13, (1,2,6-*trihapto*:3,4,5-*trihapto*cyclooctatetraene)-hexacarbonyldiruthenium(Ru–Ru)[7]

14, (1,2,3,9,10-*pentahapto*:4,5,6-*trihapto*azulene)-pentacarbonyldiiron(Fe–Fe)

15, (1,2,3,4-*tetrahapto*:5,6,7,8-*tetrahapto*cyclooctatetraene)*trans*-bis(tricarbonyliron)

16, (2,3,4,5,6,7-*hexahapto*:11,12,13,14-*tetrahapto*-tetracyclo[$6.0^{1,8}.0^{9,16}.0^{10,15}$]hexadeca-2,4,6,11,13-pentaene)hexacarbonyldiirontricarbonyliron

Finally, it will often be possible to abbreviate the proposed notation for convenience in writing formulas, by using *h* for *hapto*, and a superscript number to indicate the number of attached atoms, as a few illustrations will show.

1, $(h^1\text{-}C_5H_5)(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)MoNO$
2, $(1,2,3,4\text{-}h^4\text{-}C_8H_8)Fe(CO)_3$
4, $(h^5\text{-}C_5H_5)(1,2,5,6\text{-}h^4\text{-}C_8H_8)Co$
7, $[(h^3\text{-}C_7H_7)Co(CO)_3]$
12, $(h^8\text{-}C_8H_8)Fe_2(CO)_5$
15, *trans*-$(1,2,3,4\text{-}h^4{:}5,6,7,8\text{-}h^4\text{-}C_8H_8)[Fe(CO)_3]_2$

(7) For this structure, see F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **90**, 5412 (1968).

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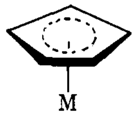
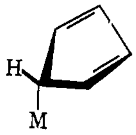
Stereochemically Nonrigid Organometallic Molecules. XVIII. A Compound Containing Three Nonequivalent Cyclopentadienyl Rings Which Are Rapidly Interconverting and Individually Rotating at Room Temperature[1]

Sir:

It is already known that there are two limiting cases of metal to cyclopentadienyl bonding, *viz.*, the $(\pi\text{-}C_5H_5)M$ case, I, which we propose[2] to designate *pentahapto*, and the $(\sigma\text{-}C_5H_5)M$ case, II, which in the same notational system[2] is called *monohapto*. The possibility of the intermediate case, III, *i.e.*, a *trihapto*-cyclopentadienylmetal configuration, is a seemingly logical possibility, but no certain example has yet been found. It is possible that such a grouping *may* exist in the methoxy(*endo*-dicyclopentadiene)platinum (or -palladium) C_5H_5 compounds,[3] but proof is as yet lacking. By far the most likely cases (though not strictly proved) are provided by $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$, both recently described by King.[4] King's formulations of these compounds would be represented in our notation as $(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)Mo(NO)I$ and $(h^3\text{-}C_5H_5)(h^5\text{-}C_5H_5)Mo(NO)CH_3$, respectively. They would, if correctly formulated, be the first molecules to contain both $h^5\text{-}C_5H_5$ and $h^3\text{-}C_5H_5$ groups bound to the same metal atom. King's nmr evidence suggests that, if there are in fact two kinds of C_5H_5 groups, they interchange their structural roles rapidly at room temperature and down to at least −55°. There are also several compounds known, *e.g.*, $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)Fe(CO)_2$[5,6] and $(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)Cr(NO)_2$,[5,7] which contain both $h^5\text{-}C_5H_5$ and $h^1\text{-}C_5H_5$ rings. The latter undergo intramolecular rearrangements rapidly at ~25°, but the two rings in each molecule have never been observed to interchange structural roles with each other.[6,7]


I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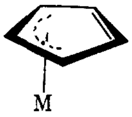
III

The foregoing considerations suggested to us that it would be possible to synthesize and interesting to study a compound containing three C_5H_5 rings (possibly one $h^5\text{-}C_5H_5$, one $h^3\text{-}C_5H_5$, and one $h^1\text{-}C_5H_5$ ring) all bound to the same metal atom. From the reaction of $[(h^5\text{-}C_5H_5)MoNOI_2]_2$ with $4TlC_5H_5$, $C_{15}H_{15}MoNO$ (reddish brown solid; mp 80.5°; ν_{NO} 1610 cm^{-1}; correct C and H analyses) was isolated. Its spectra were measured at frequent temperature intervals from +25 to ~−110°. The changes occurring in these spectra will first be described and then interpretations will be considered. Some traces showing particularly crucial features are presented in Figure 1.

Phase 1. At +25° the spectrum consists of a single sharp line which broadens (*cf.* 14° trace) on cooling, until at about −28° the spectrum of a slowly moving $h^1\text{-}C_5H_5$ ring becomes evident. On further cooling (*cf.* −52° trace) a well-developed sharp AA′BB′X spectrum due to the $h^1\text{-}C_5H_5$ ring is seen while the single line due to the remaining ten protons has again become sharp. This pattern persists to about −80°.

Phase 2. The line (τ 4.5) due to the two other C_5H_5 rings begins to broaden[8] and *at the same time* the low-τ part of the AA′BB′ resonance also begins to broaden at about −85°. The high-τ part of the AA′BB′ pattern begins to change shape but does not significantly broaden. By −95° the previously single ten-proton resonance has fully separated into two equally intense lines (τ ~3.9 and ~4.9) which become sharp by ~−110°. At −90° the low-τ part of the AA′BB′ resonance has virtually disappeared, but by ~−110° new lines of intensities corresponding to one proton each may be seen at τ ~ 2.6 and ~3.7.

Major points to be considered in interpreting these observations are the following.

(1) The molecule has an instantaneous structure in which one of the rings is clearly $h^1\text{-}C_5H_5$, *i.e.*, a σ-bonded ring, and this is so related to the other ligands that its two edges (*i.e.*, the AB and A′B′ protons) are in different environments.

(2) In the temperature range −110 to −52° some intramolecular process or processes permits two things to happen essentially simultaneously: the two edges of the $h^1\text{-}C_5H_5$ ring become (time-average) equivalent and the other two rings become (time-average) equivalent.

(3) Finally, between −52 and +14° all 15 protons become time-average equivalent.

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(1) This study was supported by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society, and by the J. F. Norris Predoctoral Fellowship, 1967–1968, to P. L.

(2) F. A. Cotton, *J. Am. Chem. Soc.*, 90, 6230 (1968).

(3) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).

(4) R. B. King, *Inorg. Chem.*, 7, 90 (1968).

(5) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

(6) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(7) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

(8) This is consistent with King's observation[4] of no broadening of the single resonance of $(C_5H_5)_2Mo(NO)I$ at −55°.

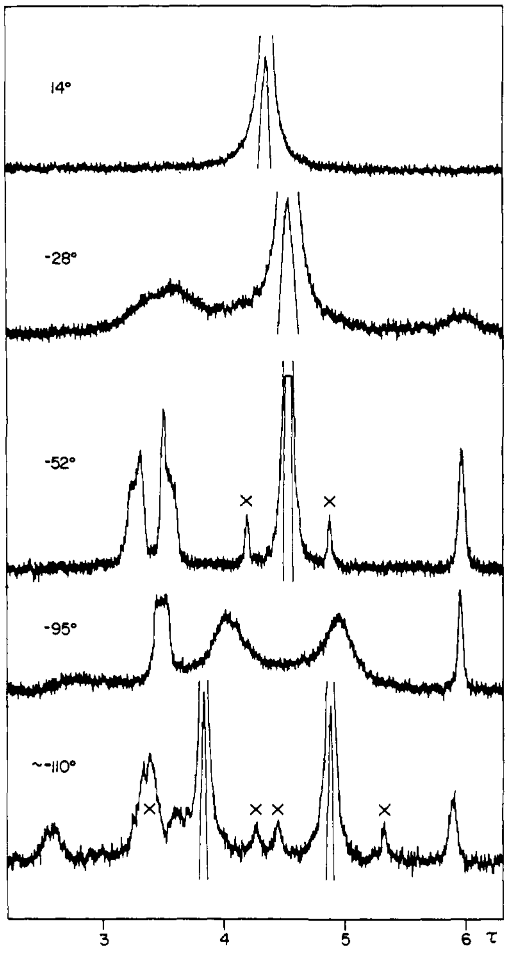

Figure 1. Nmr spectra illustrating the more critical changes which occur between +25 and ~−110°. The gain varies from trace to trace. Bands marked × are spinning side bands (spectra recorded at 60 Mc; ~0.2 *M* solution in CS_2).

(4) One possible instantaneous structure has an h^5-C_5H_5 ring and an h^3-C_5H_5 ring which at −110° is still undergoing eccentric rotation rapidly enough to average the environments of its five protons. The (h^5-C_5H_5)(h^3-C_5H_5)(NO)Mo group would then be dissymmetric and nonequivalence of the A and A′ as well as of the B and B′ protons of the h^1-C_5H_5 ring would be mandatory regardless of the rate of internal rotation, although the magnitude of the difference might be enhanced by conformational effects. This interpretation is in accord with the conventional assumptions about metal–nitrosyl and metal–C_5H_5 bonding. Thus, if NO is assumed to be a three-electron (NO^+) donor, if it is further accepted that there is one h^1-C_5H_5 ring (which is hardly debatable on the evidence), and if it is also *assumed* that the total number of ligand electrons donated to Mo must be 12, the remaining rings must jointly denote eight electrons. This suggests an h^5-C_5H_5 and an h^3-C_5H_5 ring.

(5) However, the reported experimental results do *not*, *in themselves*, demand this interpretation. It is entirely possible that there is one h^1-C_5H_5 ring and two others which do not differ in their intrinsic relation to the metal atom. The changes in the nmr spectrum between −52 and −110° *could* then be due to a freezing in of a particular orientation of the h^1-C_5H_5 ring such that the other two rings experience different degrees of shielding by the diamagnetically anisotropic h^1-C_5H_5 group.

Further studies of this and related molecules will be required in order to reach a decision between these, and perhaps other, possibilities for the instantaneous structure of the molecule.

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Chemistry of Singlet Oxygen. VII. Quenching by β-Carotene[1]

Sir:

The detrimental effects of photosensitizing dyes, light, and oxygen upon various organisms, including the human, are well known. These effects are referred to as "photodynamic action," and are the result of photosensitized oxidation of certain cell constituents.[2] Photosensitized oxygenation of olefins, dienes, and heterocyclic compounds is believed to proceed *via* the intermediacy of singlet oxygen, formed by energy transfer from triplet sensitizer.[3,4] Chlorophyll is among the most effective sensitizers for dye-sensitized photooxygenations of organic substrates.[4] Photosynthetic organisms, however, are protected from the lethal effects of their own chlorophyll by carotenoids; mutants lacking certain carotenoids are readily killed by light and oxygen; carotenoids also protect organisms against the effects of exogenous photosensitizers such as methylene blue.[5] The mechanism of this protective action has not been established, although it is known that carotenes quench triplet sensitizers efficiently.[6]

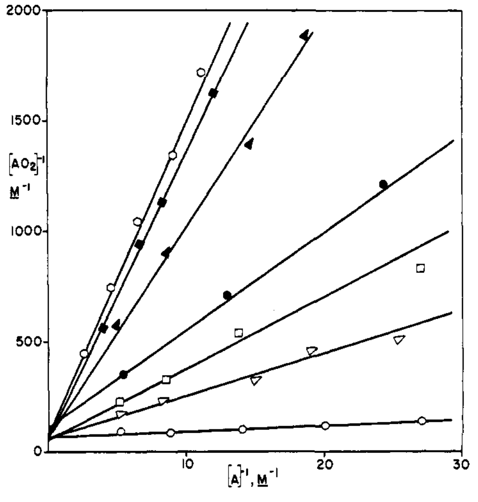

Figure 1. Methylene blue photosensitized oxygenation. β-Carotene concentrations: ○, 0.0 *M*; △, 3.10×10^{-5} *M*; ●, 3.54×10^{-5} *M*; □, 6.11 × 10-5 *M*; ▲, 8.61×10^{-5} *M*; ■, 8.95×10^{-5} *M*; ○, 9.90×10^{-5} *M*.

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[1] Supported by National Science Foundation Grants GP-5835 and GP-8293.

[2] J. D. Spikes and R. Straight, *Ann. Rev. Phys. Chem.*, **18**, 409 (1967).

[3] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[4] K. Gollnick, *Advan. Photochem.*, in press.

[5] R. Y. Stanier, *Brookhaven Symp. Biol.*, **11**, 143 (1959); W. A. Maxwell, J. D. Macmillan, and C. O. Chichester, *Photochem. Photobiol.*, **5**, 567 (1966); M. M. Mathews, *Nature*, **203**, 1092 (1964).