

the best agreement with experiment one finds 1.4 kcal./mole as the energy difference between I and II.¹²

The conformational preference for I cannot be attributed to steric effects because on the basis of internuclear distances nonbonded interactions should be more severe in I than in II. Furthermore, it has been shown that the structural equivalent of II becomes the more stable conformation when steric effects are amplified by introducing methyl groups at the cyclopropane ring *cis* to the phenyl ring.⁴ We therefore believe that electronic effects similar to those proposed by Walsh must be responsible for lowering the potential energy in conformation I.

(12) Because of the many assumptions inherent in this treatment there is little justification for attaching limits of uncertainties to this value.

(13) A. P. Sloan Foundation Research Fellow.

G. L. Closs,¹³ H. B. Klinger

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637
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Carbon-13 Nuclear Magnetic Resonance Spectra of Transition Metal Cyclopentadienyl and Carbonyl Derivatives

Sir:

C¹³ n.m.r. spectra of transition metal cyclopentadienyl and carbonyl derivatives have been relatively little investigated. Previous reports include measurements of the carbon magnetic shieldings in ferrocene,¹

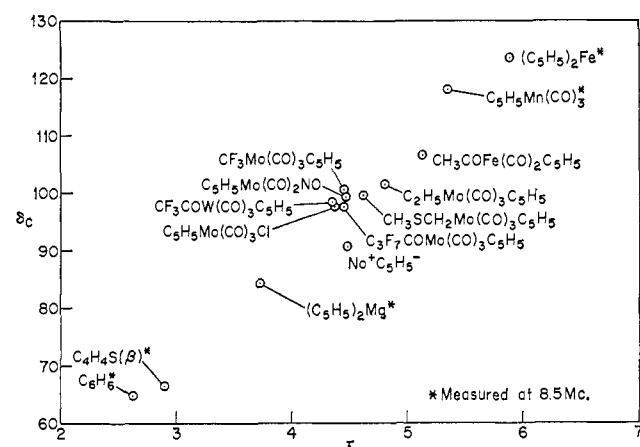


Figure 1. H¹ vs. C¹³ chemical shift in aromatic metal complexes.

iron pentacarbonyl,²⁻⁴ iron dicarbonyl nitrosyl,³ and nickel tetracarbonyl.^{3,4} We have undertaken an investigation of the C¹³ spectra of a more extensive and varied series of compounds and wish now to report our initial results.

Some of the cyclopentadienyl derivatives which we studied are listed in Table I. All of the cyclopentadienyl carbon resonances were doublets, with a carbon-hydrogen spin-spin coupling of approximately 175 c.p.s. Of particular interest is the fact that the plot in Figure 1 of the carbon shieldings against the shieldings of the corresponding protons is almost a straight line, collinear with the similar line for aromatic rings.⁵

(1) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(2) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

(3) R. Bramly, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(4) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

Table I. Cyclopentadienyl Resonances^a

Compound	C ¹³ shielding, p.p.m. ^b	H ¹ shielding, p.p.m. ^c
(C ₅ H ₅) ₂ Mg	84.2 ^d (C ₆ H ₆)	3.72 (Et ₂ O)
C ₅ H ₅ Na	90.7 ^e (THF ^f)	4.48 (THF)
C ₅ H ₅ Mo(CO) ₃ Cl	97.9 (C ₆ H ₆)	4.37 (CHCl ₃)
C ₃ F ₇ COMo(CO) ₃ C ₅ H ₅	97.9 (C ₆ H ₆)	4.45 (CHCl ₃)
CF ₃ COW(CO) ₃ C ₅ H ₅	98.7 (C ₆ H ₆)	4.35 (CHCl ₃)
C ₅ H ₅ Mo(CO) ₂ NO	99.2 (CH ₂ Cl ₂)	4.47 (CS ₂)
CH ₃ SCH ₂ Mo(CO) ₃ C ₅ H ₅	99.6 (CH ₂ Cl ₂)	4.62 (CS ₂)
CF ₃ Mo(CO) ₃ C ₅ H ₅	100.9 (C ₆ H ₆)	4.45 (CHCl ₃)
C ₂ H ₅ Mo(CO) ₃ C ₅ H ₅	101.1 (C ₆ H ₆)	4.80 (CS ₂)
CH ₃ COFe(CO) ₂ C ₅ H ₅	106.3 (C ₆ H ₆)	5.13 (CS ₂)
C ₅ H ₅ Mn(CO) ₃	118 ^d (C ₆ H ₆ , CH ₃)	5.35 (CS ₂)
(C ₅ H ₅) ₂ Fe	123.6 ^d (CS ₂)	5.89 (CS ₂)

^a Solvent given in parentheses. ^b To high field from CS₂. ^c τ -scale: G. V. D. Tiers, *J. Phys. Chem.*, **68**, 1151 (1958). Spectra measured at 60 Mc. ^d Spectrum measured at 8.5 Mc.; other carbon spectra measured at 25.143 Mc. ^e H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961). ^f Tetrahydrofuran.

Table II. Carbonyl Resonances^a

Compound	C ¹³ shielding, p.p.m. ^b
CO	11.5 ^{c,d} (gas)
Ni(CO) ₄	1.2 ^{d,e} (neat liquid)
C ₃ F ₇ Fe(CO) ₄ I	-6 ^d (CHCl ₃)
Fe(CO) ₂ (NO) ₂	-14 ^f (neat liquid)
[Fe(CO) ₃ SCH ₃] ₂	-16.6 ^d (CHCl ₃)
Fe(CO) ₅	-16.8 ^d (neat liquid)
C ₅ H ₅ Fe(CO) ₂ I	-20.9 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.4, -26.0 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.0, -25.4 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₃ Cl	-32.6 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₂ NO	-34.5 (CH ₂ Cl ₂)

^a Solvent given in parentheses. ^b To high field from CS₂. ^c R. Ettinger, P. Blume, A. Patterson, Jr., and P. C. Lauterbur, *J. Chem. Phys.*, **33**, 1547 (1960). ^d Spectrum measured at 8.5 Mc.; other spectra measured at 25.143 Mc. ^e J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). ^f R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); measured at 12.069 Mc. ^g C₇H₈ is bicyclo[2.2.1]heptadiene (norbornadiene).

The variations in carbon and hydrogen shieldings in aromatic rings seem to be dominated by the local π -charges, and a similar interpretation of the shieldings in cyclopentadienyl rings might be attempted. It appears to be very unlikely, however, that the charge separations implied by such a simple theory can be reconciled with other considerations.⁶ No convincing explanation of these results within the framework of the current approximate shielding theory has been found. It may be suggested tentatively that molecular currents similar to those responsible for high-field carbon and hydrogen shifts in acetylenes and three-membered rings may be responsible for the anomalies.⁷

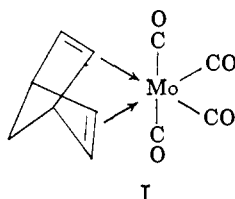
(5) P. C. Lauterbur, *Tetrahedron Letters*, No. 8, 274 (1961); H. Spiesecke and W. G. Schneider, *ibid.*, No. 8, 468 (1961).

(6) For example, ferrocene would be expected to be several orders of magnitude more reactive to electrophilic substitution than benzene or even cyclopentadienide ion, in disagreement with experimental results. [For suitable reviews of the chemistry of cyclopentadienyl derivatives see P. L. Pauson, *Quart. Rev.* (London), **9**, 391 (1955); E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1959); G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).]

(7) A fairly close analogy between the carbon-carbon triple bond and the metal-cyclopentadienyl bond may be drawn. The latter may be regarded as being made up of a σ -bond between the ring A orbitals and a metal hybrid orbital and two perpendicular π -bonds formed between

Resonances of carbonyl carbons have been more difficult to find. Some of our data are given in Table II. Conspicuously absent from the list of carbonyl resonances are those of manganese and cobalt compounds. These resonances must be split and broadened by spin-spin coupling with high-spin metal nuclei undergoing moderately rapid quadrupole-induced relaxation. In the spectrum of cyclopentadienylmanganese tricarbonyl, it has indeed been possible to observe a broad (about 170 c.p.s.), weak carbonyl resonance at about -28 p.p.m. from CS_2 . That the carbon-metal couplings in such compounds can be large is shown by the observation of a 116-c.p.s. splitting of the C^{13} satellites in the V^{51} resonance of the symmetrical $\text{V}(\text{CO})_6^-$ anion in a tetrahydrofuran solution of $[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$.

The C^{13} n.m.r. spectrum of bicyclo[2.2.1]heptadienemolybdenum tetracarbonyl (I) was found to have two resonances of approximately equal intensities in the carbonyl region. The carbon shieldings in the two types of carbonyl groups shown below must therefore



be different, but there is no way at present to associate a resonance with a particular pair of carbonyl groups.

The limited data available do not seem to provide firm grounds for any useful generalizations. A rough correlation between estimated metal-carbon bond orders and carbonyl carbon shieldings is suggested by these results, but more experimental studies are obviously required.

the ring E_1 bonding orbitals and metal hybrid orbitals. Back bonding between ring E_2 antibonding orbitals and filled metal d-orbitals is probably less important in these complexes.

P. C. Lauterbur
State University of New York
Stony Brook, Long Island, New York

R. B. King
Mellon Institute
Pittsburgh, Pennsylvania 15213
Received April 28, 1965

Homotropylium Ion and Its Molybdenum Tricarbonyl Complex¹

Sir:

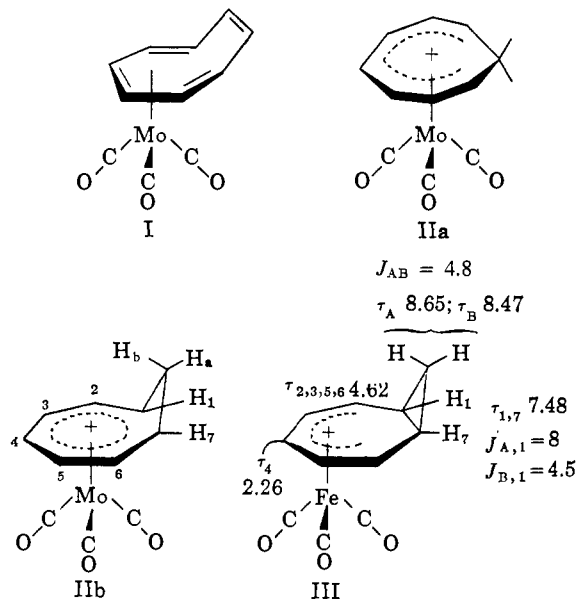
The different electronic requirements of transition metal atoms in their complexes exert a corresponding control on the resulting structure and thus constitute a powerful tool in the study of various aspects of homoconjugation, homoaromaticity, and nonclassical structures.²

We have now prepared for the first time the cyclooctatetraene complex $\text{C}_8\text{H}_8\text{Mo}(\text{CO})_3$ (I), in which this olefin is bound to a metal by six π -electrons on six carbon atoms ($6\pi-6\text{C}$). This complex can be protonated to examine the predicted $6\pi-7\text{C}$ electronic system in cation II. Especially interesting is the question whether II

(1) Research sponsored by U. S. Army Research Office (Durham) and the National Science Foundation G.P. 4175.

(2) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **81**, 6523 (1959); **83**, 3244 (1961); *Tetrahedron Suppl.*, **2**, 423 (1963).

is cyclooctatrienyl (IIa) or monohomotropylium (IIb) in character. It is of obvious importance to compare cation II with the related $\text{C}_8\text{H}_9^+\text{Fe}(\text{CO})_3$ cation (III) studied previously by Schrauzer³ and Wilkinson,⁴



and also the free C_8H_9^+ ion mentioned earlier by Pettit.⁵

Compound I is obtained as red crystals in 60–70% yield by stirring cyclooctatetraene with pale yellow diglyme-molybdenum tricarbonyl⁶ in hexane at 50° .

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{MoO}_3$: C, 46.50; H, 2.84; Mo, 33.77. Found: C, 46.74; H, 2.90; Mo, 33.36.

Nuclear magnetic resonance of I in toluene solution at 30° showed a broad band (half-width 25 c.p.s.) at $\tau 6.05$ (which became a sharp singlet at 80°).⁷ In concentrated H_2SO_4 I gives an n.m.r. spectrum summarized in Figure 1. This displays a 5:2:1:1 proton pattern with assignments as shown. Especially striking is the large chemical shift between "inside" and "outside" H_b and H_a methylene protons. From the spectrum of I in D_2SO_4 (Figure 1) it is evident that protonation is stereospecific, the proton added to the complex I becoming the "outside" proton H_a . This n.m.r. spectrum of $\text{C}_8\text{H}_9^+\text{Mo}(\text{CO})_3$ bears a striking resemblance to that of the parent cation from protonation of cyclooctatetraene in H_2SO_4 . As is clear from Figure 1 the spectrum of C_8H_9^+ in H_2SO_4 (also observed by Pettit⁵ for C_8H_9^+ in H_2SO_4 and $\text{C}_8\text{H}_9^+\text{SbCl}_6^-$ in MeNO_2) has the 5:2:1:1 pattern which in our hands was sufficiently well resolved to determine H_1-H_b , H_1-H_a , and H_a-H_b coupling constants. The chemical shift between H_b and H_a is even larger in the free ion (5.8 p.p.m.) than in the $\text{Mo}(\text{CO})_3$ complex (3.5 p.p.m.). In contrast, the n.m.r. spectrum of $\text{C}_8\text{H}_9^+\text{Fe}(\text{CO})_3$ in H_2SO_4 reported by Schrauzer³ and Wilkinson⁴ displays a 1:4:2:2 proton pattern with assignments as shown in III. In this complex, the

(3) G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961).

(4) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

(5) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).

(6) R. P. M. Werner and T. H. Coffield, *Chem. Ind. (London)*, 936 (1960).

(7) At lower temperature (-30°) the spectrum freezes to a complex pattern. This is therefore the first known complex of cyclooctatetraene whose proton magnetic resonance shows observable change from rapid to arrested valency tautomerism. We shall discuss more fully elsewhere the further study of this phenomenon and the structure of I.