

## Electronic structures of multi-decker transition metal sandwich complexes

Li Qian-shu, Yu Heng-tai and Tang Au-chin

Institute of Theoretical Chemistry, Jilin University Changchun, Jilin, P. R. of China

(Received March 12, revised July 5/Accepted August 27, 1986)

The electronic structures of multi-decker transition metal sandwich complexes are discussed according to the structure rules for transition metal heterocarboranes. A series of skeletons of the structures  $\text{Fe}_2\text{C}_5(\text{D}_{5h})$ ,  $\text{Ni}_2\text{C}_5(\text{D}_{5h})$ ,  $\text{V}_2\text{C}_6(\text{D}_{6h})$ ,  $\text{Co}_2\text{C}_6(\text{D}_{6h})$ , and  $\text{Fe}_2\text{C}_4(\text{D}_{4h})$  are calculated using the EHMO method. The calculated results show that the number of valence bonding orbitals (VBO) can vary as the distance between the metal atoms in the metallocenes is increased. This fact can be used to explain the number of valence electrons (VE) in triple-decker sandwich complexes. The conclusions are proved and discussed through a theoretical analysis of the electronic structures of such complexes and through EHMO calculations for actual compounds containing 29-34 valence electrons.

**Key words:** Transition metal complexes — Sandwich complexes — Structural rule

### Introduction

Triple-decker sandwich complexes, such as  $\text{Ni}_2\text{Cp}_3^+$ , have been prepared for about 10 years. There have been numerous investigations of the electronic structures of these multi-decker transition metal sandwich complexes [1-6]. It is interesting to note that some triple-decker sandwich complexes involving 29-34 valence electrons have been prepared. It is well known that the electronic structures of double-decker sandwich complexes can be generally explained by the 18 electron rule. However, there are also double-decker sandwich complexes which involve more than 18 valence electrons. For example  $\text{CoCp}_2$  and  $\text{NiCp}_2$

**Table 1.** Relation between the number of valence electrons and the values of  $\rho$  for  $MCp_2$  molecules

$MCp_2$	Fe	Co	Ni
VE	18	19	20
$\rho$	1.433	1.478	1.536

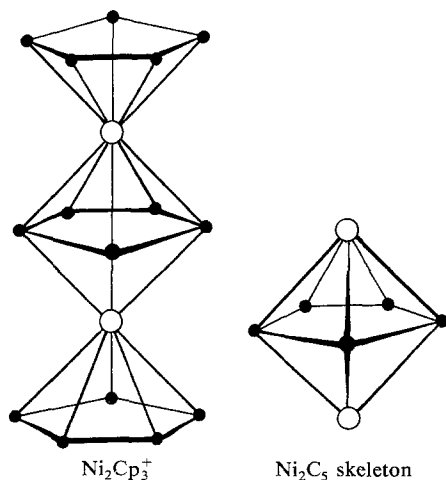
involve 19 and 20 valence electrons respectively. It is interesting to study the relation between their structures and the number of electrons. The distance between two decks in these molecules, or more precisely the ratio,  $\rho$ , of the distance between the carbon atom and the transition metal atom and that between the C—B atoms in the Cp ring increases as the number of valence electrons increases. This can be seen from Table 1.

The aforementioned observations have led us to study the relations between molecular structure and configuration in triple-decker sandwich complexes. In the present paper these relations are discussed using the structure rules of the transition metal heterocarboranes and results of calculations by the EHMO method. The conclusions obtained in this manner are then verified and discussed on the basis of a concrete analysis of triple-decker sandwich compounds which have been prepared experimentally.

### Theoretical discussion of electronic structure

A multi-decker transition metal sandwich complex can be visualized as a skeleton structure made from heterocarboranes having trigonal faces [7-8]. As an example the molecule and skeleton of  $Ni_2Cp_3^+$  are given in Fig. 1.

Using the structure rule for the heterocarboranes [9], the number of valence

**Fig. 1.** The molecule and the skeleton of  $Ni_2Cp_3^+$

bonding orbitals (VBO) is found to be

$$\text{VBO}' = 9N + \sum_{i=1}^{N-1} 4n_i - \sum_{i=1}^{N-1} F_i.$$

Where  $N$  is the number of the metal atoms in the sandwich,  $i$  is the numerical order of the  $N-1$  closo-skeletons having common connection points,  $n_i$  is the number of atoms in the main group which constitute a coordination ring in the  $i$ th closo-skeleton structure. The number of trigonal faces,  $f_i$ , is equal to  $2n_i$  for each closo-skeleton, and  $F_i = f_i + 3$ . As a consequence one has

$$\text{VBO}' = 9N + \sum_{i=1}^{N-1} (2n_i - 3).$$

In general, the number of valence electrons in a sandwich compound is the sum of the VE of the metal atoms and the number of the coordination electrons provided by the coordination rings. Therefore, the VBO corresponding to the above mentioned sandwich complexes should be equal to the VBO' minus the number of valence bonding orbitals corresponding to the  $2n_i$  bonds in each ring, i.e.

$$\text{VBO} = 9N + \sum_{i=1}^{N-1} (2n_i - 3) - \sum_{i=1}^{N-1} 2n_i = 6N + 3. \quad (1)$$

Since, in deriving this equation, the molecular symmetry is not used, Eq. (1) can be applied to molecules containing different metal atoms and mix-heterocoordination rings. Eq. (1) is obviously correct for tetra- and pentacoordination middle rings. It may be also applied to molecules having hexacoordination middle rings if the hexagonal bipyramidal skeleton is consistent with the structure rule of heterocarboranes. It can be seen from Eq. (1) that the number VBO increases by

$$\Delta\text{VBO} = 6,$$

as the number of the decks of the sandwich complex increases by one unit. In this case the molecule can involve 12 more electrons. This agrees with the results obtained by Edwin et al. [5].

In fact, Eq. (1) is derived from a "normal" range of skeleton structures. If the distance between metal atoms is increased, the VBO of the sandwich compounds can vary. As an illustration, we have calculated the orbital energies,  $E$ , of  $\text{Fe}_2\text{C}_5(\text{D}_{5h})$ ,  $\text{Ni}_2\text{C}_5(\text{D}_{5h})$ ,  $\text{Co}_2\text{C}_6(\text{D}_{6h})$  and  $\text{V}_2\text{C}_6(\text{D}_{6h})$  as a function of  $\eta$  by use of Hoffmann's EHMO method. The parameter  $\eta$  is defined as

$$\eta = \sqrt{h^2 + R^2} / d_{cc}.$$

Where  $h$  is the distance from the metal atom to the coordination ring,  $R$  is the radius of the top circle of the coordination ring, and the distance between adjacent carbon atoms in the tetra-, penta- and hexacoordination ring is denoted by  $d_{cc}$ . It is taken as 1.40, 1.42 and 1.39 Å, respectively. The parameters used in the calculations are given in Table 2.

**Table 2.** EHMO Parameters used in the calculations

		H <sub>ii</sub>	$\xi_1$	$\xi_2$	C <sub>1</sub>	C <sub>2</sub>
H	1s	-13.60	1.30			
B	2s	-15.20	1.30			
	2p	-8.50	1.30			
C	2s	-21.4	1.625			
	2p	-11.4	1.625			
S	3s	-20.0	1.817			
	3p	-13.30	1.817			
Fe	4s	-9.17	1.90			
	4p	-5.37	1.90			
	3d	-12.70	5.35	1.80	0.53659	0.66799
Co	4s	-9.21	2.0			
	4p	-5.29	2.0			
	3d	-13.18	5.55	2.10	0.56786	0.60586
Ni	4s	-9.00	2.10			
	4p	-5.00	2.10			
	3d	-14.20	5.75	2.00	0.56830	0.62920
V	4s	-8.81	1.30			
	4p	-5.52	0.875			
	3d	-11.0	4.75	1.70	0.47551	0.70521

The main results are shown in Figs. 2-6. In these figures the dashed horizontal lines indicate the 4p orbital energies of the metal atoms in the corresponding sandwich complexes. The 4p orbital energies are used as a boundary to determine VBO, the number of bonding valence orbitals.

For the Fe<sub>2</sub>C<sub>5</sub> skeleton given in Fig. 2, there are 13 antibonding orbitals in the range of  $\eta=1.18-1.33$  and, so, the molecule may contain 30 VEs in this case. When  $\eta$  is increased, the molecule can contain 34 VEs because the lowest lying antibonding orbital  $e_2''$  moves into the zone of the bonding orbitals for larger values of  $\eta$ . For the Ni<sub>2</sub>C<sub>5</sub> skeleton given in Fig. 3, the change-over point from 30 to 34 valence electrons is situated at  $\eta=1.42$  rather than at  $\eta=1.33$ .

For the V<sub>2</sub>C<sub>6</sub> skeleton given in Fig. 4, with a hexacoordination ring, the molecule may contain 26 VEs as long as  $\eta < 1.24$ . When  $1.24 < \eta < 1.36$ , the molecule will contain 28 VEs. For  $1.36 < \eta < 1.45$ , it contains 30 VEs. As the value of  $\eta$  increases further, the molecule can contain 34 VEs because the lowest lying antibonding orbital  $e_{2u}$  falls into the bonding zone. For the Co<sub>2</sub>C<sub>6</sub> skeleton given in Fig. 5, the molecule may contain 26 VEs in the case of  $\eta < 1.15$ , and 28 VEs when  $1.15 < \eta < 1.19$ . With increasing value of  $\eta$ , the lowest lying antibonding orbitals  $e_{2u}$  will fall into the bonding zone, in which case 32 VEs can be accommodated. When  $\eta=1.28$ , another antibonding orbital,  $a_{2u}$ , has also moved down into the bonding zone, which makes the molecule able to accommodate 34 VEs. In this case, since the 15th and the 16th orbital are degenerate, there is no value of  $\eta$  for which the molecule is limited to exactly 30 VEs. However it appears that, in fact, there is a range of  $\eta$  values for which some molecules do contain 30 VEs. This is presumably because real molecular structures usually do not have exact

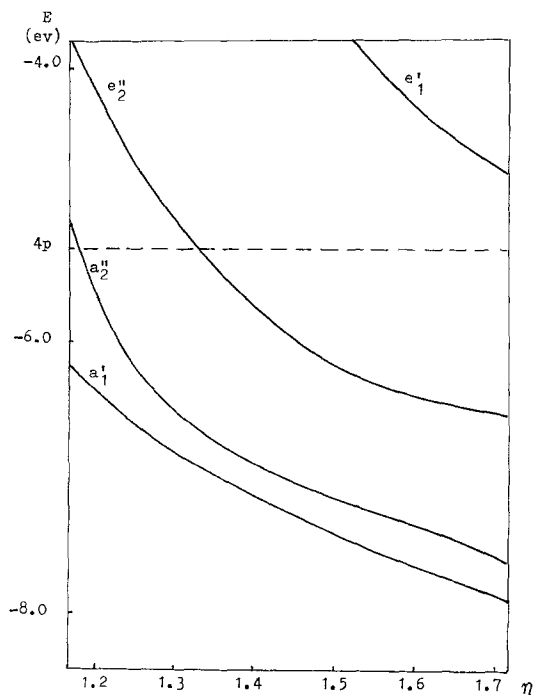


Fig. 2. Variation of the MO energies with the values of  $\eta$  for the  $\text{Fe}_2\text{C}_5(\text{D}_{5h})$  skeleton

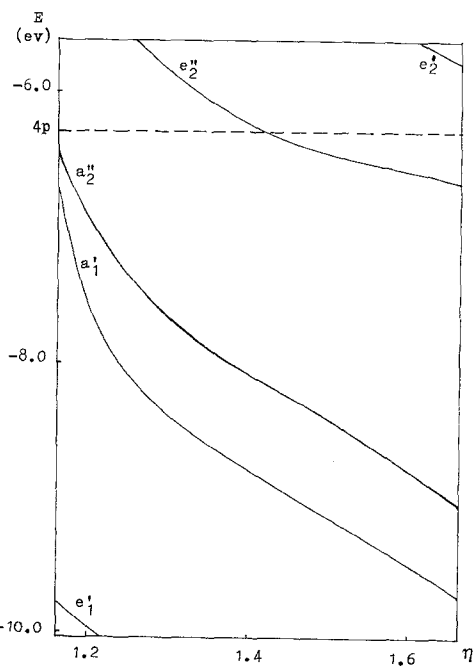


Fig. 3. Variation of the MO energies with the values of  $\eta$  for the  $\text{Ni}_2\text{C}_5(\text{D}_{5h})$  skeleton

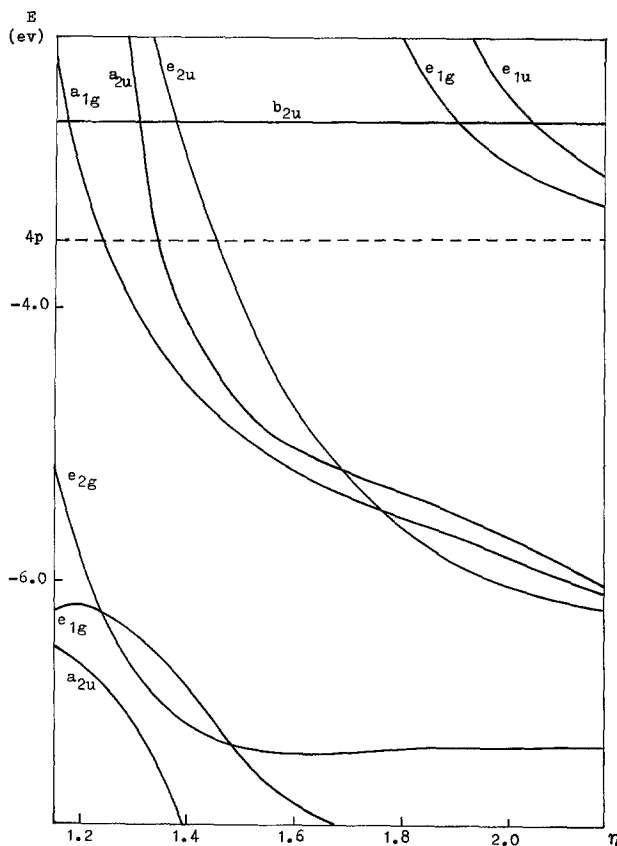


Fig. 4. Variation of the MO energies with the values of  $\eta$  for the  $V_2C_6(D_{6h})$  skeleton

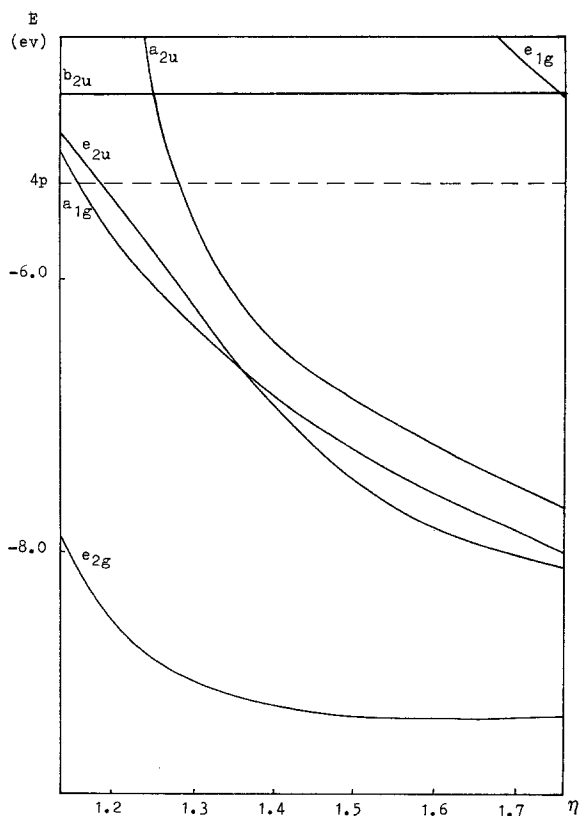
$D_{5h}$  symmetry. With the help of the distance between the metal atoms it can be estimated that a number of these compounds should contain 34 VEs.

For the  $Fe_2C_4$  skeleton given in Fig. 6, with a tetracoordination ring, the molecule may contain 30 VEs in the large range of  $1.07 < \eta < 1.614$ . For  $\eta > 1.614$ , 32 VEs can be involved, because the lowest lying antibonding orbital  $b_{1u}$  then falls into the bonding zone. But this change is very slow.

It is apparent from the preceding discussion that there is always a range of the value of  $\eta$  in which a triple-decker sandwich complex is expected to contain 30 VEs. With increasing value of  $\eta$  the molecule is able to contain 32 or 34 VEs. In some cases the valence bonding orbitals are not all filled with paired electrons. Such molecules show paramagnetism.

#### Discussion of actual triple-decker sandwich complexes

Among the pentacoordination middle rings of the triple-decker sandwich complexes which have been prepared, there exist, in addition to the Cp ring [10-13], the further rings  $C_2B_3H_5$  [14-15],  $C_3B_2H_5$  [16-18],  $C_2SB_2H_4$  [19-21] etc.



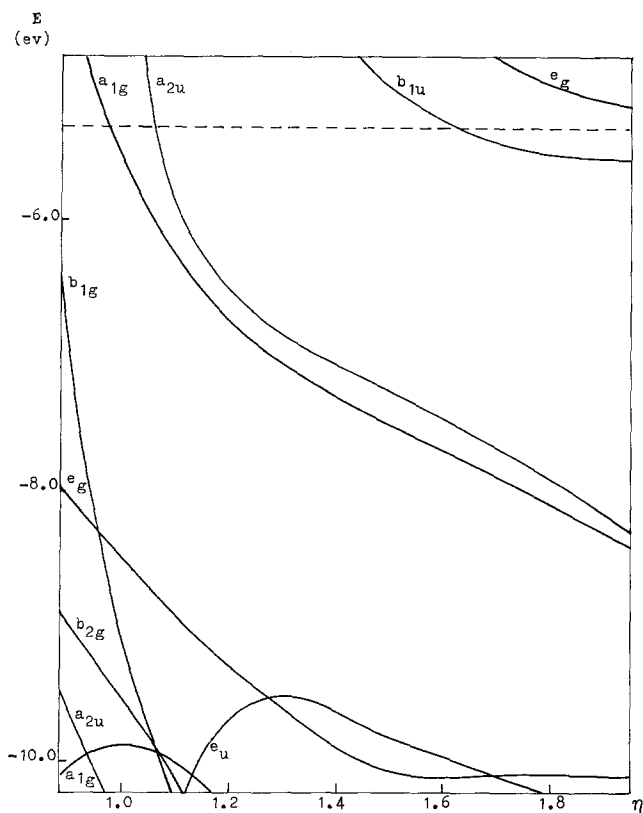
**Fig. 5.** Variation of the MO energies with the values of  $\eta$  for the  $\text{CO}_2\text{C}_6(\text{D}_{6h})$  skeleton

The valence electron number VE, the magnetic moment  $\mu$ , the spin  $S$ , the redox potentials  $M^+/M$  and  $M/M^-$ , the distance  $R_{M-M}$  between the metal atoms, the value of  $\eta$  (for which an average value for a middle heterocyclic ligand is taken), etc. of these compounds, whose structures are known experimentally, have been carefully analysed. The values obtained are given in Table 3. This analysis shows that they may be divided into two classes according to the value of VBO, namely 15 and 17 respectively. They correspond to the value of  $\eta$  being less than 1.380 and more than 1.420.

In Table 3 the value of  $\mu$  is taken from experiment and  $S$  is calculated according to the following equation

$$\mu = 2\sqrt{S(S+1)}\mu_B$$

where  $\mu_B$  is the Bohr magneton. It is evident that each case for which the spin is  $1/2$  corresponds to one orbital being occupied by a single electron. It should be noted that the molecules having 31 VEs, for example  $\text{CpCo}(\text{C}_3\text{B}_2\text{R}_5)\text{CoCp}$ , have 16 occupied orbitals. However it is easily seen from the redox potentials that the positive valence-one state having 30 VEs will be more stable. This fact



**Fig. 6.** Variation of the MO energies with the values of  $\eta$  for the  $\text{Fe}_2\text{C}_4(\text{D}_{4h})$  skeleton

shows that one valence electron occupies an antibonding orbital, and so the VBO may be still considered as 15.

To date two triple-decker sandwich complexes have been prepared which contain a hexacoordination middle ring. One of them is  $\text{Cp}_2\text{Co}_2(\text{C}_6\text{H}_6)$  and contains 34 VEs [23], while the other is  $\text{Cp}_2\text{V}_2(\text{C}_6\text{R}_6)$  ( $\text{R}=\text{H}, \text{CH}_3$ ) containing only 26 VEs [23–24]. The distance between the two V atoms is 3.403 Å and this means that  $\eta=1.58$ . It can be deduced from Fig. 3, for at such a value of  $\eta$ , it may be filled by 34 VEs. However after filling in 26 VEs, there is a large energy gap (about 2 eV) between the HOMO and the next four unoccupied bonding orbitals. This may be the reason why this compound has only 26 VE.

In principle, the preceding discussions are also applicable to other molecules having a middle coordination ring, but with terminal ligands which may not be rings. As an example the VE of the molecule  $[(\text{Co})_3\text{Mn}]_2[\text{S}(\text{BCH}_3)_2\text{C}_2\text{H}_2]$  ( $\eta=1.350$ ) is 30 [25], and that of  $(\text{CO})_2\text{Co}(\text{C}_2\text{B}_2\text{SH}_4)\text{Co}(\text{C}_2\text{B}_2\text{SH}_4)$  ( $\eta=1.313$ ) is also 30 [26].

The outlined conclusions have been confirmed by EHMO calculations of actual molecules. The  $\text{C}_3\text{B}_2\text{H}_5$  and  $\text{Cp}$  middle rings are considered as having  $\text{D}_{2h}$  ( $\text{C}_{2v}$ ,



Table 3. Properties of triple-decker sandwich complexes

Molecules	VE	$\mu$	S	Occupied orbitals	$M^+/M$	$M/M^-$	BMO	$R_{M-M}$	$\eta$	References
(CpFe) <sub>2</sub> (C <sub>2</sub> B <sub>2</sub> SH <sub>4</sub> )	30							3.236	1.291	19-21
CpFe(C <sub>2</sub> B <sub>2</sub> SH <sub>4</sub> )/CoCp	31									19-21
(C <sub>2</sub> B <sub>2</sub> SH <sub>4</sub> ) <sub>3</sub> Co <sub>2</sub>	30							3.296	1.305	19-21
(CpFe) <sub>2</sub> (C <sub>6</sub> H <sub>6</sub> BC <sub>4</sub> H <sub>3</sub> C <sub>2</sub> H <sub>5</sub> )	30							3.270	1.380	22
CpFeCpMnCp	30									22
(CpCo) <sub>2</sub> (C <sub>2</sub> B <sub>3</sub> H <sub>5</sub> )	30	2.10	$\frac{1}{2}$	15			15	3.140	1.350	14, 5
CpFe(C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )/CoCp <sup>+</sup>	29	0	0	15	-0.06	-1.77	15	3.204	1.367	5, 18, 17
CpFe(C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )/CoCp	30	0	0	15			15			5, 16-18
(CpCo) <sub>2</sub> (C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> ) <sup>+</sup>	30	0	0	15			15			5, 16-18
(CpCo) <sub>2</sub> (C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )	31	1.78	$\frac{1}{2}$	16	-0.57	-1.53	15			5, 16-18
CpNi(C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )/CoCp <sup>+</sup>	31	1.80	$\frac{1}{2}$	16						5, 16-18
CpNi(C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )/CoCp	32	2.78	1	17	0.03	-1.66	17	3.337	1.402	5, 16-18
(CpNi) <sub>2</sub> (C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> ) <sup>+</sup>	32	2.90	1	17			17			5, 16-18
(CpNi) <sub>2</sub> (C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> )	33	1.88	$\frac{1}{2}$	17	-0.13	-1.31	17	3.416	1.423	5, 16-18
(CpNi) <sub>2</sub> (C <sub>3</sub> B <sub>2</sub> R <sub>5</sub> ) <sup>-</sup>	34	0	0	17			17	3.55	1.458	5, 16-18
Cp <sub>3</sub> Ni <sup>+</sup>	34	0	0	17			17	3.576	1.466	10

**Table 4.** Orbital energies (ev) calculated by the EHMO method for several known molecules

Molecule	$E_{46}$	$E_{47}$	$E_{48}$	$E_{49}$	$E_{46}-E_{47}$	$E_{48}-E_{49}$
CpFe(C <sub>3</sub> B <sub>2</sub> H <sub>5</sub> )CoCp <sup>+</sup>	-8.6128	-9.6781	-9.7042	-11.7420	1.0653	2.0378
CpFe(C <sub>3</sub> B <sub>2</sub> H <sub>5</sub> )CoCp	-8.6128	-9.6781	-9.7042	-11.7420	1.0653	2.0378
CpCo(C <sub>3</sub> B <sub>2</sub> H <sub>5</sub> )CoCp	-9.0586	-9.9980	-10.0167	-11.9121	0.9394	1.8954
CpCo(C <sub>3</sub> B <sub>2</sub> H <sub>5</sub> )NiCp	-9.3983	-10.7711	-11.0505	-12.0406	1.3728	0.9901
CpNi(C <sub>3</sub> B <sub>2</sub> H <sub>5</sub> )NiCp	-10.3468	-11.1725	-11.2878	-12.1338	0.8257	0.8460
Cp <sub>3</sub> Ni <sub>2</sub> <sup>+</sup>	-10.4259	-11.4533	-11.4533	-12.5590	1.0274	1.1057

if the metals in the molecule are different) and D<sub>5h</sub> symmetry, respectively. The geometry parameters of the various middle coordination rings of the C<sub>3</sub>B<sub>2</sub>H<sub>5</sub> are taken as average values in the calculations. For the distances between the metal atoms and those between the metal atom and the coordination ring the experimental values are used if these values are available. Otherwise they are taken from analogous structures. The calculated results are listed in Table 4.

In Table 4,  $E_{46}-E_{49}$  denote the energies of the 46th-49th Mo's in the EHMO calculations. When the 49th orbital is doubly filled, the corresponding molecule contains 30 VEs. If the 47th orbital is filled up, the molecule contains 34 VEs. The energy split of the  $e'_2$  orbitals in D<sub>5h</sub> symmetry corresponds to the gap between the 47th and the 48th orbital. The change of the middle coordination ring obviously decreases the symmetry of system. But the value of the splitting is changed only slightly. For example, for the first three molecules this change is less than 0.03 ev, for last three molecules it is less than 0.298 ev. This shows that the results calculated by the use of D<sub>5h</sub> symmetry are applicable to the more general case. At the same time, it can be seen from Table 4 that the ( $E_{48}-E_{49}$ ) values are larger than those of ( $E_{46}-E_{47}$ ). The front-back ratio is about 2.0. The ( $E_{48}-E_{49}$ ) values of the last three molecules decrease by about  $\frac{1}{2}$ . Particularly in the molecule CpCo(C<sub>3</sub>B<sub>2</sub>H<sub>5</sub>)NiCp, the latter is much larger than the former, and the ratio is as high as 1.4. This shows that there exists a difference in the MO character between the former and the latter molecules. This inference is in agreement with the preceding analysis in that the first three and the last three molecules contain 15 and 17 valence bonding orbitals, respectively.

## References

- Summerville R H, Hoffmann R (1979) *J Am Chem Soc*: 101:3821
- Fischer R D (1963) *Theor Chim Acta* 1:418
- Lauher J W, Elian M, Summerville R H, Hoffmann R (1976) *J Am Chem Soc* 98:3219
- Werner H (1977) *Angew Chem Int Ed Eng* 16:1
- Edwin J, Bochmann M, Böhm M C, Brennan D E, Geiger W E, Krüger C, Pebler J, Pritzkow H, Siebert W, Swiridoff W, Wadepohl H, Weiss J, Zenneck U (1983) *J Am Chem Soc* 105:2582
- Tang Au-chin, Yang Zhong-zhi, Feng Sing-hong (1982) *Kexue Tongbau* 27:83
- Wade K (1971) *J Chem Soc Chem Commun* 792
- Wade K (1976) *Adv Inorg Chem Radiochem* 18:1
- Tang Au-chin, Li Qian-shu (1986) *Int J Quantum Chem* 29:579
- Schumacher E, Taubenest R (1964) *Helv Chim Acta* 47:1525

11. Werner H, Salzer A (1972) *Synth Inorg Met-org Chem* 2:239
12. Salzer A, Werner H (1972) *Angew Chem* 84:949
13. Dubler E, Textor M, Oswald H R, Salzer A (1974) *Angew Chem* 86:125
14. Beer D C, Miller V R, Sneddon L G, Grimes R N, Mathew M, Palenik G J (1973) *J Am Chem Soc* 95:3046
15. Grimes R N, Beer D C, Sneddon L G, Miller V R, Weiss R (1974) *Inorg Chem* 13:1138
16. Siebert W, Bochmann M (1978) *Angew Chem* 90:917
17. Siebert W, Bochmann M (1977) *Angew Chem Int Ed Engl* 16:857
18. Kohler F H, Zenneck U, Edwin J, Siebert W (1981) *J Organomet Chem* 208:137
19. Siebert W, Böhle C, Krüger C (1980) *Angew Chem* 92:758
20. Siebert W, Rothermel W, Bohle C, Kruger C, Brauer J (1979) *Angew Chem* 91:1014
21. Siebert W, Kinberger K (1976) *Angew Chem* 88:451
22. Siebert W (1977) *Nachr Chem* 25:597
23. Jonas V K (1985) *Angew Chem* 97:920
24. Jonas V K, Koepe G, Schieferstein L, Mynott R, Krüger C, Tsay Y H (1983) *Angew Chem Int Ed Engl* 22:620
25. Clack D W, Warren K D (1979) *Inorg Chem* 18:513
26. Siebert W, Kinberger K (1976) *Angew Chem Int Ed Engl* 15:434