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Theoretical Study of the Conformational Preferences in the $\text{Cl}_4\text{W}=\text{CH}_2$ Complex

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Tungsten(VI) carbene complexes are important because they have a high catalytic activity in olefin metathesis reactions. However, little is known about their conformational preferences. In this work a theoretical conformational study on the $\text{Cl}_4\text{W}=\text{CH}_2$ complex, in its $^1\text{A}_1$ electronic state, has been performed. Extended Hückel and ab initio methods have been used. Four conformations corresponding to a trigonal-bipyramidal structure have been considered. We have found that the equatorial parallel conformation is the most stable one. Finally, it has been shown that there exists a low-lying triplet $^3\text{B}_2$ state very close in energy to the $^1\text{A}_1$ one.

Introduction

Transition-metal carbene complexes have been postulated as catalytic intermediates of many organometallic reactions, such as olefin metathesis.¹⁻⁴ It is well-known that a great number of these metathesis catalysts contain tungsten as the transition metal,^{5,6} the most active ones being those compounds in which the metal is in a high oxidation state. In particular, tungsten(VI) carbenes exhibit high catalytic activity.

The knowledge of the structure of these metal carbene complexes is very important to understanding their reactivity. However, little is known about their equilibrium structures and conformational preferences because of the great difficulty in isolating these catalysts. To our knowledge, very few tungsten(VI) carbenes have been experimentally characterized.⁷⁻¹² For several $\text{X}_4\text{M}=\text{CR}_2$

compounds the experimental results seem to indicate that a trigonal-bipyramidal structure is the most favourable one, the carbene ligand occupying an equatorial position with its substituents in the trigonal plane.

From a theoretical point of view several metal carbenes have recently been studied.¹³⁻¹⁸ However, the arrangement of different ligands around W(VI) in a tungsten carbene complex has only been discussed by using qualitative arguments.^{19,20} In good agreement with the experimental data, these qualitative arguments predict a trigonal-bipyramidal structure in the case of the $\text{X}_4\text{M}=\text{CH}_2$ metal carbene complexes.

The object of this paper is to carry out a quantitative conformational study of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex,⁶ which is one of the simplest and more realistic tungsten(VI) carbenes that can be considered. First, the calculations have been done by assuming a singlet electronic state for the complex. However, due to the fact that we are dealing with an electron-deficient compound, the possible existence

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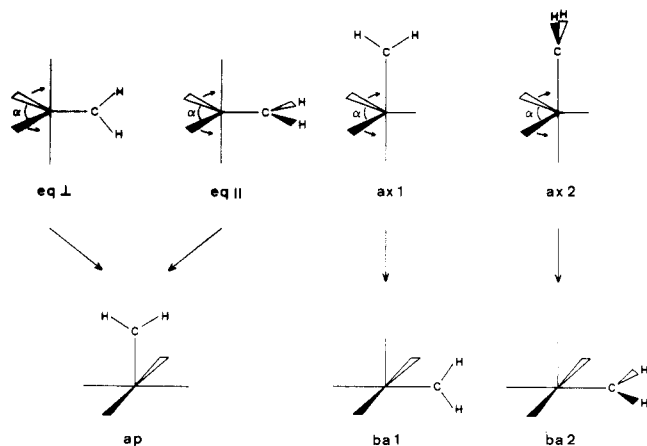


Figure 1. Studied conformations of the trigonal-bipyramidal structure of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex. The pseudorotation process leading to the square-pyramid structure is also shown.

of triplet states close in energy to the singlet state has also been considered. The calculations have been done at different levels of geometry optimization. This has permitted to discuss in which way the imposition of constraints can modify the results obtained.

Method of Calculation

As it has been mentioned in the Introduction, a trigonal bipyramidal structure seems to be the most favorable one in the case of $\text{X}_4\text{M}=\text{CH}_2$ complexes. Four different conformations of this basic structure have been considered in this paper for the $\text{Cl}_4\text{W}=\text{CH}_2$ compound. As it will be shown below, these conformations differ in the relative position of the ligands around the tungsten atom.

The relative stabilities of these four conformations have been first obtained by means of extended Hückel calculations. These calculations were carried out by using weighted H_{ij} 's. Coulomb integrals and orbitals exponents have been taken from ref 21.

Ab initio calculations of the four conformations, using a pseudopotential approach, which is implemented in a modified version of the Gaussian 86 system of programs,²² have also been carried out, first keeping invariant the geometrical parameters and then performing geometrical optimizations by means of the Schlegel algorithm.²³ These calculations have been done by using the effective core potentials of Hay et al.^{24,25} to replace the [Ne] and [Xe]4f cores of Cl and W atoms, respectively. In the case of the W atom the effective core potential incorporates relativistic effects. The minimum basis sets have been employed to represent the valence orbitals of Cl and W atoms. For H and C atoms the STO-3G basis set has been used.

To study more extensively the most stable conformation, correlation energy has been included through the perturbation theory of Møller–Plesset up to the third-order.^{26,27}

As it has been mentioned above, several triplet states have also been studied. In these cases the SCF procedure was carried out by using the ROHF method. Correlation

Table I. Total Energy, Energies of the Two Highest Occupied Orbitals, and Contribution of These Two Orbitals to the Total Energy along the Pseudorotation Process^a

	eq _⊥	eq _∥	ax ₁	ax ₂
$\alpha = 120^\circ$				
<i>E</i>	0.0	5.8	5.9	5.9
ϵ_1	0.0	5.5	3.5	3.5
ϵ_2	0.0	0.5	5.1	5.1
$2\epsilon_1 + 2\epsilon_2$	0.0	12.0	17.2	17.2
$\alpha = 140^\circ$				
<i>E</i>	-0.9	5.3	8.4	5.1
ϵ_1	-0.5	5.1	4.6	2.3
ϵ_2	-0.9	0.5	5.1	4.8
$2\epsilon_1 + 2\epsilon_2$	-2.8	11.2	19.4	14.2
$\alpha = 160^\circ$				
<i>E</i>	1.8	6.7	12.2	6.5
ϵ_1	0.7	4.8	5.5	1.6
ϵ_2	-1.4	-0.9	4.8	4.6
$2\epsilon_1 + 2\epsilon_2$	-1.4	7.8	20.6	12.4
$\alpha = 180^\circ$				
<i>E</i>	12.1		19.0	12.4
ϵ_1	4.8		6.0	1.4
ϵ_2	0.2		4.8	4.4
$2\epsilon_1 + 2\epsilon_2$	10.0		21.6	11.6
	ap		ba ₁	ba ₂

^a Energies in kcal/mol obtained at the extended Hückel level. All values are relative to the ones obtained for the eq_⊥ conformation with $\alpha = 120^\circ$.

energy has also been included in order to study the triplet–singlet energy gap at different levels of calculation.

Results and Discussion

As has been mentioned in the Introduction, the experimental results obtained for several $\text{X}_4\text{M}=\text{CH}_2$ compounds seem to indicate that the trigonal-bipyramidal structure is the most favorable one. For this structure, $\text{Cl}_4\text{W}=\text{CH}_2$ can exist in several different conformations, depending on the relative position of the carbene ligand with respect to the chlorine atoms. In this work, we have studied the four conformations presented in the upper side of Figure 1. In two of them the CH_2 group is in the equatorial position (eq_⊥ and eq_∥) while in the other two the carbene is in the axial position (ax₁ and ax₂).

Extended Hückel Results. The calculations have been carried out with the following fixed geometrical parameters: W–Cl = 2.4 Å, W–C = 2.1 Å, C–H = 1.1 Å, and HCW = 128.5°. The three XWX angles between the metal atom and the equatorial ligands have been initially fixed at 120°. However, to study the variation of the energy when this trigonal-bipyramidal structure is distorted, we have also calculated the energy variation in the Berry pseudorotation process which is schematically shown in Figure 1. One can observe that this pseudorotation leads, when $\alpha = 180^\circ$, to a square pyramid with the apical/basal angle equal to 90°. The two equatorial conformations of the trigonal bipyramid lead to the same square-pyramidal conformational in which the CH_2 group is situated in the apical position, while the two axial conformations transform into two different basal conformations of the square pyramid.

Table I presents the total energy, *E*, the energies of the two highest occupied orbitals, ϵ_1 and ϵ_2 , and the contribution of these two orbitals to the total energy for several values of the angle α (see Figure 1) leading from the trigonal bipyramidal structure ($\alpha = 120^\circ$) to the square-pyramidal one ($\alpha = 180^\circ$). All the reported values are relative to the ones obtained for the equatorial perpendicular conformation (eq_⊥) with $\alpha = 120^\circ$.

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Table II. Ab Initio Energy Values^a for the Studied Conformations of the $\text{Cl}_4\text{W}=\text{CH}_2$ Complex

	eq _⊥	eq _∥	ax ₁	ax ₂
E_{fix}	-104.6194	-104.6611	-104.6524	-104.6523
E_{part}	-104.6768	-104.6884	-104.6766	-104.6762

^a In hartree.

From the total energy values corresponding to $\alpha = 120^\circ$ one can observe that extended Hückel calculations predict that the equatorial perpendicular conformation is the most favorable situation for the $\text{Cl}_4\text{W}=\text{CH}_2$ complex. The other three conformations appear to be nearly degenerate at about 6 kcal/mol above the most stable one.

Let us now analyze the energy variation when the Berry pseudorotation process is done. One can observe that for both equatorial conformations and for one of the axial conformations (ax_2) the most stable situation is presented when $\alpha = 140^\circ$. On the contrary, the energy of the ax_1 conformation monotonically increases when α is increased, in such a way that the most favorable situation is expected to be for a value of α less than 120° .

It is also interesting to analyze the contribution of the two highest occupied orbitals to the total energy. The ϵ_1 and ϵ_2 energies of these two orbitals mainly correspond to the π and σ interactions, respectively, between the metal atom and the carbene ligand, thus representing the $\text{W}=\text{C}$ double bond. In the square-pyramidal structure ($\alpha = 180^\circ$), one can observe a qualitative correlation between the $2\epsilon_1 + 2\epsilon_2$ values and the total energy for the three studied conformations. This seems to indicate that the two highest occupied orbitals are the responsible of the relative stability of these conformations. For $\alpha \neq 180^\circ$ the correlation is worse, since ligand–ligand interactions are also responsible of the relative stability of the four studied conformations.

Ab Initio Calculations. In this section we present the ab initio calculations on the relative stability of the different conformations corresponding to the trigonal-bipyramidal structure of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex. The two equatorial and the two axial conformations depicted in the upper side of Figure 1, with $\alpha = 120^\circ$, have again been considered.

The calculations have been carried out at three different levels of geometry optimization. First, the geometrical parameters that we have used in the extended Hückel calculations have been kept unchanged. Secondly, a partial geometry optimization has been carried out. This optimization has been performed keeping invariant the dihedral angles and the $\text{X}_{\text{ax}}-\text{W}-\text{X}_{\text{eq}}$ angle which has been fixed at 90° . In this way, C_{2v} symmetry has been imposed in the equatorial conformations while C_s symmetry is maintained in the axial ones. Finally, a total optimization has also been done.

Table II presents the energy values E_{fix} and E_{part} obtained for the four conformations without geometry optimization and with partial geometry optimization, respectively. If one looks at the first row, one can observe that the lowest energy value corresponds to the eq_{\parallel} conformation in good agreement with recent experimental results for several tungsten(VI) carbene complexes.¹¹ On the contrary, our extended Hückel calculations predict the eq_{\perp} conformation to be the most stable. This discrepancy is possibly an artifact due to the parametrization that we have used for the W atom in EHT calculations, this parametrization leading to metal d orbitals too high in energy. Given that the preferred equatorial conformation depends on the relative ordering of these d orbitals and the carbene p orbital,¹⁹ a destabilization of the metal d orbitals can

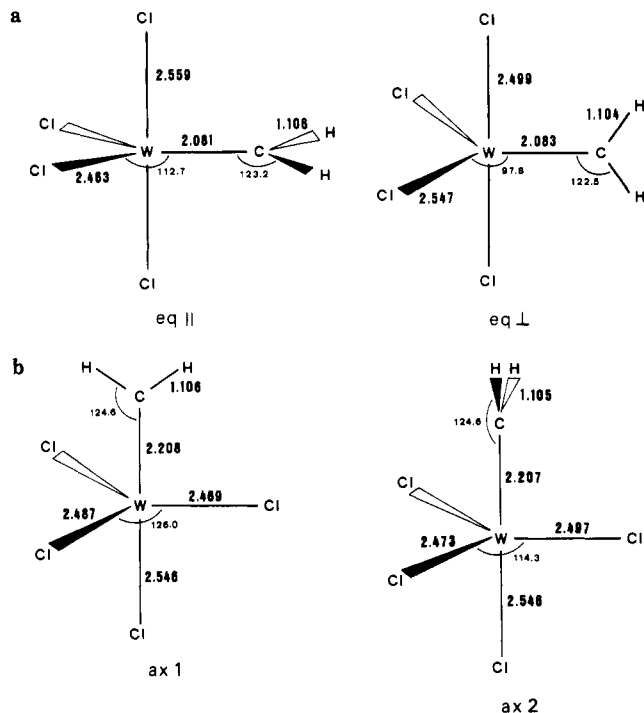


Figure 2. Ab initio partially optimized structures of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex (bond lengths in Å and angles in deg).

lead to a reverse in the relative stability of both conformations.

Regarding the energy values of the partially optimized structures, E_{part} , one can observe that these values are notoriously lower than the ones obtained with the non-optimized geometry. This energy lowering appears to be especially important in the case of the eq_{\perp} conformation for the reasons which will be discussed below. In any case, the eq_{\parallel} conformation remains the most stable one.

The structures with partial optimization are presented in Figure 2. If one looks at the geometrical parameters corresponding to the eq_{\parallel} conformation, one can observe that the W-Cl bond length greatly differs depending on the axial or equatorial position of the chlorine atom. The axial W-Cl bond length appears to be greater than the equatorial one, thus indicating that the equatorial bond is stronger. This fact has been earlier predicted by Albright et al.²⁰ for this kind of structures. Regarding the W-C bond length, the value we have obtained agrees reasonably well with the experimental data which are known for similar compounds.^{28,29} Let us now compare the geometrical parameters of the two equatorial conformations. One can observe that the main differences appear in the equatorial and in the axial W-Cl distances, the corresponding values being permuted. Furthermore, the $\text{Cl}_{\text{eq}}\text{WC}$ angle has noticeably decreased in the eq_{\perp} conformation. These facts will be understood when total optimization is allowed. Regarding the geometry of the axial conformations, it is interesting to note that the W-C bond length in both axial conformations is greater than the one obtained in the eq_{\parallel} conformation. This shows that the equatorial W-C bond is stronger than the axial one. Finally, it is worth mentioning that the values obtained for the angles XCX , where X is an equatorial ligand, are in good agreement with the extended Hückel predictions about the most favorable value of the angle α in the Berry

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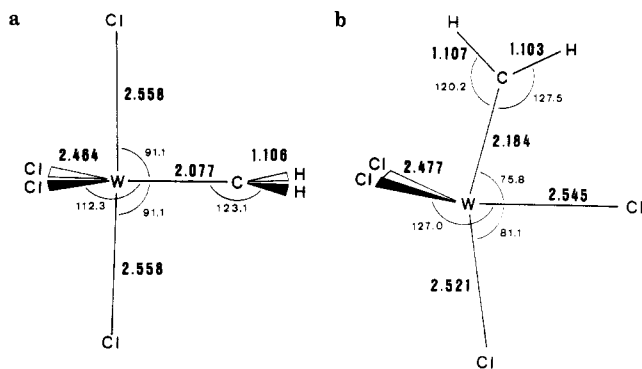


Figure 3. Ab initio totally optimized structures of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex (bond lengths in Å and angles in deg).

pseudorotation process (see Table I).

Let us now present the results obtained when total geometry optimization is allowed. In this case only two minimum energy structures have been found, which correspond to the optimization of the eq_{\parallel} and of the ax_1 conformations, respectively. It has to be outlined that both structures correspond to real minima, since they do not present any imaginary frequency. When the eq_{\perp} conformation is optimized without constraints, it transforms into the eq_{\parallel} one. This indicates that the eq_{\perp} conformation does not correspond to a real minimum in the potential energy surface. So, the eq_{\perp} structure presented in Figure 2 was only due to the constraints imposed in the optimization which avoided its transformation into the eq_{\parallel} conformation. In the case of the ax_2 conformation, the elimination of constraints has not lead to a minimum energy structure corresponding to this region of the potential energy surface.

Figure 3 presents the two fully optimized structures. If one compares these structures with the corresponding ones in Figure 2, one can observe that the eq_{\parallel} conformation only slightly changes when total optimization is carried out, while more important changes are produced in the ax_1 conformation. As a direct consequence, total optimization stabilizes the ax_1 structure more than the eq_{\parallel} one, although this latter is still the most stable. The energies of the equatorial and axial conformations are -104.6885 au and -104.6852 au, respectively, leading to a relative energy difference of about 2 kcal/mol. This difference increases to about 13 kcal/mol when the electron correlation is introduced at the MP2 level, using the fully optimized HF geometries.

Another interesting aspect is the difference in the W-C bond lengths that can be observed when both optimized structures are compared. The fact that this bond length in the axial isomer is about 0.11 Å longer than in the equatorial one may be due to the use of a HF level of calculation, since the electron correlation for M-C π bonding has been shown to be important.³⁰ To investigate this problem we have calculated the energy of both structures at the MP2 level for several W-C distances, the rest of geometrical parameters being kept unchanged. We have found that electron correlation leads to a decrease of the W-C distance, this decrease being of about 0.08 Å for the equatorial conformation and of about 0.11 Å for the axial one.

Up to here, the conformational study of the $\text{Cl}_4\text{W}=\text{CH}_2$ complex has been done considering that the ground state of this molecule is a closed-shell singlet state. However, since this complex is an electron-deficient compound, there could be some triplet states close in energy to the singlet

Table III. ROHF Energy Values^a for Several Triplet States of the $\text{Cl}_4\text{W}=\text{CH}_2$ Complex

	${}^3\text{B}_2$	${}^3\text{A}_2$	${}^3\text{A}_1$	${}^3\text{B}_1$
<i>E</i>	-104.6977	-104.6814	-104.6275	-104.6121

^a In hartree.

Table IV. Energy Values^a of the ${}^1\text{A}_1$ and ${}^3\text{B}_2$ States of $\text{Cl}_4\text{W}=\text{CH}_2$ at Different Levels of Calculation^b

	HF	MP2	MP3
${}^1\text{A}_1$	-104.6885 (-104.9847)	-104.8862 (-105.2390)	-104.8785
${}^3\text{B}_2$ ^c	-104.7211 (-105.0379)	-104.8749 (-105.2362)	-104.8831

^a In hartree. ^b Values in parentheses correspond to calculations with the double- ζ basis set. ^c At the UHF level of calculation.

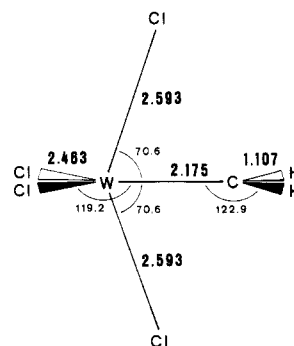


Figure 4. Ab initio ROHF total optimized structure of the ${}^3\text{B}_2$ state (bond lengths in Å and angles in deg).

one. Although the study of the triplet states is not the main purpose of this paper, we have carried out some preliminary calculations in order to determine which is the ground state. As a starting point we have calculated the energy of four different triplet states at the ROHF level keeping unchanged the geometry of the most stable singlet state conformation, the eq_{\parallel} one (see Figure 3). The energy values obtained in this way are presented in Table III.

One can observe that the most stable triplet is a B_2 symmetry state. This state has been obtained through the occupancy of a b_1 and a_2 symmetry orbitals. The b_1 orbital corresponds to the π interaction between the d_{zz} metal orbital and the p_x orbital of the carbon atom, whereas the a_2 orbital is mainly the d_{xy} metal orbital (the z axis follows the direction of the W-C bond).

If one compares the energy value of the ${}^3\text{B}_2$ state with the one of the ${}^1\text{A}_1$ state, it appears that the triplet state is lower in energy. However, to discuss which is the ground state it is necessary to calculate both states in a higher level of calculation. So, we have completely optimized the geometry of the triplet state at the ROHF level, and then we have introduced electron correlation in both states by using the MP perturbation theory. Given that the minimal basis set has only single- ζ flexibility, calculations using a double- ζ quality basis set for the s and d metal orbitals and a 3-21G basis set for the C and H have also been carried out.

The optimized structure for the ${}^3\text{B}_2$ state is presented in Figure 4. When one compares this geometry with the one obtained for the singlet ${}^1\text{A}_1$ state (see Figure 3), one can observe that the distance between the tungsten atom and the carbon atom is longer for the triplet. This fact was to be expected if one considers that now the orbital which is responsible for the π interaction between the metal atom and the carbene is occupied by only one electron. Another interesting fact is that $\text{Cl}_{\text{ax}}\text{WC}$ angle is appreciably smaller in the triplet state in such a way that the minimum energy structure is now quite far from the

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idealized trigonal-bipyramidal geometry.

The energy values obtained for both electronic states at different levels of calculation are presented in Table IV. It must be remarked that all these energy values have been obtained by keeping the geometrical parameters optimized at the HF level unchanged by using the minimal basis set (see Figures 3 and 4). In the case of the triplet, although the optimization has been carried out at the ROHF level of calculation, electron correlation has been introduced over one UHF determinant, this procedure being the one implemented in the GAUSSIAN 86 system of programs. In these UHF calculations the spin contamination is very small, since the values of S^2 are 2.06 or 2.07 depending on the basis set which is used.

Let us first examine the results obtained with the minimal basis set. As was to be expected, the introduction of electron correlation stabilizes the singlet 1A_1 state more than the 3B_2 state. As a consequence the singlet state is the most stable at the MP2 level although the situation is again reversed when third-order corrections are taken into account. This difference in the relative stability of both states at the MP2 and MP3 levels is probably due to the fact that MP2 calculations overestimate the energy lowering. Given that the energy gap is only of about 3 kcal/mol at the MP3 level, these calculations permit only the conclusion that both states lie very close in energy.

The results obtained with the double- ζ quality basis set are qualitatively very similar. In this case, calculations at the MP3 level have not been carried out since they are not feasible with the facilities available in our laboratory. However, given that the singlet state is only 2 kcal/mol lower at the MP2 level, the triplet state is again expected to be more stable if third-order corrections are introduced. Calculations at a much higher level would be necessary to obtain a definitive answer about which is the ground state of this molecule.

Conclusion

In this work we have carried out a quantitative conformational study of the $Cl_4W=CH_2$ complex in its 1A_1 electronic state. We have found that in a trigonal-bipyramidal structure the equatorial parallel ($eq_{||}$) conformation is the most stable one. A preliminary study of different triplet states has also shown that there is a low-lying 3B_2 state very close in energy to the singlet 1A_1 state. So, calculations at a much higher level of calculation would be necessary to obtain a definitive answer about which is the ground state of this molecule.

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Binuclear Organometallic Electron Reservoirs: Syntheses and Electrochemistry of the Fulvalene Complexes



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Ligand exchange reaction between ferrocene (1) and C_6Me_6 in the presence of $AlCl_3$ and Al powder in decahydronaphthalene (140 °C) provides $[Fe_2(Fv)(HMB)_2]^{2+}$ (2, (Fv = $\mu_2, \eta^{10}-C_{10}H_8$, HMB = $\eta^6-C_6(CH_3)_6$) isolated as a PF_6^- crystalline salt, as well as analogues containing other arenes (C_6H_6 (bz), 3; $C_6H_5CH_3$ (tol), 4; $C_6H_5CH_2CH_3$ (Etbz), 5; $C_6H_3(CH_3)_3$ (mes), 6). The dissymmetric dicationic complex $[Fe_2(Fv)(bz)(HMB)]^{2+}(PF_6^-)_2$ (7) is made from $[Fe_2(Fv)(Cp)(bz)]^+PF_6^-$ (8) and HMB (Cp = $\eta^5-C_5H_5$). Permethylation of 2 using potassium *tert*-butoxide and methyl iodide in THF gives the perethylated complex $[Fe_2(Fv)(HEB)_2]^{2+}(PF_6^-)_2$ (HEB = $\eta^6-C_6(CH_2CH_3)_6$) (9) (one-pot formation of 12 C-C bonds). The cyclic voltammograms (CV) of 2 in DMF at -35 °C at Hg cathode show three reversible waves and a fourth, quasi-reversible one (i_a/i_c close to unity, charge-transfer coefficient $\alpha = 0.5$; heterogeneous rate constant $k_s \approx 10^{-3} \text{ cm s}^{-1}$). The other dicationic complexes $[Fe_2(Fv)(arene)_2]^{2+}$ (arene = bz, tol, Etbz, mes) including the dissymmetric complex $[Fe_2(Fv)(C_6H_6)(HMB)]^{2+}$ (7) show an analogous electrochemical behavior. The chemical reversibility of the waves increases with the number of methyl groups on the arene ligands (20 °C). The comproportionation constants for the formation of the mixed-valence $Fe^I Fe^{II}$ complexes (arene = HMB (10), benzene (11), toluene (12), ethylbenzene (13), and mesitylene (14) and complex 15) and $Fe^0 Fe^I$ species were estimated from ΔE values.

Introduction

Sandwich compounds have recently received considerable attention in material science for the design of molecular ferromagnets,² for energy conversion,³ and in

stoichiometric^{4a} and catalytic electron transfer processes.^{4b} Many studies have already been performed.^{5,6} The bi-

(1) (a) *Organometallic Electron Reservoirs*. 34. For part 33, see: Morrow, J.; Catheline, D.; Desbois, M.-H.; Manriquez, J.-M.; Ruiz, J.; Astruc, D. *Organometallics* 1987, 6, 2605. (b) This paper overlaps with parts of the third cycle thesis of M.-H.D..

(2) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* 1988, 88, 201. (b) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* 1988, 21, 114.

(3) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 702.

(4) (a) Astruc, D. *Chem. Rev.* 1988, 27, 643. (b) Astruc, D. *Angew. Chem.* 1988, 100, 602; *Angew. Chem., Int. Ed. Engl.* 1988, 27, 643.