times 10^4$  (1400);  $\nu_{\text{methyl}} = +1.233 \times 10^4$ ]. The discrepancy is not fully understood at present, but, on the basis of the broader line observed by Fritz *et al.*, it is felt that partial oxidation to Ni(C<sub>6</sub>H<sub>7</sub>)<sub>2</sub><sup>+</sup> may have occurred in the other work.

expected for the simple  $\pi$  delocalization model.<sup>3</sup> We are thus forced to conclude that other delocalization mechanisms are involved. Accordingly we are studying in detail the problem of spin delocalization in the metallocenes. In this connection, studies of 1,1'-diphenylmetallocenes, interactions of the metallocenes with  $\pi$ -acids, low-temperature solution n.m.r. spectra, and wide-line n.m.r. spectra of the solid complexes are under way, and are expected to be of value in the clarification of this problem.

(Received, November 8th, 1966; Com. 869.)

<sup>1</sup> H. M. McConnell and C. A. Holm, *J. Chem. Phys.*, 1957, **27**, 314.

<sup>2</sup> H. M. McConnell and C. A. Holm, *J. Chem. Phys.*, 1958, **28**, 749.

<sup>3</sup> D. A. Levy and L. E. Orgel, *Mol. Phys.*, 1960, **3**, 583.

<sup>4</sup> H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 1958, **28**, 107.

<sup>5</sup> A. D. McLachlan, *Mol. Phys.*, 1958, **1**, 233.

<sup>6</sup> L. T. Reynolds and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1959 **9**, 86.