termediate can accumulate. Under these conditions mechanism 19 can be written as eq 21, in which the formed dinuclear complex

$$\begin{array}{l} Pt(CN)_4^{2-} + AuCl_3OH_2 \\ \quad K_1'' \updownarrow \\ Pt(CN)_4\cdots Cl\text{-}AuCl_2\text{-}OH_2^{2-} \qquad (21) \\ \quad k_2'' \downarrow + H_2O \\ H_2O\cdots Pt(CN)_4\text{-}Cl\text{-}AuCl_2\cdots OH_2^{2-} \end{array}$$

represents the intermediate produced in reaction 1a. With $K_1''[Pt(CN)_4^{2-}] \ll 1$, the pseudo-first-order rate constant is

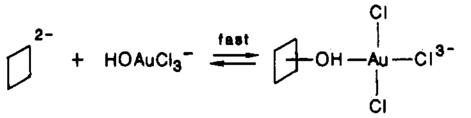
$$k = K_1''k_2''[Pt(CN)_4^{2-}] \qquad (22)$$

which agrees with rate law 4. The intermediate $H_2O\cdots Pt(CN)_4\text{-}Cl\text{-}AuCl_2\cdots OH_2^{2-}$ is best described as a precursor complex. Electron transfer to Pt(IV) and Au(I) (or Pt(III) and Au(II)) is expected to result in rapid split of the dimer since both Pt(III) and Au(I) complexes are substitution-labile. However, a certain amount of electron displacement within the dimer must have taken place, since the intense UV peak of $Pt(CN)_4^{2-}$ around 253 nm disappears when it is formed; cf. the spectra of Figure 2c,d.

The presence of an aqua ligand at the platinum side of the dimer is supported by the fact that *trans*-$Pt(CN)_4ClOH_2^-$ is formed as the product of electron transfer and split. The acceleration of this split by addition of chloride can be interpreted as a replacement of the aqua ligand at platinum by chloride, which facilitates electron transfer and split according to mechanism 19.

Oxidation of $PtCl_4^{2-}$ by $AuCl_4^-$ in aqueous solution with high concentrations of chloride (>0.25 M) has also been reported to be independent of the concentration of chloride,[7] with a rate law of the same form as the present eq 4 and with a rate constant of the same order of magnitude (830 $M^{-1}$ $s^{-1}$) as that of reaction 1a. Since no product analysis was made in that study, it is not possible to relate those results to the present ones, however.

For reaction with $AuCl_3OH^-$, hydroxide bridging with $Pt(CN)_4^{2-}$ might also occur, for instance according to eq 23. This



(23)

is not expected to result in electron transfer. The somewhat slower reaction observed in the experiment of Figure 2a (26% $AuCl_3OH^-$) compared to that of Figure 2b (100% $AuCl_4^-$) might be due to such hydroxide bridging.[12]

**Acknowledgment.** Thanks are due to Eva Bredenfeldt and Bodil Jönsson for experimental assistance and to the Swedish Natural Science Research Council for financial support.

**Registry No.** $Pt(CN)_4^{2-}$, 15004-88-3; $AuCl_4^-$, 14337-12-3; $AuCl_3OH_2$, 16561-67-4; $AuCl_3OH^-$, 56781-99-8.

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(12) Such decrease in rate is only observed when reactions are studied under second-order conditions.

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Contribution from the Department of Chemistry,
Peking University, Beijing, China

# Localized INDO Study on the Dimer of Bis($\eta^5$-methylcyclopentadienyl)ytterbium Chloride

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An INDO calculation has revealed that the dimer $(Yb(CH_3C_5H_4)_2Cl)_2$ is a covalent compound. Among the AO's of Yb atoms, the 5d orbitals make the main contribution to bonding, while the 4f orbitals are localized. With use of the Edmiston–Ruedenberg technique, the canonical orbitals of the dimer were transformed to localized molecular orbitals. The nonbonding mixing of atomic orbitals in some canonical molecular orbitals is discussed. The weak interaction between Yb atoms is due to the existence of chlorine bridges that consist of Yb–Cl $\sigma$ bonds and Cl→Yb dative bonds.

## Introduction

Because of the longstanding controversy over the nature of chemical bonding of lanthanide compounds, the electronic structure of these molecules is one of the most attractive topics. Although a series of papers published previously by us[1-8] have revealed some characteristics of the chemical bonds in monomeric lanthanide compounds, there are few theoretical papers concerning the electronic structure of dimers. Recently, we have presented a study on the dimer of bis($\eta^5$-cyclopentadienyl)methylytterbium based on delocalized INDO wave functions,[9] in which the main conclusions obtained in the case of monomers were confirmed. However, there were some unexpected results in it. For example, the 4f orbitals on two different Yb atoms are mixed to form 4f-like molecular orbitals, while the bond orders between the 4f subshells of the atoms are of negligible values. Moreover, the assignment of molecular orbitals to chemical bonds, which are more acceptable for chemists, is rather difficult in terms of these delocalized MO wave functions.

In this investigation, the electronic structure of the dimer of bis($\eta^5$-methylcyclopentadienyl)ytterbium chloride, which is the first organolanthanide dimer characterized by X-ray analysis,[10] is studied by INDO calculation. The wave functions obtained were transformed by a localization procedure and therefore are comparable with the traditional chemical bonds. As expected, the formal mixing of the 4f orbitals from different Yb atoms and that of the 4f orbitals and ligand atoms vanished after localization.

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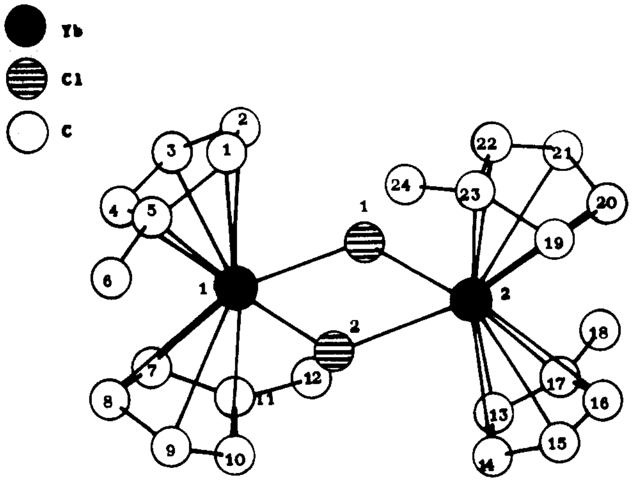

**Figure 1.** Molecular structure of $(Yb(CH_3C_5H_4)_2Cl)_2$.

Interaction between the two Yb atoms, which is weaker than that in $(YbCp_2Me)_2$, is observed and is attributed to the existence of the bridging chlorine atoms rather than a direct bonding interaction between the Yb atoms.

## Method and Parameters

An unrestricted INDO method suitable for lanthanide compounds and the parameters involved were published previously.[2,3] The structural data were taken from ref 10 and shown in Figure 1. The calculations was performed on a Honeywell DPS 8/52 computer.

The Edmiston–Ruedenberg localization method[11] was used to transform the INDO wave functions into localized molecular orbitals (LMO's). Under the INDO approximation the rotational angle $\theta$ should be determined as follows:

$$A_{ij} = \sum_{\alpha}^{a}\sum_{\beta}^{b}(c_{i\alpha}c_{j\alpha}c_{i\beta}c_{j\beta} - \tfrac{1}{4}(c_{i\alpha}{}^2 - c_{j\alpha}{}^2)(c_{i\beta}{}^2 - c_{j\beta}{}^2))\gamma_{ab} + \sum_{\alpha\beta\delta\nu}^{a}(c_{i\alpha}c_{j\beta}c_{i\delta}c_{j\nu} - \tfrac{1}{4}(c_{i\alpha}c_{i\beta} - c_{j\alpha}c_{j\beta})(c_{i\delta}c_{i\nu} - c_{j\delta}c_{j\nu}))(\alpha\beta|\delta\nu) \quad (1)$$

$$B_{ij} = \sum_{\alpha}^{a}\sum_{\beta}^{b}c_{i\beta}c_{j\beta}(c_{i\alpha}{}^2 - c_{j\alpha}{}^2)\gamma_{ab} + \sum_{\alpha\beta\delta\nu}^{a}(c_{i\alpha}c_{j\beta}c_{i\delta}c_{j\nu} - c_{j\alpha}c_{j\beta}c_{i\delta}c_{j\nu})(\alpha\beta|\delta\nu) \quad (2)$$

$$\theta = \tfrac{1}{4}\arctan\,(-B_{ij}/A_{ij}) \quad (3)$$

where the subscripts i and j and $\alpha$, $\beta$, $\delta$, and $\nu$ refer to MO's and AO's, respectively. $\gamma_{ab}$ is the Coulomb integral between two different atoms a and b. The coefficients, $c$'s, of eigenfunctions are obtained from the INDO calculation. $(\alpha\beta|\delta\nu)$ is the one-center–two-electron integral. Generally, only Coulomb and exchange types are considered.

The rotational invariance is an essential prerequisite for a unitary transformation. However, it has been pointed out that the rotational invariance will not hold when an spd[12] or spdf[13] basis set is used in the INDO calculation. As a remedy, the one-center–two-electron integrals appearing in eq 1 and 2 should be calculated completely or replaced by weighted-average values.[12,13]

The iterative procedure of the Edmiston–Ruedenberg method is similar to Jacobi diagonalization. Although the convergence behavior is rather good, the extent of CPU time is not encouraging. In the subroutine written by us, the appropriate MO's of a complicated system can be chosen in any stage of calculation to be transformed while others remain unchanged. In the investigation, moreover, only $\alpha$-spin canonical molecular orbitals are discussed in order to save CPU time.

Generally, the wave functions $\Psi^{UHF}$ obtained under the INDO approximation are not necessarily the eigenfunctions of the operator $\hat{S}^2$. Because the contamination from the high-spin excited states is rather small, it is possible to produce an almost pure state with a spin of $s'$ by annhiliating the state with a spin of $s' + 1$ in the wave functions $\Psi^{UHF}$. In this investigation, the spin annihilator

$$\hat{A}_{s+1} = \hat{S}^2 - (s' + 1)(s' + 2) \quad (4)$$

was used and the "pure" wave functions were obtained.

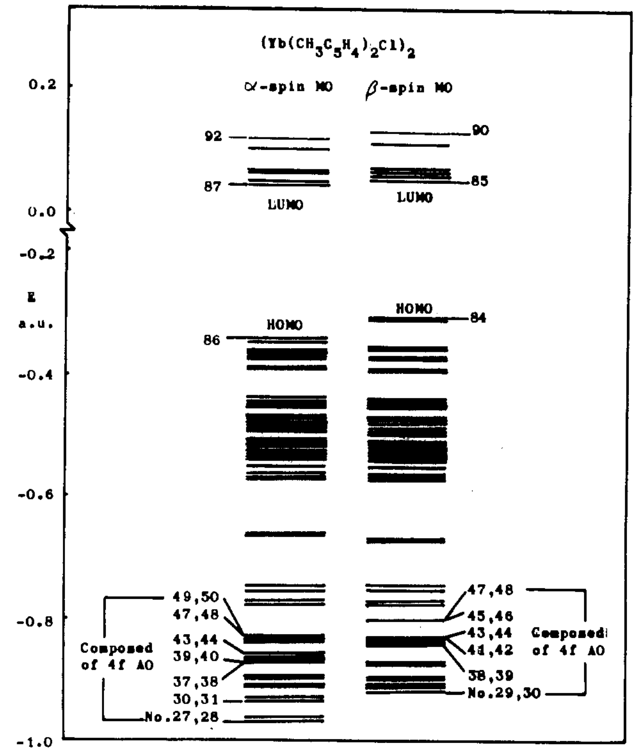

**Figure 2.** Energy level diagram of the canonical MO's of $(Yb(CH_3C_5H_4)_2Cl)_2$.

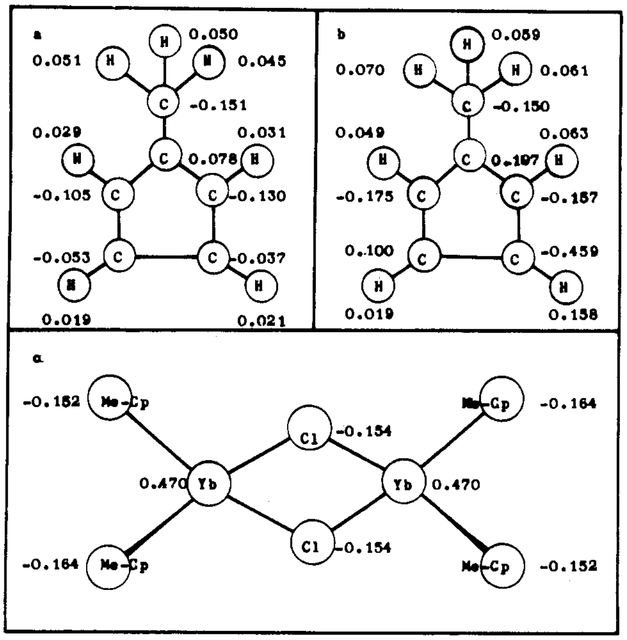

**Figure 3.** Net charge distribution of $(Yb(CH_3C_5H_4)_2Cl)_2$: (a) methylcyclopentadienyl group 1; (b) methylcyclopentadienyl group 2; (c) dimer.

## Results and Discussion

**I. Electronic Structure of $(Yb(CH_3C_5H_4)_2Cl)_2$.** The energy level, net charge, and Mulliken population of $\alpha$- and $\beta$-spin MO's are calculated. Figure 2 is an energy level diagram of some MO's. The charge distribution of the dimer is shown in Figure 3. Mulliken population data are listed in Table I.

From Figure 2, it is seen that the energy difference between the HOMO and the LUMO is about 9 eV. Different from the dimer $(YbCp_2Me)_2$,[9] both the HOMO and the LUMO as well as the neighboring MO's are mainly composed of the 2p orbitals of the ligand carbon atoms, showing no possibility of charge-

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**Table I.** Population Data of $(Yb(CH_3C_5H_4)_2Cl)_2$

| | | subshell | | | | |
|---|---|---|---|---|---|---|
| | | Yb 6s | Yb 6p | Yb 5d | Yb 4f | bond order |
| | | Orbital Populations | | | | |
| | | 0.354 | 0.594 | 1.582 | 13.000 | |
| | | Overlap Populations | | | | |
| Yb | 6s | 0.037 | 0.078 | 0.004 | 0.000 | 0.214 (Yb–Yb) |
| | 6p | 0.078 | 0.000 | 0.004 | 0.000 | |
| | 5d | 0.004 | 0.004 | 0.005 | 0.000 | |
| | 4f | 0.000 | 0.000 | 0.000 | 0.000 | |
| C(Cp) | 2s | 0.041 | 0.077 | 0.031 | 0.000 | 0.272 (Yb–C) |
| | 2p | 0.013 | 0.012 | 0.098 | 0.000 | |
| Cl | 3s | 0.070 | 0.144 | 0.048 | 0.000 | 0.480 (Yb–Cl) |
| | 3p | 0.025 | 0.037 | 0.156 | 0.000 | |

transfer spectra. This is in good agreement with experiment,[14] in which the spectra of the species $Cp_2LnR$ are different from those of the species $Cp_2LnCl$ by a charge-transfer band.

It is seen from Figure 3 that the net charge on Yb atoms is much lower than the value estimated by the ionic model, +3. The electrons transfer from the metal atoms to the ligands during the formation of the compound, clearly indicating the covalent nature of the chemical bonds in $(Yb(CH_3C_5H_4)_2Cl)_2$.

The result of the population analysis listed in Table I shows that the covalency is due to the participation of 5d, 6s, and 6p orbitals of Yb atoms in bond formation, while the 4f orbitals are strongly localized. The bond order between Yb and the cyclopentadienyl ring is comparable to those in other $\eta^5$ organolanthanide compounds.[4-8]

**II. Localized Bonds of $(Yb(CH_3C_5H_4)_2Cl)_2$.** With use of the Edmiston–Ruedenberg technique, the 86 occupied $\alpha$-spin canonical INDO wave functions were transformed to 86 LMO's. In comparison to the case for the canonical molecular orbitals (CMO's) the assignment of the LMO's to chemical bonds is much easier and more reliable.

The 86 LMO's, which correspond to 66 chemical bonds and 20 lone pairs, can be divided into four groups, depending on the distribution of the energy levels. The C–H bonds have lower energies (ranging from −1.828 to −0.790 au). The C–C $\sigma$ bonds and Yb–Cl $\sigma$ bonds are at the high position of the energy level diagram (−1.549 to −0.883 au). The 14 localized 4f orbitals are located at a higher position (−0.937 to −0.850 au). At the top of the energy level diagram (−0.856 to −0.379 au), there are the C–C $\pi$ bonds and the lone pairs of electrons on the Cl atoms. It is also noted that each $\pi$ orbital in $\eta^5$ rings could not be definitely localized on two atoms. This is in agreement with the concept of delocalization of $\pi$-bond systems. The 4 Cp rings are coordinated to Yb atoms through 12 C–C $\pi$ bonds, which mainly consist of the 2p AO's of C atoms and the 5d AO's of Yb atoms.

In the result of the canonical molecular orbitals, there are two things that are in conflict with the nonbinding nature of 4f atomic orbitals of lanthanides. First, the 4f AO's from two different Yb atoms form MO's with approximately equal coefficients. Second, in some neighboring MO's of the 4f-like MO's, the 4f composition is up to 20%. However, the population analysis shows that there is no interaction between the AO's mentioned above. This kind of mixing of basis orbitals in some MO's, which makes no contribution to bonding, may be called nonbonding mixing or formal mixing.

On the basis of the interaction, the mixing of the 4f AO's from different atoms is easily understood. Two degenerated 4f orbitals from different Yb atoms, $\chi_1$ and $\chi_2$, form two MO's, $\psi_1$ and $\psi_2$:

$$\psi_1 = \pm\frac{1}{(2 + 2S_{12})^{1/2}}(\chi_1 + \chi_2)$$
$$\psi_2 = \pm\frac{1}{(2 - 2S_{12})^{1/2}}(\chi_1 - \chi_2) \quad (5)$$

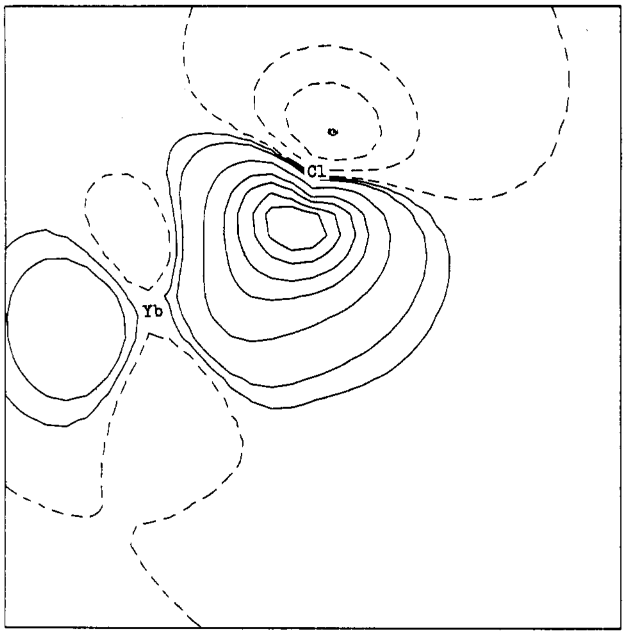

**Figure 4.** Localized molecular orbital contour map of the bond Yb1–Cl1 on the plane Yb1–Cl1–Yb2–Cl2.

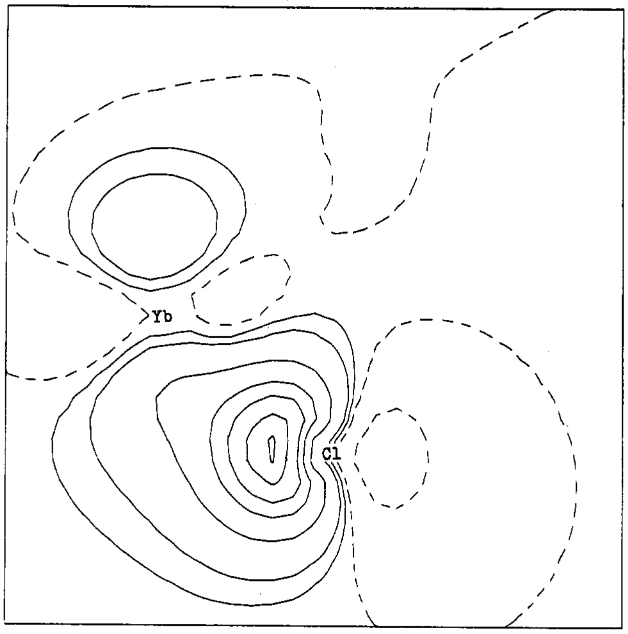

**Figure 5.** Localized molecular orbital contour map of the bond Cl2→Yb1 on the plane Yb1–Cl1–Yb2–Cl2.

where $S_{12}$ denotes the overlap integral between $\chi_1$ and $\chi_2$. The corresponding MO energies are

$$e_1 = \frac{e_1^0 + \Delta_{12}}{1 + S_{12}} \qquad e_2 = \frac{e_1^0 - \Delta_{12}}{1 - S_{12}} \quad (6)$$

where $\Delta_{12} = \langle\chi_1|\hat{H}^{\mathrm{eff}}|\chi_2\rangle \propto -S_{12}$. The population between $\chi_1$ and $\chi_2$ is

$$P_{12} = -\frac{4S_{12}^2}{1 - S_{12}^2} \quad (7)$$

Because of the long distance between the two Yb atoms and the contractive character of the 4f AO's, $S_{12}$ should be extremely small.[15] Therefore, the interaction between two 4f orbitals is too weak to be felt and makes no contribution to chemical bonding. It is expected that $e_1 = e_2 \cong e_1^0$ and $p_{12} \cong 0$ as shown in the

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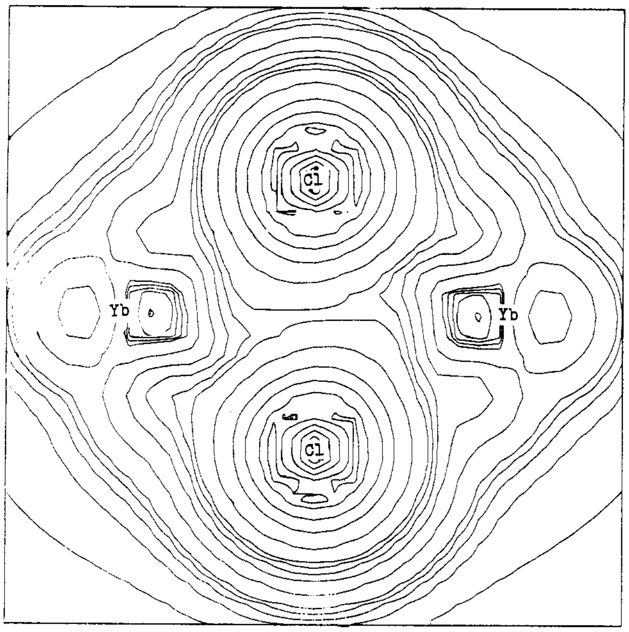

**Figure 6.** Density contour map of the dimer on the plane Yb1–Cl1–Yb2–Cl2.

calculation, although the two 4f orbitals are mixed with considerable coefficients.

The considerable amount of 4f orbitals in some MO's may be explained by the perturbational molecular orbital theory.[16] A ligand group orbital and a 4f AO may be considered as "molecular orbitals" of two fragments $\psi_{il}^0$ and $\psi_{jf}^0$, which form a molecular orbital of the complex, $\psi_i$:

$$\psi_i = (1 + t_{ii}^{(2)})\psi_{il}^0 + t_{ji}^{(1)}\psi_{jf}^0 \qquad (8)$$

where

$$t_{ji}^{(1)} = \frac{\Delta_{ij} - e_{ij}^0 S_{ij}}{e_{il}^0 - e_{jf}^0} \propto \frac{-S_{ij}}{e_{il}^0 - e_{jf}^0}$$
$$t_{ii}^{(2)} = -\left(S_{ij}t_{ji}^{(1)} + \frac{1}{2}(t_{ji}^{(1)})^2\right) \qquad (9)$$

where $S_{ij}$ denotes the overlap integral between $\psi_{il}^0$ and $\psi_{jf}^0$ and $e_{il}^0$ and $e_{jf}^0$ refer to the energies of $\psi_{il}^0$ and $\psi_{jf}^0$, respectively. Then the energy of $\psi_i$ is

$$e_i = e_{il}^0 + e_i^{(1)} + e_i^{(2)} + ... \qquad (10)$$

As a second approximation, $e_i^{(1)} = 0$ and $e_i^{(2)} = (\Delta_{ij} - e_{ij}^0 S_{ij})^2/(e_{il}^0 - e_{jf}^0) \propto S_{ij}^2/(e_{il}^0 - e_{jf}^0)$ gives $e_i = e_{il}^0 + e_i^{(2)}$.

It is clear now that in some special cases where both the values of $S_{ij}$ and $e_{il}^0 - e_{jf}^0$ are extremely small, $t_{ji}^{(1)}$ may be of considerable value, while $e_i^{(2)}$ is still insignificant, implying that the mixing of the fragment orbitals makes no contribution to chemical bonding.

With the increase of the number of atoms in a molecule, the nonbonding mixing will be more common, because in such cases the energies of the ligand group orbitals may fall in the range of those of 4f orbitals.

This nonbonding mixing will vanish after a proper transformation of the CMO's. In fact, after the localization transformation the 4f orbitals are localized completely on each Yb atom (99.9% Yb1 or Yb2) and the 4f composition in other MO's entirely vanishes.

**III. Chlorine Bridge Bonds.** According to the assignment of the LMO's to chemical bonds, it is seen that there are two Yb–Cl σ bonds and two Cl→Yb dative bonds in the dimer. Figures 4 and 5 show the contour maps of these LMO's. The density contour map of the dimer on the plane Yb1–Cl1–Yb2–Cl2 is shown in Figure 6.

It is interesting to notice that although the bond orders between each chlorine atom and any one of the two Yb atoms are the same, the energy of a Cl→Yb bond is much higher than that of a Yb–Cl σ bond, implying that the Cl→Yb bonds may be more active and easier to be broken in some conditions.

Like the case of $(YbCp_2Me)_2$,[9] there is a weak interaction between the two Yb atoms in the dimer. However, the distance between the Yb atoms is longer than that in $(YbCp_2Me)_2$. This fact may be attributed to the difference between the bonding character of the bridges of the two systems, namely, the two three-center–two-electron bonds in $(YbCp_2Me)_2$ and the two covalent bonds and two dative bonds in $(Yb(CH_3C_5H_4)_2Cl)_2$. It is not likely that there is a strong Yb–Yb bonding interaction in the dimer. The weak interaction between two Yb atoms may be attributed to the bridges rather than the direct bonding of two metal atoms.

**Acknowledgment.** We are grateful to the National Natural Science Foundation of China for support.

**Registry No.** $(Yb(CH_3C_5H_4)_2Cl)_2$, 54365-60-5.

**Supplementary Material Available:** Details of the α-spin localized molecular orbitals of $(Yb(CH_3C_5H_4)_2Cl)_2$ (Table S1) and the comparison of some LMO's and CMO's (Table S2) (6 pages). Ordering information is given on any current masthead page.

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