

A DFT investigation of the molecular and electronic structures of 19-electron transition-metal sandwich complexes

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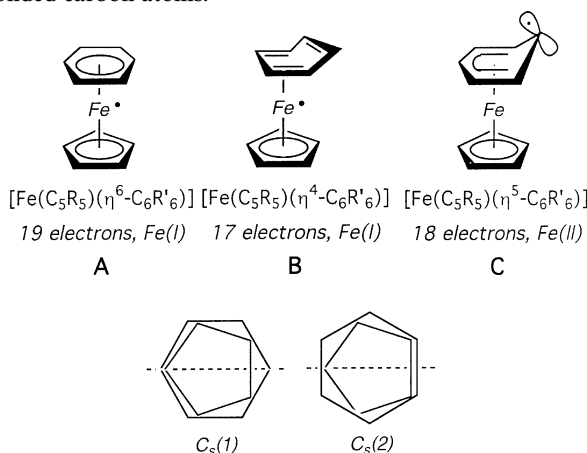
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Received (in Montpellier, France) 20th January 2000, Accepted 28th February 2000

Published on the Web 13th April 2000

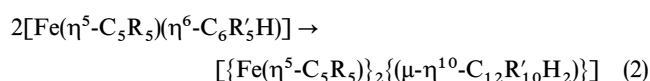
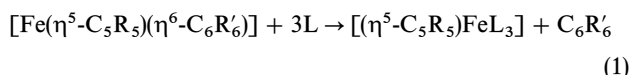
DFT calculations indicate that the 19-electron transition-metal complexes $[\text{M}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{R}'_6)]$ ($\text{R}, \text{R}' = \text{H}, \text{Me}$) have a metal-centered SOMO, a rather flexible molecular structure and that in their ground state the arene ring does not always adopt a perfect η^6 coordination mode.

Stable, isolable 19-electron transition-metal complexes of the general type $[\text{Fe}^{\text{I}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{R}'_6)]$ ($\text{R}, \text{R}' = \text{H}, \text{alkyl}$) behave as electron reservoirs, and their useful stoichiometric and catalytic electron-transfer chemistry has been largely developed.¹ It has been suggested that these electron-reservoir properties rely on the localisation of the extra electron on the metal site protected by the ligand shell in structure **A** (Scheme 1) established from spectroscopic data in solution and in the solid state. Indeed, the X-ray crystal structure of $[\text{Fe}^{\text{I}}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{Me}_6)]$ (**1c**) has been determined^{1b} and shows the pseudo-cylindrical structure **A** in which the arene ring is bonded in an η^6 mode to the metal. However, other molecular structures, namely **B** and **C**, have been proposed to be in fast equilibrium with **A** in solution, in order to account for the reactivity of this series of compounds.^{1a,c} The existence in the mechanism of reaction (1) of a 17-electron η^4 intermediate such as **B** would account for the formation of the 19-electron $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\eta^4\text{-C}_6\text{R}'_6)\text{L}]$ intermediate adduct, which is more likely to exist than the 21-electron species $[\text{Fe}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{R}'_6)\text{L}]$. On the other hand, the existence of the η^5 conformation **C** could explain radical reactions occurring at the arene ring, such as, for example, the dimerization reaction (2), in which coupling between the two rings occurs through H-bonded carbon atoms.



Scheme 1

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The DFT method has recently proved to be invaluable in determining the electronic and molecular structure of organometallic complexes.² Thus, we have undertaken such a study³ for the series of complexes $[\text{Fe}^{\text{I}}(\eta^5\text{-C}_5\text{R}_5)(\eta^6\text{-C}_6\text{R}'_6)]$ ($\text{R}, \text{R}' = \text{H}$: **1a**; $\text{R} = \text{Me}, \text{R}' = \text{H}$: **1b**; $\text{R} = \text{H}, \text{R}' = \text{Me}$: **1c**; $\text{R} = \text{R}' = \text{Me}$: **1d**) in order to answer the following questions. (i) Are **1a–d** metal-centered 19-electron complexes unlike many other so-called 19-electron complexes, which have, in fact, a ligand-based singly occupied molecular orbital (SOMO)?^{1a,7} (ii) Are structures **A**, **B** and **C** mesomers or tautomers (*i.e.* do **B** and **C** correspond to secondary energy minima on the potential energy surface)? Two ideal conformations of C_s symmetry were assumed, namely $\text{C}_s(1)$ and $\text{C}_s(2)$ (Scheme 1). It is well known that the strong $\text{C}_{\infty v}$ pseudo-symmetry of conformation **A** induces an almost exact degeneracy of the pseudo- e_1 singly occupied level of **1a**.⁸ Therefore, assuming exact C_s symmetry for conformation **A** of **1a**, two different electronic states are possible, depending on which of the pseudo- e_1 components (a' or a'') is occupied.

Full geometry optimisations were carried out on conformation **A** of **1a** at the UNLDA level. The results obtained for the four considered cases: two states ($^2\text{A}'$ and $^2\text{A}''$) for two different C_s geometries, are summarised in Fig. 1. They all correspond to conformation **A** and are almost isoenergetic. For each individual ring, the average Fe–C and C–C separations

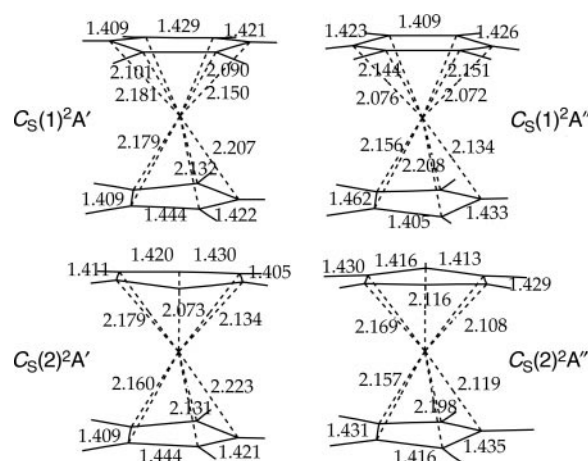


Fig. 1 The four geometries of C_s symmetry corresponding to the pseudo-cylindrical ground state $^2\text{E}_1$ of **1a** (UNLDA optimisations).

Table 1 SOMO localization, averaged Fe–C bond distances and ionization potentials (IP) computed at the ULDA level for the **1a–d** series and experimental reduction potentials of their 18-electron parents ($E_{1/2}$ vs. [FeCp₂] in acetonitrile)

Compound	SOMO localisation (%) ^a			Fe–C(C ₅ R ₅)/Å	Fe–C(C ₅ R' ₆)/Å	IP/eV ^b	$E_{1/2}$ /V ^c
	Fe	C ₅ R ₅	C ₆ R' ₆				
(C ₅ H ₅)Fe(C ₆ H ₆) (1a)	66	21	13	2.098	2.058	4.71	–1.84
(C ₅ Me ₅)Fe(C ₆ H ₆) (1b)	62	18	19	2.133	2.053	4.27	–2.07
(C ₅ H ₅)Fe(C ₆ Me ₆) (1c)	65	20	15	2.096	2.066	4.36	–2.02
(C ₅ Me ₅)Fe(C ₆ Me ₆) (1d)	54	21	25	2.085	2.088	4.00	–2.24

^a From a Mulliken population analysis. ^b Calculated with Slater's transition state method (see ref. 10). ^c From ref. 12.

are very close, confirming the $C_{\infty v}$ pseudo-symmetry. Consistently, the rotation barrier was found to be less than 0.3 kcal mol^{–1}. A Mulliken population analysis of the SOMO led to Fe, C₅H₅ and C₆H₆ fragment participations of 70, 17 and 13%, respectively. These values are in reasonable agreement with previous X α calculations.^{8c} The Fe–C bond lengths optimised for **1a** are in good agreement with the X-ray crystal structure of **1c**.^{1b}

The ionization potential of **1a**, calculated as the energy difference between the optimised structures of **1a** and **1a**⁺ (4.95 eV), also compares well with the experimental value (4.68 eV) reported for **1c**.⁹ As expected from the moderate structural reorganisation of **1a** upon oxidation, it is not very different from the calculated vertical ionization potential (see below and Table 1). Calculations using Slater's transition state method¹⁰ found the visible optical absorption band (λ = 720 nm)^{1c} to be associated with a transition between the pseudo-²E₁ ground state and the lowest pseudo-²E₂ excited state for which the SOMO has a large $\pi^*(C_6H_6)$ character (Fe: 12; C₅H₅: 3; C₆H₆: 85%).

After having checked that ULDA calculations on **1a** give quite similar results to those obtained at the higher UNLDA level (see Table 1), a detailed exploration of the potential energy surface of **1a** was carried out at the ULDA level. In particular, the decoordination pathway of **A** towards structures **B** and **C** has been investigated through a series of full geometry optimisations in which the Fe···C(decoordinated) distance was fixed at different constant values. Calculations confirmed that conformations **B** and **C** do not correspond to local minima. Partial decoordination of one or two C atoms of the C₆H₆ ring leads to destabilisation. However, the potential energy surface is particularly flat around the energy minimum **A**. Assuming distortions towards **B** and **C**, by increasing two or one Fe–C distances by 0.3 Å, destabilises **1a** by less than 2 and 4 kcal mol^{–1}, respectively. Obviously, conformations **B** and **C** are attainable through thermal motion. Calculations indicate that a distortion towards **C** does not considerably localise the SOMO on the arene ring. Rather, **1a** remains mainly a Fe(i) complex, suggesting that the localisation of the spin density is probably not the key factor responsible for the dimerization reaction (2). In fact, preliminary results obtained on model reactions of the attack of **1a**

by H⁺ suggest that reaction (2) is likely to be thermodynamically rather than kinetically controlled.

The series of the methylated derivatives **1b–d** was investigated at the ULDA level, assuming conformation C_s(1). The major results are summarised in Table 1. All the complexes adopt the sandwich structure **A**, except for **1d**, which exhibits significant distortion towards structure **C**, with one partly decoordinated C atom (Fe–C = 2.291 Å) on which the SOMO has an 18% localisation. This is in agreement with the fact that the related compound [Fe(C₅Me₅)Fe(C₆Me₅H)] dimerizes faster than **1a**.¹ Consistent with the composition of the SOMO, the permethylation of one of the ligands tends to increase its distance from the metal. Permethylation of both ligands leads to a more complicated situation in which various electronic and steric effects are involved and induces a distortion towards **C**. A Mulliken analysis of the SOMO localisation of compounds **1a–d** (Table 1) indicates a quite similar composition within the series, with a dominant metal character,¹¹ the partially decoordinated **1d** behaving slightly differently to the others. The ionization potentials (IPs) of the **1a–d** series have been computed at the ULDA level by using Slater's transition state method.¹⁰ A nice linear correlation is found between the IP values and the recently reported reduction potentials of their 18-electron parents in acetonitrile (least-squares correlation factor = 0.998; see Table 1).¹²

Interestingly, full geometry optimisation of [Ru(C₅H₅)(C₆H₆)] (**2a**) at the UNLDA level found a ground state structure intermediate between **A** and **B** (Fig. 2). The bending angle β of the arene ring is 16°. The bending is even larger in the case of the osmium derivative (β = 21°, Os–C(C₆H₆) = 2.178, 2.248 and 2.691°; ULDA calculations). Similar computations on the Co/Rh/Ir isoelectronic series led to a similar trend (β = 0, 12 and 15°, respectively). Consistent with these results, UNLDA calculations on the hypothetical **1a**[–] anion found conformation **B** (18-electron diamagnetic species) to be only 2.3 kcal mol^{–1} more stable than conformation **A** (20-electron diradical species), while this energy difference is much larger (18.4 kcal mol^{–1}) in the case of **2a**[–]. We are currently investigating the electronic structure of isoelectronic sandwich complexes.

Acknowledgements

The authors thank Prof. D. R. Tyler for communicating results prior to publication. F. O. thanks Prof. A. J. Baerends for introducing him to the ADF code (European Program ERBCHRXCT-930156). The Centre de Ressources Informatiques (CRI) of Rennes and the Institut de Développement et de Ressources en Informatique Scientifique (IDRIS-CNRS) are acknowledged for computing facilities.

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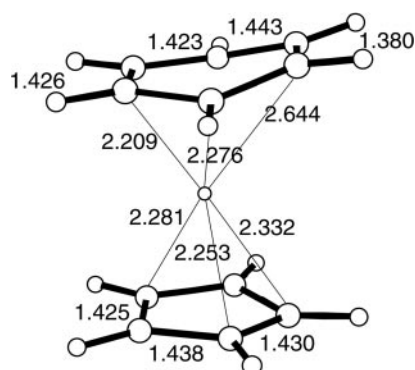


Fig. 2 UNLDA optimised structure of **2a**.

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