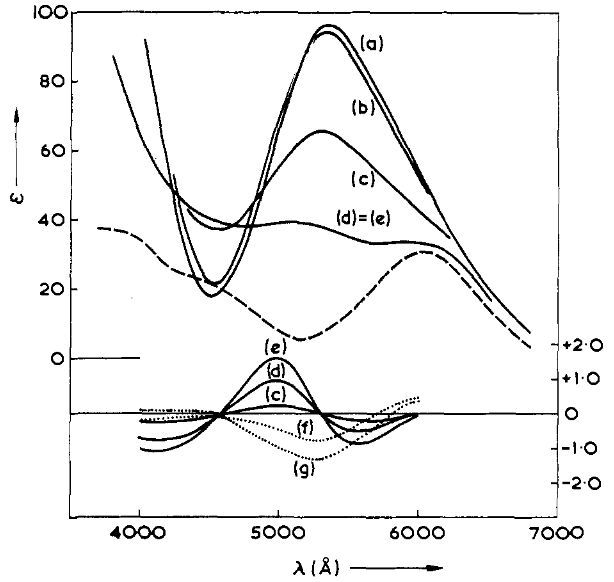

Figure 1. The changes in absorption and associated circular dichroism spectra (solid lines) of solutions of racemic *cis*-[Co(en)$_2$-Cl$_2$]B(C$_6$H$_5$)$_4$ in (−)-2,3-butanediol at 30°. The time intervals are t = 0 (a); t = 0.33 hr (b); t = 4.00 hr (c); t = 19.00 hr (d); t = 96.00 hr (e). Also shown is the absorption spectrum of *trans*-[Co(en)$_2$Cl$_2$]$^+$ in (−)-2,3-butanediol (– – –) and the circular dichroism spectra (·····) of (+)-*cis*-[Co(en)$_2$Cl$_2$]$^+$ in water (f) and (−)-2,3-butanediol (g). The circular dichroism spectrum of (−)-*cis*-[Co-(en)$_2$Cl$_2$]$^+$ in (−)-2,3-butanediol is enantiomorphic (±5%) to (g). The circular dichroism spectra c, d, and e were computed on the basis of unit concentration of *cis* species as calculated from ε(*cis* species at 5200 Å) = 90 and ε(*trans*-[Co(en)$_2$Cl$_2$]$^+$ at 5200 Å) = 6.0.

the solvent interchange reaction on the previously prepared complex *cis*-[Co(en)$_2$Cl(DMF)](ClO$_4$)$_2$ (DMF = dimethylformamide).[19] In all analogous solvent-interchange reactions, this complex reacts to an equilibrium of *cis*-solvent-containing species.[19] Furthermore, this complex in (−)-2,3-butanediol reacts to give an identical circular dichroism with that found for the *cis*-dichloro reaction and a visible absorption spectrum which is consistent with that found for the *cis*-dichloro reaction after the spectral contribution of *trans*-[Co(en)$_2$Cl$_2$]$^+$ has been subtracted.

The solubility measurements reported here and the consideration of the thermodynamic terms involved allow us to draw certain conclusions about the problem of attempting to resolve compounds through fractional crystallization from an optically active solvent.[16,7,8] We wish to make the following observations.

(i) Attempts at resolution through fractional crystallization from a solution containing equal numbers of *d* and *l* forms in an optically active solvent will only be successful under thermodynamically reversible conditions if the chemical potential of crystals containing equal numbers of *d* and *l* forms (racemic compound) is greater than that of crystals which contain exclusively only one hand. This is evident from the equation given in footnote 16 and is clearly not the case here because the less soluble form is the racemic compound (Table I). It might be possible in unfavorable thermodynamic circumstances to achieve resolution through kinetic differences which may become manifest by "seeding" one enantiomer.

(ii) In the absence of other complicating factors, allowing the enantiomerization to occur before the crystallization is attempted will tend to decrease the possibility of the racemic compound precipitating, but the chances of fractionally crystallizing the enantiomers are not greatly improved because the solution-stabilized form is also more soluble.

Acknowledgment. One of us (D. W. W.) wishes to acknowledge a Fulbright–Hays Australian–American Government Educational Committee Travel Grant and the invitation of Professor J. Lewis to work at University College, London.

B. Bosnich
William Ramsay and Ralph Forster Laboratories
University College, London W.C.1, England

D. W. Watts
School of Chemistry, The University of Western Australia
Nedlands 6009, Western Australia

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[19] I. R. Lantzke and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 815 (1967); *Australian J. Chem.*, **19**, 1821 (1966).

Proposed Nomenclature for Olefin–Metal and Other Organometallic Complexes

Sir:

Hundreds of molecules containing polyolefins and other organic molecules bound to metal atoms are now known. More are being prepared every day, and both the olefins themselves and the manner of their attachment to the metal atom (or atoms) are becoming increasingly complex. Existing nomenclature is, in general, inadequate.

I wish to propose the following scheme for *all* compounds containing organic residues bound to metal atoms.[1] It is applicable whether bonding occurs through σ or π electrons or both. Indeed, one of its chief advantages is that it *avoids* implications and, hence, subjective judgments about bonding details; it simply gives a topological description of the structure by indicating the connexity of atoms. The rules are as follows.

(1) The olefin or other organic moiety is named and, if necessary, numbered as it would be when unattached to the metal atom(s). Hence, existing nomenclature and notation are employed as fully as possible. While the olefin whose name is chosen should be the one most similar in structure to that known or assumed to exist in the organometallic compound (usually, it will be the one from which the compound is prepared), the use of the name is not necessarily intended as a literal specification of the arrangement of multiple bonds in the organic moiety after it is part of the organometallic molecule.

(2) The adjectival prefix *hapto* (from the Greek *haptein*, ηαπτειν, to fasten, denoting contact or combination[2a]) is placed before the name of the olefin.[2b]

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[1] Unsaturated compounds which contain heteroatoms may also be accommodated (*cf.* example **10**), and the emphasis here on olefins is not intended to exclude such other cases as the scheme may appropriately and conveniently be applied to. The system is applicable to olefinic ligands of great complexity (*cf.* examples **9** and **16**) and heterocyclic ligands without modification so long as a name and numbering scheme are established for the ligand. It is indeed possible that the principle of using the *hapto* prefix with numerical modifiers may be applicable to more conventional polydentate ligands where the points of attachment to a metal atom need to be specified. For example, a compound where only the first, second, and fourth nitrogen atoms of a tetradentate tetramine ligand are coordinated could be so described.

(3) The number of atoms of the organic moiety which are attached to the metal atom is specified by the appropriate Greek numerical prefix, *mono, di, tri, tetra, penta, hexa, hepta, octa,* etc.

(4) When it is necessary to specify which atoms are attached to the metal, they may be cited by number, the set of numbers being placed before the numerical prefix and *hapto*.

The utility of this scheme can best be demonstrated by some illustrations. These have been chosen, for the most part, to illustrate how the proposed notation provides a straightforward, unambiguous, and information-bearing name in cases where otherwise no such name—or at best a very ambiguous one—can be devised. References are cited for the more arcane or very recently characterized compounds.

1, (*monohapto*cyclopentadienyl)(*trihapto*cyclopentadienyl)(*pentahapto*cyclopentadienyl)nitrosylmolybdenum[3]

2, (1,2,3,4-*tetrahapto*cyclooctatetraene)tricarbonyliron

3, (1,2,3,4,5,6-*hexahapto*cyclooctatetraene)tricarbonylchromium

4, (1,2,5,6-*tetrahapto*cyclooctatetraene)(*pentahapto*cyclopentadienyl)cobalt

5, (*trihapto*-2-methylallyl)tetracarbonylmanganese

6, (1,2,7-*trihapto*-4-methylbenzyl)(*pentahapto*cyclopentadienyl)dicarbonylmolybdenum[4]

7, (1,2,3-*trihapto*cycloheptatrienyl)tricarbonylcobalt

8, (*heptahapto*cycloheptatrienylium)tricarbonylmolybdenum

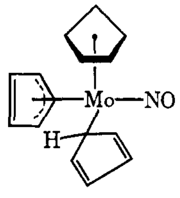
9, (1,2,3,4-*tetrahapto*-1-phenyl-6-*p*-tolyl-1,3,5-hexatriene)tricarbonyliron

10, (2,3,4,5-*tetrahapto*-1-carboxyethyl-1-azacycloheptatriene)tricarbonyliron[5]

11, (1,2,3,4,5,6-*hexahapto*cycloheptatriene)tricarbonylmolybdenum. (Note that it is possible to name this compound unequivocally without regard to whether the details of bonding favor representation a or b.)

The notation can be also used for polynuclear molecules. The rules remain the same as those already discussed for the mononuclear compounds, except that, where desired, the prefix indicating points of attachment may be partitioned using colons to indicate that different parts of the olefin are bound to different metal atoms. To be even more specific, this may be done with the understanding that its parts will apply successively to the several metal-containing moieties which will be listed in corresponding sequence. For example:

12a, (1,2,3,4,5-*pentahapto*:1,5,6,7,8-*pentahapto*cyclooctatetraene)-μ-carbonyl-tetacarbonyldiiron(Fe–Fe)[6]



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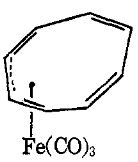

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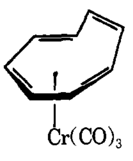

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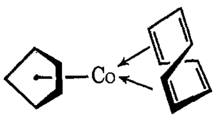

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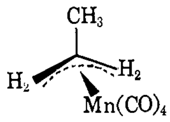

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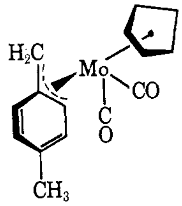

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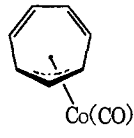

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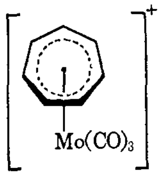

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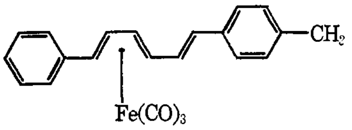

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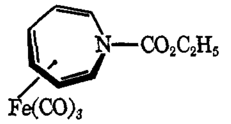

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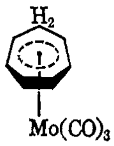
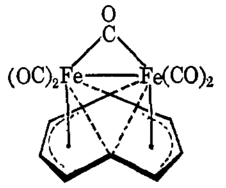
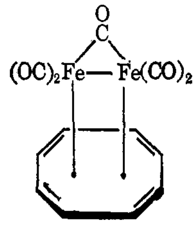


11a

11b



12a



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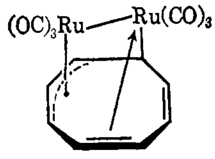

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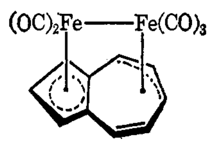

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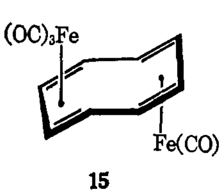

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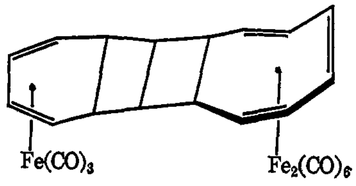

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(2) (a) *Cf.* "Webster's Third New International Dictionary," unabridged, 1961, G. and C. Merriam Co., Springfield, Mass. (b) Use of italic letters is important for indexing purposes.

(3) F. A. Cotton and P. Legzdens, *J. Am. Chem. Soc.*, **90**, 6232 (1968). The structure implied by this name has not been proved correct, and it may not be; the notation does, however, afford a means of giving the structure a self-explanatory name, thus facilitating discussion. Where two or more of the same olefiin are present but differently bound they should be listed in order of increasing "hapticity."

(4) F. A. Cotton and M. D. LaPrade, *ibid.*, **90**, 5418 (1968). The compound lacking the methyl group was earlier reported by R. B. King and A. Fronzaglia, *ibid.*, **88**, 709 (1966).

(5) H. Gunther and R. Wenzl, *Tetrahedron Letters*, 4155 (1967).

(6) Were it not known whether **12a** (which is correct) or **12b** (which was originally proposed) is the correct structure for this compound, one could simply have assumed that the Fe$_2$(CO)$_5$ moiety will interact with all double bonds and thus with all carbon atoms and called the compound (*octahapto*cyclooctatetraene)-μ-carbonyltetracarbonyldiiron-(Fe–Fe).

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

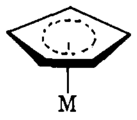
(7) For this structure, see F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **90**, 5412 (1968).

F. A. Cotton
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received July 5, 1968

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 (π-C_5H_5)M case, I, which we propose[2] to designate *pentahapto*, and the (σ-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 $(C_5H_5)_2$-$Mo(NO)CH_3$, both recently described by King.[4] King's formulations of these compounds would be represented in our notation as (h^3-C_5H_5)(h^5-C_5H_5)Mo(NO)I and (h^3-C_5H_5)(h^5-C_5H_5)$Mo(NO)CH_3$, respectively. They would, if correctly formulated, be the first molecules to contain both h^5-C_5H_5 and h^3-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-C_5H_5)(h^5-C_5H_5)$Fe(CO)_2$,[5,6] and (h^1-C_5H_5)(h^5-C_5H_5)$Cr(NO)_2$,[5,7] which contain both h^5-C_5H_5 and h^1-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]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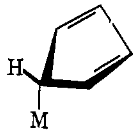
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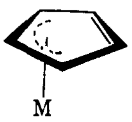
III

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-C_5H_5, one h^3-C_5H_5, and one h^1-C_5H_5 ring) all bound to the same metal atom. From the reaction of $[(h^5$-$C_5H_5)MoNOI_2]_2$ 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-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-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-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-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.

---

(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°.