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Systematic Enumeration of Ferrocene Derivatives by Unit-Subduced-Cycle-Index Method and Characteristic-Monomial Method

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The unit-subduced-cycle-index method and the characteristic-monomial method have been applied to the combinatorial enumeration of ferrocene derivatives. The enumeration has been itemized with respect to formulas as well as to symmetries, where the symmetry of each derivative is characterized by a factor group $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ and its subgroups. The chirality/achirality of ligands and of ferrocene derivatives has been discussed.

From the discovery of ferrocene (bis(η^5-cyclopentadienyl)iron) in 1951,[1] its unusual structure (sandwich structure) has attracted the interests of inorganic, organic, and theoretical chemists.[2—4] In particular, the stereochemistry of ferrocene derivatives has been extensively investigated in terms of optical isomerism[5,6] and positional isomerism.[7] Their chirality/achirality nature has been discussed on the basis of an assumption that rotation about the molecular axis (C_5-axis) is unrestricted. For example, there exists one 1,1′-disubstituted ferrocene, which is a "*meso* form" on the average because of rapid racemization at room temperature.[8] The positional isomerism of ferrocenes has been investigated and reported in many papers.[7,9] However, the discussions on ferrocene stereochemisty have been rather qualitative because of a lack of any sound mathematical framework. As summarized in an excellent review,[10] the characterization of isomers has been based on an eclipsed model of $\mathbf{D}_{5h}$-symmetry and a staggered one of $\mathbf{D}_{5d}$-symmetry, where the rotation around the C_5-axis has been taken into implicit consideration only. Such fixed models are too insufficient to obtain the numbers of positional isomers or to discuss their chirality/achirality more strictly. This means that there have been no quantitative approach suitable to formulate the rotation concerning ferrocene derivatives. Hence, another model that explicitly takes account of the rotation is necessary so that the model is consistent with the modern knowledge that ferrocene is polymorphic ($\mathbf{D}_{5h}$ or $\mathbf{D}_5$ according to crystal conditions).[3]

In a previous paper,[11] we have proposed the concept of promolecules with a subsymmetry of $\mathbf{D}_{\infty h}$ and applied it to a combinatorial enumeration of ethane derivatives rotatable around the centeral C–C bond (C_3-axis). This method is expected to be applicable to the enumeration of ferrocene derivatives, since the rotation around the C_5-axis can be regarded as being parallel with the rotation of ethane around the C_3-axis. For this purpose, however, we have to prepare tables indispensable to such enumeration, i.e. a mark table, its inverse, and a unit-subduced-cycle-index (USCI) table for the point group $\mathbf{C}_{5v}$.

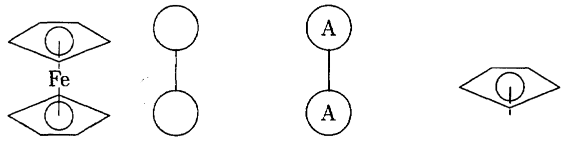
More recently, we have proposed the concept of characteristic monomials,[12—16] which has been applied to enumerate chiral and achiral isomers.[17] If this method is combined with the concept of promolecules, a further approach to the enumeration of ferrocene derivatives can be established.

As clarified in the preceding paragraphs, the first target is to enumerate ferrocene derivatives after the preparation of the tables indispensable to the USCI approach. The second target is to apply characteristic monomials to the enumeration of ferrocene derivatives.

Results

1 Promolecules for Ferrocene Derivatives. Figure 1 shows the methodology for discussing the stereochemistry of ferrocene derivatives. Ferrocene (**1**) itself is regarded as a molecule derived from a promolecule (**3**) of $\mathbf{D}_{\infty h}$, where each proligand A is replaced by a cyclopentadienyl ligand (**4**) of $\mathbf{C}_{5v}$-symmetry. Note that the proligand A is presumed to be a hypothetical achiral ligand without structure, while the cyclopentadienyl ligand (**4**) is regarded as a ligand with structure. The promolecule A–A is in turn generated from a skeleton (**2**) of $\mathbf{D}_{\infty h}$.

When the cyclopentadienyl ligand (**4**) is substituted by a given set of atoms, the resulting ligand belongs to a subsym-



1 ferrocence
2 skeleton
3 promolecule with proligands A
4 ligand for proligand A

Fig. 1. Ferrocene and promolecule.

metry of $\mathbf{C}_{5v}$, which is chiral ($\mathbf{C}_1$ or $\mathbf{C}_5$) or achiral ($\mathbf{C}_s$ or $\mathbf{C}_{5v}$) in accord with the substitution pattern. According to the conversion process of the ligand symmetry, the proligand A is considered to be converted into a chiral proligand (p) or another achiral one (B). Thereby, a promolecule substituted by the resulting proligands is generated so that it belongs to a subsymmetry of $\mathbf{D}_{\infty h}$.

Promolecules of $\mathbf{D}_{\infty h}$ and its subsymmetries are represented schematically, as shown in Fig. 2, where the symbols A and B represent achiral proligands and the symbols p, $\overline{\text{p}}$, and q represent chiral proligands. A symbol with an overline is used to represent an enantiomeric proligand; thus, the proligand $\overline{\text{p}}$ is the enantiomer of the proligand p. A factor group $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ (= $\mathbf{K}$) has been introduced to treat the infinite nature of $\mathbf{D}_{\infty h}$ as found in the bottom of Fig. 2.[11] The chirality/achirality nature of such proligands is maintained in this treatment. To enumerate ferrocene derivatives, each of the proligands is replaced by a substituted cyclopentadienide anion as a ligand.

2 Enumeration of Cyclopentadienyl Ligands by the SCI Method. A cyclopentadienide anion is assumed to belong to point group $\mathbf{C}_{5v}$ as a ligand for a ferrocene derivative. Our first problem is to enumerate ligand derivatives based on the the cyclopentadienyl ligand of $\mathbf{C}_{5v}$-symmetry. For this purpose, we first have to prepare a mark table (Table 1), its inverse (Table 2), and a USCI table (Table 3). These are generated from the coset representations of $\mathbf{C}_{5v}$-group by using the method described in Ref. 18.

Table 1. Mark Table for $\mathbf{C}_{5v}$

$\mathbf{C}_{5v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_5$	$\mathbf{C}_{5v}$
$\mathbf{C}_{5v}(/\mathbf{C}_1)$	10	0	0	0
$\mathbf{C}_{5v}(/\mathbf{C}_s)$	5	1	0	0
$\mathbf{C}_{5v}(/\mathbf{C}_5)$	2	0	2	0
$\mathbf{C}_{5v}(/\mathbf{C}_{5v})$	1	1	1	1

Table 2. Inverse of the Mark Table for $\mathbf{C}_{5v}$

	$\mathbf{C}_{5v}(/\mathbf{C}_1)$	$\mathbf{C}_{5v}(/\mathbf{C}_s)$	$\mathbf{C}_{5v}(/\mathbf{C}_5)$	$\mathbf{C}_{5v}(/\mathbf{C}_{5v})$	Sum
$\mathbf{C}_1$	$\frac{1}{10}$	0	0	0	$\frac{1}{10}$
$\mathbf{C}_s$	$-\frac{1}{2}$	1	0	0	$\frac{1}{2}$
$\mathbf{C}_5$	$-\frac{1}{10}$	0	$\frac{1}{2}$	0	$\frac{2}{5}$
$\mathbf{C}_{5v}$	$\frac{1}{2}$	-1	$-\frac{1}{2}$	1	0

Table 3. USCIs for $\mathbf{C}_{5v}$

$\mathbf{C}_{5v}$	$\mathbf{C}_1$		$\mathbf{C}_s$		$\mathbf{C}_5$		$\mathbf{C}_{5v}$	
$\mathbf{C}_{5v}(/\mathbf{C}_1)$	s_1^{10}	(b_1^{10})	s_2^5	(c_2^5)	s_5^2	(b_5^2)	s_{10}	(c_{10})
$\mathbf{C}_{5v}(/\mathbf{C}_s)$	s_1^5	(b_1^5)	$s_1 s_2^2$	$(a_1 c_2^2)$	s_5	(b_5)	s_5	(a_5)
$\mathbf{C}_{5v}(/\mathbf{C}_5)$	s_1^2	(b_1^2)	s_2	(c_2)	s_1^2	(b_1^2)	s_2	(c_2)
$\mathbf{C}_{5v}(/\mathbf{C}_{5v})$	s_1	(b_1)	s_1	(a_1)	s_1	(b_1)	s_1	(a_1)
Sum	$\frac{1}{10}$		$\frac{1}{2}$		$\frac{2}{5}$		0	

Suppose that five atoms selected from the set of atoms of five different kinds (H, W, X, Y, and Z) are placed on the five vertices of the cyclopentadienyl ligand. Then, we aim at counting ligand derivatives of the formula $H^h W^w X^x Y^y Z^z$, to which we assign the partition $[h,w,x,y,z]$ where $h+w+x+y+z = 5$. Since the five vertices construct an orbit governed by a coset representation $\mathbf{C}_{5v}(/\mathbf{C}_s)$, the subduced cycle indices (SCIs) is equal to the USCIs selected from the $\mathbf{C}_{5v}(/\mathbf{C}_s)$ row of Table 3, into which the following inventory is introduced:

$$s_d = H^d + W^d + X^d + Y^d + Z^d. \tag{1}$$

Thereby, we have the following generating functions for the numbers of fixed isomeric ligands:

$$\mathbf{C}_1 : (H+W+X+Y+Z)^5, \tag{2}$$

$$\mathbf{C}_s : (H+W+X+Y+Z)(H^2+W^2+X^2+Y^2+Z^2)^2, \tag{3}$$

$$\mathbf{C}_5, \mathbf{C}_{5v} : H^5+W^5+X^5+Y^5+Z^5. \tag{4}$$

After the expansion of each equation, the coefficients of the term $H^h W^w X^x Y^y Z^z$ are collected to give a column of a matrix. The term is represented by the partition $[h,w,x,y,z]$, as shown on the left-hand side of Eq. 5. The resulting matrix is multiplied by the inverse (M^{-1}, Table 2) to give the following equation:

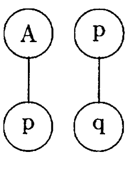
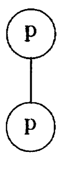
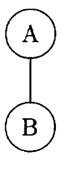
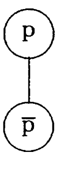
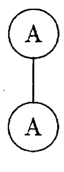
Promolecule					
$\mathbf{D}_{\infty h}$ $\mathbf{K} = \mathbf{K}_5$	$\mathbf{C}_{\infty}$ $\mathbf{K}_1$ $= \mathbf{C}_{\infty}/\mathbf{C}_{\infty}$	$\mathbf{D}_{\infty}$ $\mathbf{K}_2$ $= \mathbf{D}_{\infty}/\mathbf{C}_{\infty}$	$\mathbf{C}_{\infty v}$ $\mathbf{K}_3$ $= \mathbf{C}_{\infty v}/\mathbf{C}_{\infty}$	$\mathbf{C}_{\infty h}$ $\mathbf{K}_4$ $= \mathbf{C}_{\infty h}/\mathbf{C}_{\infty}$	$\mathbf{D}_{\infty h}$ $\mathbf{K}_5$ $= \mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$
$\mathbf{K}(/\mathbf{K}_3)$	b_1^2	b_2	a_1^2	c_2	a_2

Fig. 2. Promolecules of $\mathbf{D}_{\infty h}$ and its subsymmetries.

$$\begin{array}{c} \\ [5,0,0,0,0] \\ [4,1,0,0,0] \\ [3,2,0,0,0] \\ [3,1,1,0,0] \\ [2,2,1,0,0] \\ [2,1,1,1,0] \\ [1,1,1,1,1] \end{array} \begin{array}{cccc} \mathbf{C}_1 & \mathbf{C}_s & \mathbf{C}_5 & \mathbf{C}_{5v} \\ \end{array} \left(\begin{array}{cccc} 1 & 1 & 1 & 1 \\ 5 & 1 & 0 & 0 \\ 10 & 2 & 0 & 0 \\ 20 & 0 & 0 & 0 \\ 30 & 2 & 0 & 0 \\ 60 & 0 & 0 & 0 \\ 120 & 0 & 0 & 0 \end{array} \right) \mathrm{M}^{-1}$$

$$= \begin{array}{c|cccc} & \mathbf{C}_1 & \mathbf{C}_s & \mathbf{C}_5 & \mathbf{C}_{5v} \\ \hline [5,0,0,0,0] & 0 & 0 & 0 & 1 \\ [4,1,0,0,0] & 0 & 1 & 0 & 0 \\ [3,2,0,0,0] & 0 & 2 & 0 & 0 \\ [3,1,1,0,0] & 2 & 0 & 0 & 0 \\ [2,2,1,0,0] & 2 & 2 & 0 & 0 \\ [2,1,1,1,0] & 6 & 0 & 0 & 0 \\ [1,1,1,1,1] & 12 & 0 & 0 & 0 \end{array} \qquad (5)$$

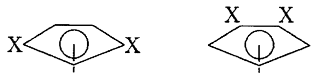
Each row of the resulting matrix represents the numbers of ligand derivatives of $[h,w,x,y,z]$, which are itemized with respect of the subsymmetries of $\mathbf{C}_{5v}$. For example, the [3,2,0,0,0]-row shows that there appear two ligands of $\mathbf{C}_s$-symmetry, while the [3,1,1,0,0]-row indicates that two ligands belong to $\mathbf{C}_1$-symmetry. To illustrate these results, Fig. 3 shows two H^3X^2, $\mathbf{C}_s$-ligands (achiral ligands) and two H^3XY, $\mathbf{C}_1$-ligands (chiral ligands). It should be noted that there exist no isomers of $\mathbf{C}_5$ in this enumeration.

Figure 3 also involves two H^3X^2Y, $\mathbf{C}_s$-ligands (achiral ligands) and two H^3X^2Y, $\mathbf{C}_1$-ligands (chiral ligands). The numbers of these isomers are found in the [2,2,1,0,0]-row of the right-hand side of Eq. 5.

Figure 4 shows six H^2XYZ, $\mathbf{C}_1$-ligands (chiral ligands). The number of these isomers is found in the [2,1,1,1,0]-row of Eq. 5.

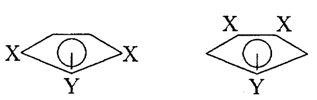
In the light of Lemma 3 described in Appendix 2 of Ref. 19, the data of the matrix of Eq. 5 give the following inventories

[3,2,0,0,0],$\mathbf{C}_s$-ligands:



[3,1,1,0,0],$\mathbf{C}_1$-ligands:

[2,2,1,0,0],$\mathbf{C}_s$-ligands:



[2,2,1,0,0],$\mathbf{C}_1$-ligands:

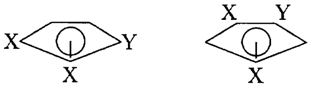


Fig. 3. $\mathbf{C}_s$- and $\mathbf{C}_1$-Ligands.

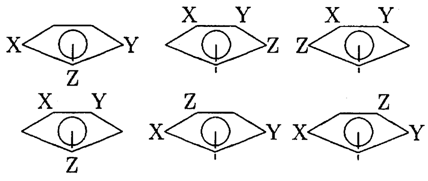


Fig. 4. [2,1,1,1,0], $\mathbf{C}_1$-Ligands.

for enumerating ferrocene derivatives:

$$\begin{aligned} a_d = {} & [(H^5)^d + (W^5)^d + \cdots] + [(H^4W)^d + (H^4X)^d + \cdots] \\ & + [2(H^3W^2)^d + 2(H^3X^2)^d + \cdots] + [2(H^2W^2X)^d + 2(H^2W^2Y)^d + \cdots], \end{aligned} \qquad (6)$$

$$\begin{aligned} b_d = c_d = {} & [(H^5)^d + (W^5)^d + \cdots] + [(H^4W)^d + (H^4X)^d + \cdots] \\ & + [2(H^3W^2)^d + 2(H^3X^2)^d + \cdots] + [2(H^2W^2X)^d + 2(H^2W^2Y)^d + \cdots] \\ & + 2[2(H^3WX)^d + 2(H^3WY)^d + \cdots] + 2[2(H^2W^2X)^d + 2(H^2W^2Y)^d + \cdots] \\ & + 2[6(H^2WXY)^d + 6(H^2WXZ)^d + \cdots] + 2[12(HWXYZ)^d]. \end{aligned} \qquad (7)$$

Note that a_d is related to the data of achiral ligands ($\mathbf{C}_s$ and $\mathbf{C}_{5v}$), while b_d (or c_d) is related to the data of achiral ($\mathbf{C}_s$ and $\mathbf{C}_{5v}$) and chiral ligands ($\mathbf{C}_1$ and $\mathbf{C}_5$).

3 Enumeration of Cyclopentadienyl Ligands by the PCI Method. The same results are obtained by partial-cycle-index (PCI) method described in the Chapter 16 of our book.[18] For the purpose of obtaining PCIs, we regard the $\mathbf{C}_{5v}(/\mathbf{C}_s)$-row of Table 3 as a formal row vector:

$$(s_1^5, s_1s_2^2, s_5, s_5),$$

which is multiplied by M^{-1}. The formal matrix calculation gives the following PCIs:

$$\mathrm{PCI}(\mathbf{C}_1; s_d) = \frac{1}{10}s_1^5 - \frac{1}{2}s_1s_2^2 - \frac{1}{10}s_5 + \frac{1}{2}s_5 = \frac{1}{10}s_1^5 - \frac{1}{2}s_1s_2^2 + \frac{2}{5}s_5, \qquad (8)$$

$$\mathrm{PCI}(\mathbf{C}_s; s_d) = s_1s_2^2 - s_5, \qquad (9)$$

$$\mathrm{PCI}(\mathbf{C}_5; s_d) = \frac{1}{2}s_5 - \frac{1}{2}s_5 = 0, \qquad (10)$$

$$\mathrm{PCI}(\mathbf{C}_{5v}; s_d) = s_5. \qquad (11)$$

The zero value of $\mathrm{PCI}(\mathbf{C}_5;s_d)$ is consistent with the fact that there are no $\mathbf{C}_5$-isomers in this enumeration. After the introduction of the inventory (Eq. 1) into Eqs. 8, 9, 10, and 11, these are expanded to give generating functions as follows:

$$\begin{aligned} f_{\mathrm{C}_1} = {} & (2H^3WX + 2H^3WY + \cdots) + (2H^2W^2X + 2H^2W^2Y + \cdots) \\ & + (6H^2WXY + 6H^2WXZ + \cdots) + 12HWXYZ, \end{aligned} \qquad (12)$$

$$\begin{aligned} f_{\mathrm{C}_s} = {} & (H^4W + H^4X + \cdots) + (2H^3W^2 + 2H^3X^2 + \cdots) \\ & + (2H^2W^2X + 2H^2W^2Y + \cdots), \end{aligned} \qquad (13)$$

$$f_{\mathrm{C}_5} = 0, \qquad (14)$$

$$f_{\mathrm{C}_{5v}} = H^5 + W^5 + X^5 + Y^5 + Z^5, \qquad (15)$$

where the coefficient of each term of $[h,w,x,y,z]$ represents the isomer number of the corresponding symmetry. The values of each equation are equivalent to the ones collected in the corresponding column of the matrix of Eq. 5.

In the light of Lemma 3 described in Appendix 2 of Ref. 19, the data of the generating functions (Eqs. 12, 13, 14, and 15) give the inventories for enumerating ferrocene derivatives, which are equivalent to the results obtained by the SCI method (Eqs. 6 and 7). The comparison between the set of Eqs. 12, 13, 14, and 15 and the set of Eqs. 6 and 7 reveals the relationship between the coefficients of their terms.

4 Enumeration of Cyclopentadienyl Ligands by the Characteristic-Monomial Method. The inventories obtained by the SCI or PCI method (Eqs. 6 and 7) are concerned with proligands not with ligands. More precisely speaking, they are concerned with the chirality/achirality nature of a ligand. Hence, the characteristic-monomial method for enumerating achiral and chiral isomers[17] is applicable to the calculation of the inventories. For this purpose, the **Q**-conjugacy character table for $\mathbf{C}_{5v}$ (Table 4) is generated from the character table for $\mathbf{C}_{5v}$,[20] where the E_1- and E_2-rows of the latter table are summed up to give the E-row of Table 4. Note that the conjugacy classes ($2C_5$ and $2C_5^2$) coalesce into a **Q**-conjugacy class during this procedure. Characteristic monomials for $\mathbf{C}_{5v}$, which are calculated by means of the procedures described in Refs. 12, 13, 14, 15, and 16, are collected in Table 5. The necessary coefficients for such applications (N_j, $N_j^{(m)}$, $N_j^{(e)}$, and $N_j^{(a)}$) are also collected in Table 5.

The five positions of an unsubstituted cyclopentadienyl ligand give a fixed-point vector (FPV), which is obtained to be (5,1,0) under the operations of $\mathbf{C}_1$, $\mathbf{C}_s$, and $\mathbf{C}_5$. The FPV is multiplied by the inverse of the **Q**-conjugacy character table (Table 4) to give

$$(5,1,0)\begin{pmatrix} \frac{1}{10} & \frac{1}{10} & \frac{1}{5} \\ \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{2}{5} & \frac{2}{5} & -\frac{1}{5} \end{pmatrix} = (1,0,1). \tag{16}$$

This result indicates that the **Q**-conjugacy representation corresponding to the FPV is reduced into A_1+E. This result is alternatively obtained in the light of the markaracter table for $\mathbf{C}_{5v}$ (Table 6), where the $\mathbf{C}_{5v}(/\mathbf{C}_s)$-row is equal to the FPV.

Table 4. **Q**-Conjugacy Characters for $\mathbf{C}_{5v}$

$\mathbf{C}_{5v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_5$
A_1	1	1	1
A_2	1	−1	1
E	4	0	−1

Table 5. Characteristic Monomials for $\mathbf{C}_{5v}$

$\mathbf{C}_{5v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_5$	Remarks
A_1	s_1	s_1	s_1	$\mathbf{C}_{5v}(/\mathbf{C}_{5v})$
A_2	s_1	$s_1^{-1}s_2$	s_1	$\mathbf{C}_{5v}(/\mathbf{C}_5)-\mathbf{C}_{5v}(/\mathbf{C}_{5v})$
E	s_1^4	s_2^2	$s_1^{-1}s_5$	$\mathbf{C}_{5v}(/\mathbf{C}_s)-\mathbf{C}_{5v}(/\mathbf{C}_{5v})$
N_j	$\frac{1}{10}$	$\frac{1}{2}$	$\frac{2}{5}$	Achiral isomers and enantiomeric pairs
$N_j^{(m)}$	$\frac{1}{5}$	0	$\frac{4}{5}$	Achiral and chiral isomers
$N_j^{(e)}$	$\frac{1}{10}$	$-\frac{1}{2}$	$\frac{2}{5}$	Enantiomeric pairs ($N_j^{(m)}-N_j$)
$N_j^{(a)}$	0	1	0	Achiral isomers ($N_j-N_j^{(e)}$)

Table 6. Markaracters for $\mathbf{C}_{5v}$

$\mathbf{C}_{5v}$	$\mathbf{C}_1$	$\mathbf{C}_s$	$\mathbf{C}_5$	Reduction
$\mathbf{C}_{5v}(/\mathbf{C}_1)$	10	0	0	A_1+A_2+2E
$\mathbf{C}_{5v}(/\mathbf{C}_s)$	5	1	0	A_1+E
$\mathbf{C}_{5v}(/\mathbf{C}_5)$	2	0	2	A_1+A_2
$\mathbf{C}_{5v}(/\mathbf{C}_{5v})$	1	1	1	A_1

According to the reduction A_1+E, characteristic monomials are collected from Table 5 to give subduced cycle indices (SCI) for the cyclic subgroups of $\mathbf{C}_{5v}$:

$$\begin{array}{ccc} \mathbf{C}_1 & \mathbf{C}_s & \mathbf{C}_5 \\ \hline (s_1)(s_1^4)=s_1^5 & (s_1)(s_2^2)=s_1s_2^2 & (s_1)(s_1^{-1}s_5)=s_5 \end{array}.$$

By using these monomials and the coefficients collected in the $N_j^{(m)}$-row of Table 5, we have a cycle index $CI^{(m)}$ for counting achiral and chiral ligands based on the cyclopentadienyl ligand.

$$CI^{(m)}(\mathbf{C}_{5v};s_d)=\frac{1}{5}s_1^5+\frac{4}{5}s_5. \tag{17}$$

On the other hand, the $N_j^{(a)}$-row of Table 5 gives a cycle index $CI^{(a)}$ for counting achiral ligands.

$$CI^{(a)}(\mathbf{C}_{5v};s_d)=s_1s_2^2. \tag{18}$$

The inventory represented by Eq. 1 is introduced into these cycle indices, giving the following generating functions for the numbers of chiral/achiral isomeric ligands.

$$\begin{aligned} f^{(m)} &= (H^5+W^5+X^5+Y^5+Z^5)+(H^4W+H^4X+\cdots) \\ &\quad +(2H^3W^2+2H^3X^2+\cdots)+(2H^2W^2X+2H^2W^2Y+\cdots) \\ &\quad +2(2H^3WX+2H^3WY+\cdots)+2(2H^2W^2X+2H^2W^2Y+\cdots) \\ &\quad +2(6H^2WXY+6H^2WXZ+\cdots)+2(12HWXYZ), \end{aligned} \tag{19}$$

$$\begin{aligned} f^{(a)} &= (H^5+W^5+X^5+Y^5+Z^5)+(H^4W+H^4X+\cdots) \\ &\quad +(2H^3W^2+2H^3X^2+\cdots)+(2H^2W^2X+2H^2W^2Y+\cdots). \end{aligned} \tag{20}$$

These equations give the inventories represented by Eqs. 6 and 7, which are alternatively obtained by the SCI and PCI methods

5 Enumeration of Ferrocene Derivatives. The SCIs for the enumeration of ferrocene derivatives are listed in the bottom of Fig. 2. The figure inventories a_d, b_d, and c_d (Eqs. 6 and 7) are introduced into the SCIs, giving the following generating functions:

$\mathbf{K}_1=\mathbf{C}_\infty/\mathbf{C}_\infty$:

$$\begin{aligned} b_1^2 &= \{(H^5+W^5+X^5+Y^5+Z^5)+(H^4W+H^4X+\cdots) \\ &\quad +(2H^3W^2+2H^3X^2+\cdots)+(2H^2W^2X+2H^2W^2Y+\cdots) \\ &\quad +2(2H^3WX+2H^3WY+\cdots)+2(2H^2W^2X+2H^2W^2Y+\cdots) \\ &\quad +2(6H^2WXY+6H^2WXZ+\cdots)+2(12HWXYZ)\}^2. \end{aligned} \tag{21}$$

$\mathbf{K}_2 = \mathbf{D}_\infty/\mathbf{C}_\infty$:

$$\begin{aligned} b_2 = {} & (H^{10}+W^{10}+X^{10}+Y^{10}+Z^{10})+(H^8W^2+H^8X^2+\cdots) \\ & +(2H^6W^4+2H^6X^4+\cdots)+(2H^4W^4X^2+2H^4W^4Y^2+\cdots) \\ & +2(2H^6W^2X^2+2H^6W^2Y^2+\cdots)+2(2H^4W^4X^2+2H^4W^4Y^2+\cdots) \\ & +2(6H^4W^2X^2Y^2+6H^4W^2X^2Z^2+\cdots)+2(12H^2W^2X^2Y^2Z^2). \end{aligned} \tag{22}$$

$\mathbf{K}_3 = \mathbf{C}_{\infty v}/\mathbf{C}_\infty$:

$$\begin{aligned} a_1^2 = {} & \{(H^5+W^5+X^5+Y^5+Z^5) \quad +(H^4W+H^4X+\cdots) \\ & +(2H^3W^2+2H^3X^2+\cdots)+(2H^2W^2X+2H^2W^2Y+\cdots)\}^2. \end{aligned} \tag{23}$$

$\mathbf{K}_4 = \mathbf{C}_{\infty h}/\mathbf{C}_\infty$:

$$c_2 = b_2. \tag{24}$$

$\mathbf{K}_5 = \mathbf{D}_{\infty h}/\mathbf{C}_\infty$:

$$\begin{aligned} a_2 = {} & (H^{10}+W^{10}+X^{10}+Y^{10}+Z^{10})+(H^8W^2+H^8X^2+\cdots) \\ & +(2H^6W^4+2H^6X^4+\cdots)+(2H^4W^4X^2+2H^4W^4Y^2+\cdots). \end{aligned} \tag{25}$$

These equations are expanded and the resulting coefficients are collected to give a matrix, which is multiplied by the inverse of the mark table of the factor group **K** as follows:

$$\begin{array}{l} \\ {[10,0,0,0,0]} \\ {[9,1,0,0,0]} \\ {[8,2,0,0,0]} \\ {[8,1,1,0,0]} \\ {[7,3,0,0,0]} \\ {[7,2,1,0,0]} \\ {[7,1,1,1,0]} \\ {[6,4,0,0,0]} \\ {[6,3,1,0,0]} \\ {[6,2,2,0,0]} \\ {[6,2,1,1,0]} \\ {[6,1,1,1,1]} \\ {[5,5,0,0,0]} \\ {[5,4,1,0,0]} \\ {[5,3,2,0,0]} \\ {[5,3,1,1,0]} \\ {[5,2,2,1,0]} \\ {[5,2,1,1,1]} \\ {[4,4,2,0,0]} \\ {[4,4,1,1,0]} \\ {[4,3,3,0,0]} \\ {[4,3,2,1,0]} \\ {[4,3,1,1,1]} \\ {[4,2,2,2,0]} \\ {[4,2,2,1,1]} \end{array} \begin{array}{c} \begin{array}{rrrrr} \mathbf{K}_1 & \mathbf{K}_2 & \mathbf{K}_3 & \mathbf{K}_4 & \mathbf{K}_5 \end{array} \\ \left(\begin{array}{rrrrr} 1 & 1 & 1 & 1 & 1 \\ 2 & 0 & 2 & 0 & 0 \\ 5 & 1 & 5 & 1 & 1 \\ 10 & 0 & 2 & 0 & 0 \\ 8 & 0 & 8 & 0 & 0 \\ 24 & 0 & 8 & 0 & 0 \\ 48 & 0 & 0 & 0 & 0 \\ 10 & 2 & 10 & 2 & 2 \\ 40 & 0 & 8 & 0 & 0 \\ 60 & 4 & 20 & 4 & 0 \\ 120 & 0 & 8 & 0 & 0 \\ 240 & 0 & 0 & 0 & 0 \\ 12 & 0 & 12 & 0 & 0 \\ 52 & 0 & 12 & 0 & 0 \\ 104 & 0 & 24 & 0 & 0 \\ 208 & 0 & 0 & 0 & 0 \\ 312 & 0 & 24 & 0 & 0 \\ 624 & 0 & 0 & 0 & 0 \\ 126 & 6 & 30 & 6 & 2 \\ 252 & 0 & 12 & 0 & 0 \\ 168 & 0 & 24 & 0 & 0 \\ 504 & 0 & 24 & 0 & 0 \\ 1008 & 0 & 0 & 0 & 0 \\ 756 & 12 & 60 & 12 & 0 \\ 1512 & 0 & 24 & 0 & 0 \end{array} \right) \end{array}$$

$$\times \begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = \tag{26}$$

This gives the following matrix:

$$\begin{array}{l} \\ {[10,0,0,0,0]} \\ {[9,1,0,0,0]} \\ {[8,2,0,0,0]} \\ {[8,1,1,0,0]} \\ {[7,3,0,0,0]} \\ {[7,2,1,0,0]} \\ {[7,1,1,1,0]} \\ {[6,4,0,0,0]} \\ {[6,3,1,0,0]} \\ {[6,2,2,0,0]} \\ {[6,2,1,1,0]} \\ {[6,1,1,1,1]} \\ {[5,5,0,0,0]} \\ {[5,4,1,0,0]} \\ {[5,3,2,0,0]} \\ {[5,3,1,1,0]} \\ {[5,2,2,1,0]} \\ {[5,2,1,1,1]} \\ {[4,4,2,0,0]} \\ {[4,4,1,1,0]} \\ {[4,3,3,0,0]} \\ {[4,3,2,1,0]} \\ {[4,3,1,1,1]} \\ {[4,2,2,2,0]} \\ {[4,2,2,1,1]} \end{array} \begin{array}{c} \begin{array}{rrrrr} \mathbf{K}_1 & \mathbf{K}_2 & \mathbf{K}_3 & \mathbf{K}_4 & \mathbf{K}_5 \end{array} \\ \left(\begin{array}{rrrrr} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 & 1 \\ 2 & 0 & 1 & 0 & 0 \\ 0 & 0 & 4 & 0 & 0 \\ 4 & 0 & 4 & 0 & 0 \\ 12 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4 & 0 & 2 \\ 8 & 0 & 4 & 0 & 0 \\ 8 & 2 & 10 & 2 & 0 \\ 28 & 0 & 4 & 0 & 0 \\ 60 & 0 & 0 & 0 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 10 & 0 & 6 & 0 & 0 \\ 20 & 0 & 12 & 0 & 0 \\ 52 & 0 & 0 & 0 & 0 \\ 72 & 0 & 12 & 0 & 0 \\ 156 & 0 & 0 & 0 & 0 \\ 22 & 2 & 14 & 2 & 2 \\ 60 & 0 & 6 & 0 & 0 \\ 38 & 0 & 8 & 0 & 0 \\ 120 & 0 & 12 & 0 & 0 \\ 252 & 0 & 0 & 0 & 0 \\ 168 & 6 & 30 & 6 & 0 \\ 372 & 0 & 12 & 0 & 0 \end{array} \right) \end{array} \tag{27}$$

Each row of the resulting matrix represents the numbers of ligand derivatives of $[h,w,x,y,z]$ ($h+w+x+y+z = 10$), which are itemized with respect of the subsymmetries of **K**. Note that cases lower than $[3,w,x,y,z]$ are abbreviated for the sake of simplicity.

To illustrate the results of this enumeration, Fig. 5 shows ferrocene derivatives with H^8X^2. The numbers of the derivatives, which are itemized with respect to symmetries, are found in the [8,2,0,0,0]-row of Eq. 27. For the sake of simplicity, the conformation of each ferrocene derivative is fixed to be a staggered form. Thus, there appear two $\mathbf{K}_3$-isomers and one $\mathbf{K}_5$-isomer. They are all achiral, since $\mathbf{K}_3 = \mathbf{C}_{\infty v}/\mathbf{C}_\infty$ and $\mathbf{K}_5 = \mathbf{D}_{\infty h}/\mathbf{C}_\infty$.

On the other hand, Fig. 6 shows ferrocene derivatives with H^8XY, the isomer numbers of which are found in the [8, 1,1,0,0]-row of Eq. 27. Thus, there appear two $\mathbf{K}_1$-isomers (chiral) and one $\mathbf{K}_3$-isomer (achiral). Each of the $\mathbf{K}_1$-isomers illustrated in Fig. 6 is an arbitrary enantiomer selected from a pair of enantiomers.

Discussion

1 Chiral and Achiral Isomers. The present enumeration

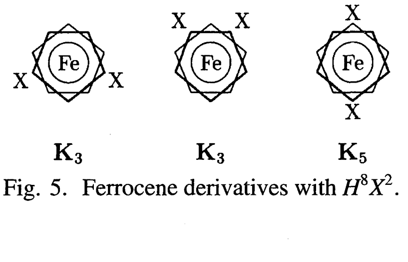


Fig. 5. Ferrocene derivatives with H^8X^2.

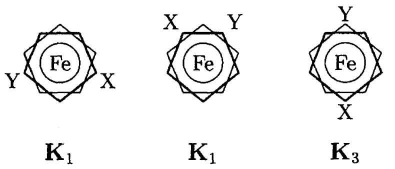


Fig. 6. Ferrocene derivatives with H^8XY.

is based on the concept of promolecules, which provides us with a useful criterion to characterize the chirality/achirality of an enumerated ferrocene derivative. For example, the homoannular disubstituted derivatives with H^8X^2 (the two isomers depicted in the left-hand part of Fig. 5 are achiral because $\mathbf{K}_3$ ($=\mathbf{C}_{\infty v}/\mathbf{C}_{\infty}$) is ascribed to them. This fact is further confirmed by referring to Fig. 2 after we find that each $\mathbf{K}_3$-derivative contains an unsubstituted ligand as one achiral proligand A and a disubstituted ligand (shown in the first row of Fig. 3) as the other achiral proligand B. The remaining heteroannular disubstituted derivative of Fig. 5 is deduced to be achiral, since it belongs to $\mathbf{K}_5$ ($=\mathbf{D}_{\infty h}/\mathbf{D}_{\infty}$) or it is ascribed to the type A–A (Fig. 2).

On the other hand, the two H^8XY-isomers depicted in the left-hand of Fig. 6 are homoannular disubstituted derivatives, which belong to $\mathbf{K}_1$ ($=\mathbf{C}_{\infty}/\mathbf{C}_{\infty}$) and are deduced to be chiral. They are ascribed to type A–p (Fig. 2), because the unsubstituted ligand is an achiral proligand A and the disubstituted ligand (shown in the second row of Fig. 3) is regarded as a chiral proligand p. The remaining heteroannular disubstituted derivative of Fig. 6 is categorized into the type A–B ($\mathbf{K}_3=\mathbf{C}_{\infty v}/\mathbf{C}_{\infty}$).

Since the present methodology takes account of the chirality/achirality of an intervening proligand, its enumeration scheme is so systematic that it prevents us from getting erroneous results. For example, the [7,2,1,0,0]-row of Eq. 27 indicates the presence of four $\mathbf{K}_1$-derivatives (chiral) and four $\mathbf{K}_3$-ones (achiral), which is exemplified by eight ferrocene derivatives with H^7X^2Y depicted in Fig. 7. Note that all of the $\mathbf{K}_1$-derivatives are categorized into the type A–p and that all of the $\mathbf{K}_3$-derivatives are categorized into the type A–B (see the ligands depicted in Fig. 3). This result is different from a previous one reported in Table 1 of Ref. 10 (three chiral and five achiral derivatives for H^7X^2Y).

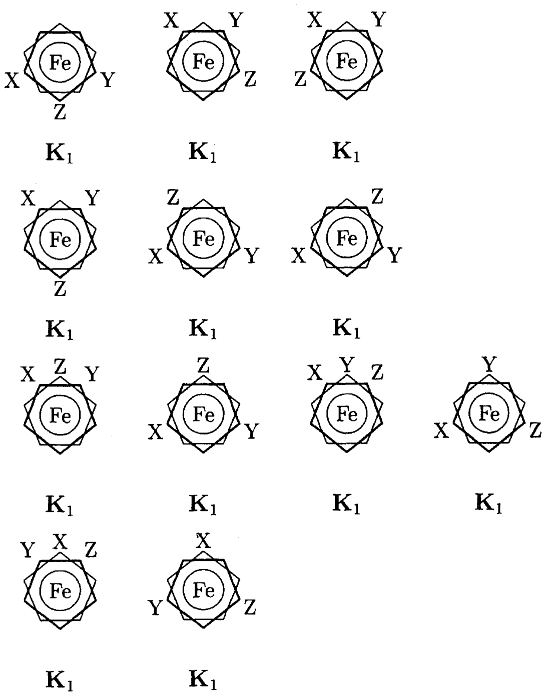


Fig. 8. Ferrocene derivatives with H^7XYZ.

The [7,1,1,1,0]-row of Eq. 27 indicates the presence of twelve $\mathbf{K}_1$-derivatives (chiral). In agreement with this value, Fig. 8 shows twelve ferrocene derivatives with H^7XYZ. This result is different from a previous one reported in Table 1 of Ref. 10 (thirteen chiral derivatives for H^7XYZ). The validity of our result can be tested by considering the division of H^7XYZ into two terms ($H^5\times H^2XYZ$, $H^4Z\times H^3XY$, $H^4Y\times H^3XZ$, and $H^4X\times H^3YZ$). The six derivatives in the first and second rows of Fig. 8 are homoannular trisubstituted derivatives, which correspond to the division $H^5\times H^2XYZ$. The latter term H^2XYZ indicates the six $\mathbf{C}_1$-ligands depicted in Fig. 4. On the other hand, the remaining six derivatives in the third and fourth rows are heteroannular trisubstituted derivatives (with mono- and di-substitution), which correspond to the divisions $H^4Z\times H^3XY$, $H^4Y\times H^3XZ$, and $H^4X\times H^3YZ$. Each of the latter terms, H^3XY, H^3XZ, or H^3YZ, indicates the two isomeric $\mathbf{C}_1$-ligands depicted in the second row of Fig. 3 (for H^3XY). The twelve derivatives depicted in Fig. 8 are all ascribed to type A–p (Fig. 2).

2 Derivatives with Given Symmetries. Several derivatives enumerated in the $\mathbf{K}_5$-column of Eq. 27 are depicted in Fig. 9. Note that each ligand is achiral.

Let us here consider the process of replacing proligands

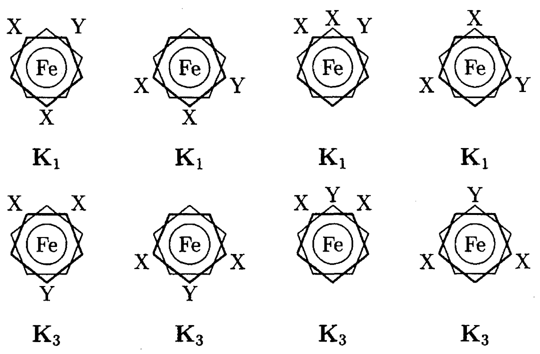


Fig. 7. Ferrocene derivatives with H^7X^2Y.

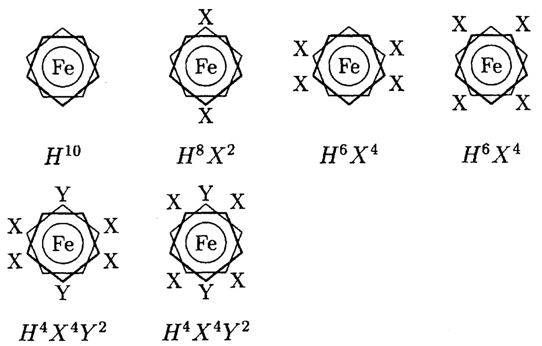


Fig. 9. Several ferrocene derivatives of $\mathbf{K}_5$-symmetry.

by ligands. Since the $\mathbf{K}_5$-derivatives are represented by A–A (Fig. 2), the two ligands of each $\mathbf{K}_5$-derivative are identical with each other. As a result, the term shown in each derivative collected in Fig. 9 is divided into two equal parts, i.e. $H^5 \times H^5$ from H^{10}, $H^4X \times H^4X$ from H^8X^2, $H^3X^2 \times H^3X^2$ from H^6X^4, and $H^2X^2Y \times H^2X^2Y$ from $H^4X^4Y^2$. The term H^5 (for H^{10}) corresponds to the [5,0,0,0,0]-row of Eq. 5. Hence, the number (1) appearing at the intersection between the [5, 0,0,0,0]-row and the $\mathbf{C}_{5v}$-column is equal to the number of $\mathbf{K}_5$-derivatives with H^{10}. Similarly, the term H^4X (for H^8X^2) corresponds to the number (1) appearing at the intersection between the [4,1,0,0,0]-row and the $\mathbf{C}_s$-column (Eq. 5). The ligand number (2) at the intersection between the [3,2,0,0, 0]-row and the $\mathbf{C}_s$-column (Eq. 5) shows the presence of two kinds of achiral ligands with H^3X^2 and accordingly the presence of two $\mathbf{K}_5$-derivatives with H^6X^4. The term $H^2X^2Y^1$ (for $H^4X^4Y^2$) corresponds to the ligand number (2) appearing at the intersection between the [2,2,1,0,0]-row and the $\mathbf{C}_s$-column (Eq. 5).

So-called "*meso*"-derivatives of ferrocene are characterized by the $\mathbf{K}_4$-symmetry in the present approach. The $\mathbf{K}_4$-symmetry is symbolically represented by p–$\overline{\text{p}}$, where p and $\overline{\text{p}}$ are enantiomeric to each other. This situation can be checked by using $\mathbf{K}_4$-derivatives shown in Fig. 10. Their numbers are found in the $\mathbf{K}_4$-column of Eq. 27.

Each of the two isomers with $H^6X^2Y^2$ (Fig. 10) is constructed from a pair of enantiomeric ligands with H^3XY. The number of isomers corresponds to the number of such pairs, which appears at the intersection between the [3,1,1,0,0]-row and the $\mathbf{C}_1$-column of Eq. 5. The ligand number (2) at the intersection between the [2,2,1,0,0]-row and the $\mathbf{C}_1$-column (Eq. 5) shows the presence of two kinds of achiral ligands with H^2X^2Y and accordingly the presence of two $\mathbf{K}_5$-derivatives with $H^4X^4Y^2$. The six isomers shown in the second and third rows of Fig. 10 are consistent with the number appearing at the intersection between the [2,1,1,1,0]-row and the $\mathbf{C}_1$-column (Eq. 5).

3 Partial Enumeration. In the expansion of the generating functions (Eqs. 21, 22, 23, 24, and 25), the term $H^6X^2Y^2$ (for [6,2,2,0,0]) is generated from $H^5 \times HX^2Y^2$, $H^4X \times H^2XY^2$, $H^4Y \times H^2X^2Y$, $H^3Y^2 \times H^3Y^2$, and $H^3XY \times H^3XY$. If we focus our attention on the combination $H^3XY \times H^3XY$, we can enumerate isomers with two cyclopentadienyl ligands, each of which is substituted by H^3XY. The fixed-point vector (FPV) is calculated to be (16,4,0,4,0); for example, we have 16 (= 4×4) by the square of the coefficient of the term H^3XY in Eq. 21. The FPV is multiplied by the inverse described above to give

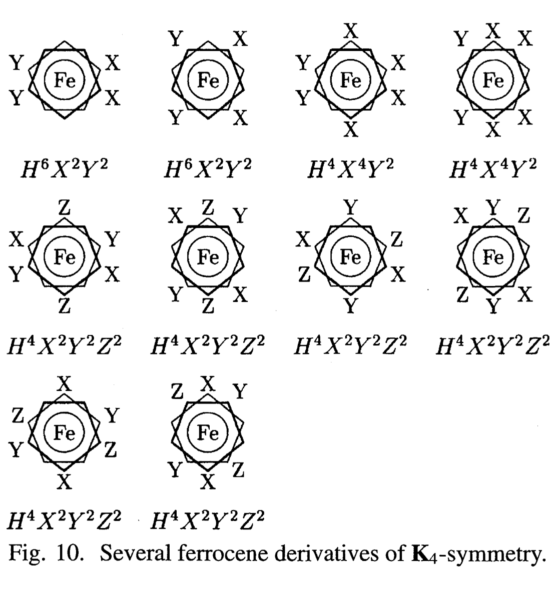
$$(16,4,0,4,0)\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (2,2,0,2,0) \tag{28}$$

This result indicates that there are two $\mathbf{K}_1$-isomers, two $\mathbf{K}_2$-isomers, and two $\mathbf{K}_4$-isomers. Let us represent the two types of ligands with H^3XY (as found in the [3,1,1,0,0]-row of Eq. 5) by the symbols p and q (and their antipodes by $\overline{\text{p}}$ and $\overline{\text{q}}$). Note that each ligand H^3XY is chiral. Thereby, the chiral $\mathbf{K}_1$-isomers are represented by p–q and p–$\overline{\text{q}}$; the chiral $\mathbf{K}_2$-isomers are represented by p–p and q–q; and the achiral $\mathbf{K}_4$-isomers are represented by p–$\overline{\text{p}}$ and q–$\overline{\text{q}}$. They are depicted in Fig. 11. This result is consistent with a previous one reported in Table 1 of Ref. 10 (four chiral and two achiral derivatives for H^7X^2Y).

Let us next focus our attention on the combination $H^2XYZ \times H^2XYZ$, which generates the term $H^4X^2Y^2Z^2$ (for [4,2,2,2,0]). This corresponds to the enumeration of isomers with two cyclopentadienyl ligands, each of which is substituted by H^2XYZ. The fixed-point vector is calculated to be (144,12,0,12,0), which is multiplied by the inverse described above to give

$$(144,12,0,12,0)\begin{pmatrix} \frac{1}{4} & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & \frac{1}{2} & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{2} & 0 & 0 \\ -\frac{1}{4} & 0 & 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix} = (30,6,0,6,0). \tag{29}$$

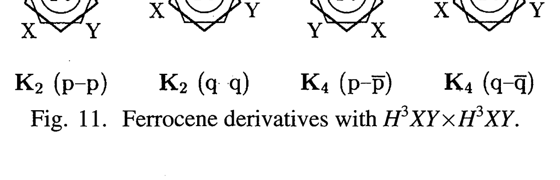
This result indicates that there are 30 $\mathbf{K}_1$-isomers (chiral), six $\mathbf{K}_2$-isomers (chiral), and six $\mathbf{K}_4$-isomers (achiral). Since there are six types of ligands with H^2XYZ as found in the


$H^6X^2Y^2$ $H^6X^2Y^2$ $H^4X^4Y^2$ $H^4X^4Y^2$

$H^4X^2Y^2Z^2$ $H^4X^2Y^2Z^2$ $H^4X^2Y^2Z^2$ $H^4X^2Y^2Z^2$

$H^4X^2Y^2Z^2$ $H^4X^2Y^2Z^2$

Fig. 10. Several ferrocene derivatives of $\mathbf{K}_4$-symmetry.


$\mathbf{K}_1$ (p q) $\mathbf{K}_1$ (p–$\overline{\text{q}}$)

$\mathbf{K}_2$ (p–p) $\mathbf{K}_2$ (q q) $\mathbf{K}_4$ (p–$\overline{\text{p}}$) $\mathbf{K}_4$ (q–$\overline{\text{q}}$)

Fig. 11. Ferrocene derivatives with $H^3XY \times H^3XY$.

[2,1,1,1,0]-row of Eq. 5 (see the six $\mathbf{C}_1$-ligands depicted in Fig. 4), there appear 15 isomers of type p–q (5+4+3+2+1 = 15) and 15 isomers of type p–$\overline{\text{q}}$ (5+4+3+2+1 = 15). It follows that the total number of $\mathbf{K}_1$-isomers is equal to 30. Obviously, there appear six isomers of type p–p ($\mathbf{K}_2$) and six isomers of type p–$\overline{\text{p}}$ ($\mathbf{K}_4$). The latter six isomers have been illustrated in the second and third rows of Fig. 10. This inspection of the promolecules is consistent with our result shown in Eq. 29, which is different from a previous one reported in Table 1 of Ref. 10 (eight chiral and five achiral derivatives for $H^2XYZ \times H^2XYZ$). Thus, the facts that we can obtain such numbers as itemized with respect to formulas and subsymmetries and that we can easily check the numbers by using the promolecule concept emphasize the advantages of the present approach over the previous enumeration.[10]

Conclusion

Ferrocene derivatives with a given formula and a given symmetry are enumerated by means of the unit-subduced-cycle-index method and the characteristic-monomial method. Their symmetries are characterized by means of the promolecule concept, where each derivative is ascribed to a factor group $\mathbf{D}_{\infty h}/\mathbf{C}_{\infty}$ and its subgroups ($\mathbf{C}_{\infty}/\mathbf{C}_{\infty}$, $\mathbf{D}_{\infty}/\mathbf{C}_{\infty}$, $\mathbf{C}_{\infty v}/\mathbf{C}_{\infty}$, and $\mathbf{C}_{\infty h}/\mathbf{C}_{\infty}$). The chirality/achirality of ligands and of derivatives is discussed.

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