Structure and Conformational Equilibrium in Substituted [(η^4-butadiene)Fe(CO)$_3$] Complexes: A Density Functional Study

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Abstract: The energy profiles corresponding to C–C rotation in several carbonyl- and olefin-substituted derivatives of [(η^4-butadiene)Fe(CO)$_3$] have been studied through density functional calculations. The energy differences between s-*cis* and s-*trans* conformations show an excellent correlation with the diastereoselectivities experimentally observed in several reactions. These energy differences have been rationalized through an analysis of the iron–butadiene bond, and the role played by the metal in the conformational preferences is discussed.

Keywords: asymmetric synthesis · conformation analysis · density functional calculations · iron · nucleophilic additions

Introduction

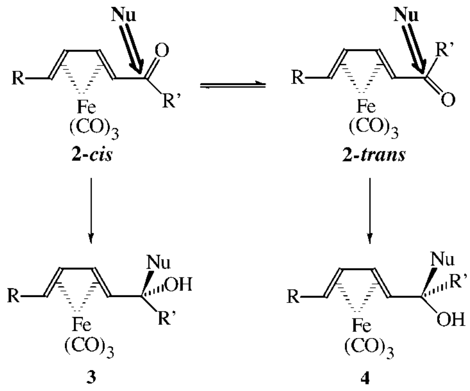
Organoiron complexes are now routinely used in organic synthesis thanks to the extensive research developed in this field during the last 20 years.[1–5] Besides their easy access, even in optically pure form, the acyclic diene-tricarbonyliron complexes appear especially useful for two main reasons: the iron-tricarbonyl unit is a very efficient protecting group for a 1,3-diene and it facilitates an excellent chirality transfer to the stereogenic centers created close to it.[6–8] A key issue for the developement of this chemistry is then a clear understanding of the factors governing the diastereoselectivity of the reactions of unsaturated systems in positions vicinal to the organometallic unit.

The experimental results strongly suggest, as discussed below, a possible correlation between the ground state conformations of the complexes and the stereochemistry of their adducts. This hypothesis takes into account the very large Fe(CO)$_3$ unit, with all reagents entering *anti* to this bulky group. Such correlations should be valid only if the conformations of the transition structures mimic the ground state conformations and if there are no conformational switches.[9] It appeared then to be of much interest to test this hypothesis by computational methods.

Recently, several theoretical studies have been devoted to the parent [(butadiene)Fe(CO)$_3$] complex (**1**).[10–12] The gas-phase structure[13, 14] and the vibrational spectra[15–17] are well reproduced by density functional calculations.[10] Moreover, the computed conformational barrier[10] corresponding to the turnstile rotation[18] of the butadiene ligand relative to the Fe(CO)$_3$ moiety is in excellent agreement with experiment.[19–24]

The organoiron complexes studied here have π systems vicinal to the organometallic unit and they can be separated in two groups: the derivatives substituted with a carbonyl group (aldehyde or ketone), **2**, and the olefinic systems, **5**.

Many examples of nucleophilic additions on aldehyde (R′ = H) derivatives have been already reported:[6–8] they yield in almost every case mixtures of the two diastereomers **3** and **4** (see Scheme 1), even if the diastereomeric ratios



2a	R=H	R'=H
2b	R=H	R'=Me
2c	R=CN	R'=H
2d	R=OMe	R'=H

Scheme 1. Reaction scheme of the nucleophilic addition to the carbonyl derivatives.

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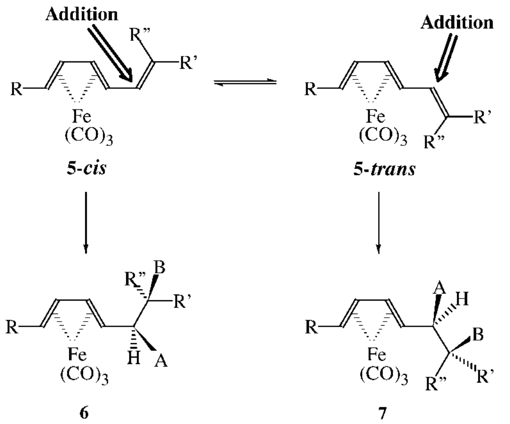
(typically from 4:1 to 2:3) are somewhat dependent upon the nature of the nucleophile and the reaction conditions (temperature, solvent, etc.). A similar result has been obtained in hetero Diels–Alder reactions.[25] Addition of the nucleophiles *anti* to the $Fe(CO)_3$ group on both the ***2-cis*** and the ***2-trans*** conformers (probably in rapid equilibrium) has been generally accepted as the reason for these results.

For the ketone derivatives (R′ = H), the nucleophilic additions are highly stereoselective giving in almost every case exclusively type **3** adducts. Exclusive reactions of the more stable ***2-cis*** conformers could explain these results.

For the olefinic derivatives, the results are mainly dependent on the size of the R″ substituent (Scheme 2). If R″ is larger than H, all reactions are highly stereoselective giving exclusively type **7** compounds. Furthermore, it is important to point out that this result is independent both from the nature of R″ and from the type of reaction. Typical examples include osmylation[26–28] or diazopropane cycloaddition[29] on *Z* olefins (R′ = H). The reactions on *gem*-disubstituted olefins (R′ and R″ ≠H) are also relevant: cyclopropanations with sulfur ylides,[30] dichlorocarbene additions,[31] and diazoacetate chemistry[32] have been reported. Similar stereoselectivities are obtained during Diels–Alder reactions[33] and Michael type additions.[34, 35] All these results appear in agreement with reactions occurring *anti* to the $Fe(CO)_3$ group on the ***5-trans*** conformer.



5a	R=H	R'=H	R"=H
5b	R=H	R'=H	R"=Me
5c	R=H	R'=Me	R"=H
5d	R=H	R'=Mc	R"=Mc

Scheme 2. Reaction scheme for the addition to the olefinic derivatives.

If R″ is a hydrogen atom, the reactions give mixtures (around 1:9) of the type **6** and type **7** diastereoisomers. This was observed in the case of the nitrile oxide,[36, 37] diazopropane cycloadditions,[29] and osmylations.[26–28] It is interesting to note that similar results are obtained also during additions on imines[38, 39] and iminium salts.[40] All these data appear to be in agreement with reactions occurring, in these case, on both conformers ***5-cis*** and ***5-trans***.

It is also interesting to note that both the nature of the substituents on the diene and the ligands on the iron seem to have a limited influence on such diastereoselectivities.[41] However, this should be taken with caution since few systematic studies dealing with this aspect have been reported until now.

The purpose of this paper is to study the conformational equilibrium of complexes **2** and **5** and to compare the relative stabilities of s-*cis* and s-*trans* conformers with the observed diastereoselectivity of the above-mentioned reactions.

Computational Methods

All the calculations were done with the ADF program.[42–44] The molecular geometries were optimized with the method developed by Versluis and Ziegler.[45] All geometries were optimized within the local density approximation (LDA),[46] with the parametrization in accordance with Vosko et al.[47] Gradient corrections to the exchange and correlation potentials in accordance with Becke[48] and Perdew,[49] respectively, were included in all energy calculations. The 1s shell of C, N, and O, and the 1s2s2p shells of Fe have been treated by the frozen core approximation.[43] For the representation of the valence shells of C, N, and O we used an uncontracted double-ζ basis set of Slater orbitals (STO) augmented with a set of 3d polarization functions.[50] For H we also used a double-ζ basis set augmented with a set of 2p polarization functions.[50] Finally, for Fe we used a triple-ζ basis set.[50] A set of auxiliary s, p, d, f, and g STO functions,[51] centered on all nuclei, was used to fit the molecular density and to represent the Coulomb and exchange correlation potentials in each SCF cycle.

Results and Discussion

We have computed the energy profiles corresponding to the ***2-cis*** →***2-trans*** and ***5-cis*** →***5-trans*** interconversion for all the complexes studied. A model energy profile is presented in Figure 1. For each complex we computed eight points along the profile with increments of 45 degrees. The corresponding energy minima were fully optimized. Figure 2 presents the optimized geometries of the s-*cis* and s-*trans* conformations of **2a** and **5a**. Table 1 presents the most relevant geometric parameters obtained for these structures, along with the

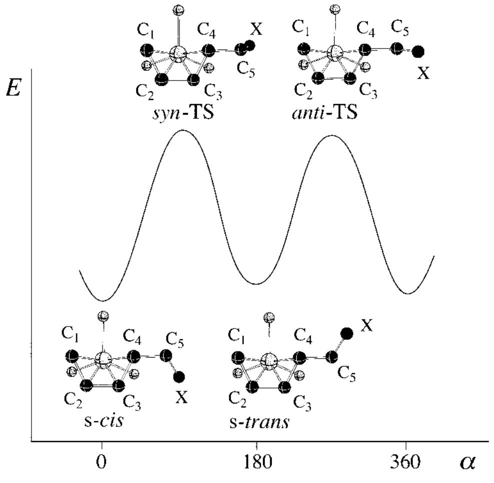
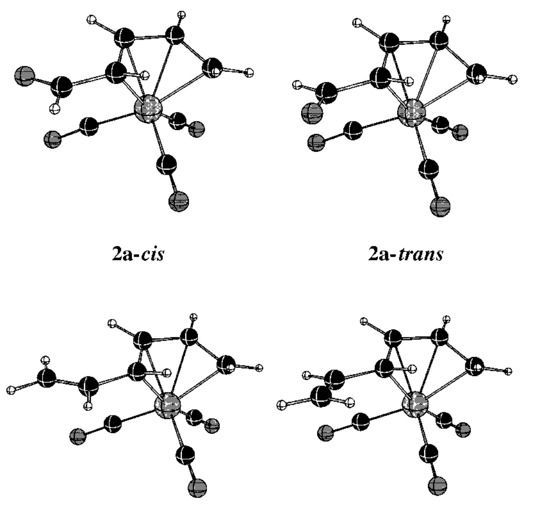


Figure 1. Model energy profile for the rotation around the C_4–C_5 bond for carbonylic derivatives (X = CR′O) and for olefinic derivatives (X = CR′R″) of the $[(\eta^4\text{-butadiene})Fe(CO)_3]$ complexes. α defines the C_3–C_4–C_5–X dihedral angle (in degrees).



2a-*cis* **2a-*trans***

5a-*cis* **5a-*trans***

Figure 2. Optimized structures for the s-*cis* and the s-*trans* conformers of **2a** and **5a**.

Table 1. Selected geometric parameters[a] computed for several [(η^4-butadiene)Fe(CO)$_3$] complexes.

	1[b]	**2a**-*cis*	**2a**-*trans*	**5a**-*cis*	**5a**-*trans*
Fe–C$_1$	2.071	2.070	2.073	2.065	2.068
Fe–C$_2$	2.022	2.026	2.024	2.016	2.016
Fe–C$_3$	2.022	2.014	2.009	2.026	2.020
Fe–C$_4$	2.071	2.080	2.079	2.116	2.111
C$_1$–C$_2$	1.414	1.416	1.415	1.416	1.416
C$_2$–C$_3$	1.407	1.404	1.405	1.407	1.407
C$_3$–C$_4$	1.414	1.423	1.424	1.418	1.420
isolated dienes[c]					
C$_1$–C$_2$	1.332	1.334	1.334	1.335	1.335
C$_2$–C$_3$	1.451	1.438	1.439	1.440	1.439
C$_3$–C$_4$	1.332	1.341	1.341	1.342	1.344

[a] Bond distances in Ångstroms. [b] Ref. [10]. [c] Structures with an s-*cis* C$_1$–C$_2$–C$_3$–C$_4$ arrangement have been considered to be comparable with the complexes.

results corresponding to the isolated dienes. The geometric parameters corresponding to **2b** are very similar to those obtained for **2a**, while the geometries obtained for the remaining olefinic derivatives are very similar to that of **5a**. Table 1 shows that in all cases carbon atoms C$_1$ and C$_4$ are further from Fe than C$_2$ and C$_3$. Furthermore, the presence of the substituent on C$_4$ in **2a** and **5a** makes the bond length from C$_4$ to Fe longer than the Fe–C$_1$ bond. It should be noted that the difference between the Fe–C$_1$ and Fe–C$_4$ distances is larger for **5a** than for **2a**. Thus, the olefinic substituent seems to have more steric requirements than the carbonylic one. With regard to the Fe–C$_2$ and Fe–C$_3$ distances, we observe that for **2a** the Fe–C$_2$ distance is slightly longer than the Fe–C$_3$ one, while for **5a** the ordering is reversed.

Carbon–carbon distances in the butadiene moiety of the diene show the same trends upon complexation that have already been reported for **1**[10] and show only slight variations upon substitution on C$_4$. Finally, the comparison between the s-*cis* and s-*trans* conformers for each complex does not show any significant difference.

Table 2 presents the relative energies of the most significant points of the energy profiles that correspond to **2** and **5**. We did not locate the transition states, and the energy barriers reported in Table 2 are only estimated values computed from the maxima of the energy profiles.

Table 2. Energies relative to the s-*cis* conformer for selected points of the conformational profile of the butadiene complexes.[a]

	2a	**2b**	**5a**	**5b**	**5c**	**5d**
s-*cis*	0.0	0.0	0.0	0.0	0.0	0.0
syn-TS[b]	7.5	7.5	3.5	5.2	3.5	5.7
s-*trans*	0.5	3.0	−2.3	−3.7	−2.3	−4.6
anti-TS[b]	7.2	8.0	3.5	0.8	3.9	0.4
isolated diene						
s-*cis*	0.0	0.0	0.0	0.0	0.0	0.0
s-*trans*	−1.9	0.1	−4.2	−3.7	−4.4	−3.9

[a] All energies in kcal mol^{-1}. [b] See Figure 1.

We can observe that for the carbonylic derivatives (**2**) the s-*cis* conformer is the most stable one, with a smaller difference for the aldehyde, as expected. On the other hand, for the olefinic derivatives (**5**) the s-*trans* conformer is the most favorable one. Isolated dienes always prefer the s-*trans* conformation, with only the exception of the ketone.

For the s-*cis* and s-*trans* structures of **2a** we have computed the harmonic vibrational frequencies and the corresponding zero-point vibrational energies. The inclusion of these corrections leads to an energy difference of 0.4 kcal mol^{-1} in favor of the s-*cis* structure. This result shows that the zero-point energy correction has a minor effect on the relative energies of the s-*cis* and s-*trans* conformations.

As a general rule for all the dienes, it seems that the metal fragment tends to stabilize the s-*cis* conformer relative the s-*trans* one. Nevertheless, when the olefin has a methyl group in the *cis* position (complexes **5b** and **5d**), the s-*trans* conformer can be further stabilized relative to the s-*cis* one.

With regard to the conformational barriers, we can consider two different transition states connecting the s-*cis* and s-*trans* conformers: *syn*-TS and *anti*-TS (see Figure 1). Both structures have similar energies except for **5b** and **5d**, in which the presence of the methyl group in the *cis* position produces an important steric repulsion with the Fe(CO)$_3$ moiety in the *syn* transition state.

If we assume that the equilibrium distribution at a given temperature between s-*cis* and s-*trans* conformers is determined by their energy difference, we can calculate the s-*cis*/s-*trans* ratio at 298 K. The results obtained are presented in Table 3. We can observe that for **2b**, **5b**, and **5d** only one conformer is significantly populated. For **5a** and **5c** only a

Table 3. Relative composition of equilibrium s-*cis*/s-*trans* mixtures at 298 K computed for substituted [(η^4-butadiene)Fe(CO)$_3$] complexes.

	cis:*trans*
2a	2.34:1
2b	157:1
5a	1:51.3
5b	1:510
5c	1:50.8
5d	1:2532

small amount of s-*cis* conformer would be present. Finally, for **2a** the s-*cis* conformer would be more populated, but a noticeable amount of the s-*trans* conformer would also be present. These results qualitatively agree with the diastereomeric ratios experimentally observed for several reactions (see above), thus supporting the hypothesis that the diastereoselectivity of the processes is determined by the ground-state conformations of the reactants. A similar conclusion has already been suggested by Frenking et al.[52, 53] for the nucleophilic addition to uncomplexed carbonyl compounds.

Let us now discuss the role played by the metal complexation in the conformational equilibrium of the studied dienes. From the extended transition state method,[54, 55] an expression for the bonding energy (BE) between a butadiene ligand and a $Fe(CO)_3$ fragment can be formulated [Eq. (1)], in which

$$BE = -(E_{\mathrm{prep}} + E_{\mathrm{st}} + E_{\mathrm{orb}}) \qquad (1)$$

E_{prep} is the preparation energy and represents the energy needed to distort the fragments from their ground-state equilibrium geometries to the geometries adopted upon complexation. For $Fe(CO)_3$ the preparation term was computed from the $^3A_2$ ground state of a C_{3v} structure,[56, 57] while in the complex we have considered it to exist in a singlet state.[10] For the butadiene fragments we have considered the distortion from their minimum energy conformation, that is, an s-*trans* arrangement for the $C_1{-}C_2{-}C_3{-}C_4$ moiety to the s-*cis* arrangement in the complex.

E_{st} is the steric interaction term. This term represents the interaction energy between the two prepared fragments with the electron densities that each fragment would have in the absence of the other fragment. This term can be decomposed into an exchange repulsion or Pauli term (E_{Pauli}) and an electrostatic term (E_{elstat}). Finally, the orbital interaction term, E_{orb}, represents the stabilization produced when the electron density is allowed to relax. This term comes from the two-orbital two-electron stabilizing interactions between both fragments. The orbital term can be decomposed into a contribution arising from the butadiene → Fe electron donation, a contribution from the Fe → butadiene back-donation, and a synergic term that appears when both interactions are allowed.

The different terms of the bonding energy partition for the most stable conformer of each carbonylic and olefinic derivative of **1** are presented in Table 4. We can see that the preparation of $Fe(CO)_3$ requires about the same amount of energy for all the dienes, while the preparation energy of all substituted dienes is lower than that of the parent compound. The presence of the carbonyl or olefinic substituent produces an increase in the steric interaction term with respect to the value obtained for **1**. This variation is dominated by the variation of the Pauli repulsion term except for **2a**, in which there is also a significant contribution from the electrostatic term.

Table 4. Analysis of the diene–$Fe(CO)_3$ bonding energy[a] for the most stable conformer of each complex.

		1[b]	**2a**-*cis*	**2b**-*cis*	**5a**-*trans*	**5b**-*trans*	**5c**-*trans*	**5d**-*trans*
E_{prep}	$Fe(CO)_3$	24.7	24.7	24.6	24.0	24.0	23.8	24.0
	diene	38.2	36.2	35.7	34.3	33.0	32.1	32.2
	Total	62.9	60.9	60.3	58.3	57.0	55.9	56.2
E_{st}	Pauli	234.4	240.4	241.5	238.6	238.3	239.4	239.8
	Elstat	–166.2	–162.4	–165.1	–166.0	–166.4	–167.6	–168.2
	Total	68.2	78.0	76.4	72.6	71.9	71.8	71.6
E_{orb}	don	–72.7	–70.6	–71.4	–71.1	–70.7	–71.6	–71.6
	back	–100.4	–108.5	–107.1	–99.3	–98.1	–97.6	–97.0
	syn	–18.0	–17.7	–17.9	–17.3	–16.9	–16.8	–16.4
	Total	–191.1	–196.8	–196.4	–187.7	–185.7	–186.0	–185.0
BE		59.9	57.9	59.7	56.8	56.8	58.3	57.2

[a] Values in kcal mol^{-1}. See text for definitions. [b] Ref. [10].

The steric interaction term of the carbonylic derivatives **2** is larger than for the olefinic derivatives **5**. This is due to the different values of the $Fe{-}C_4$ bond lengths in the substituted complexes, since this bond is shorter for **2a** and **2b** than for the olefinic derivatives **5** (see Table 1).

In all cases, the orbital term largely overcomes the destabilizing preparation and steric terms; thus, this gives the main contribution to the bond.[10] The decomposition of this term shows a bond that is clearly dominated by the back-donation interaction. The presence of the electron-withdrawing carbonylic group in **2a** and **2b** makes the diene a stronger acceptor, thus enhancing the back-donation from the metal to the diene with respect to that of **1**. This fact can be related to the values of the energy of the LUMO of each diene ligand shown in Table 5. We observe that the presence of the carbonyl substituent produces a significant lowering of the energy of the LUMO of the diene, so that the back donation is favored. This increase in the back-donation term leads to a total orbital term that is more stabilizing than in the butadiene complex **1**. However, the increase of the steric term overcomes the stabilization due to the orbital term, so that the Fe–diene bonding energy of **2a** and **2b** is lower than that of **1**.

Table 5. LUMO energies of the studied dienes.[a]

	E_{LUMO}
1	–2.681
2a	–4.069
2b	–3.758
5a	–3.121
5b	–3.057
5c	–2.924
5d	–2.873

[a] Values in eV computed for an s-*cis* $C_1{-}C_2{-}C_3{-}C_4$ arrangement.

For the olefinic derivatives **5**, both the donation and the back-donation terms decrease in absolute value with respect to **1**. The presence of an olefinic substituent on C_4 produces a lowering of the energy of the LUMO of the diene ligand with respect to that of the parent compound **1** (see Table 5). However, this lowering is less pronounced than for the carbonylic derivatives. According to this fact, one should expect a small increment of the back-donation term, but the lengthening of the $Fe{-}C_4$ bond length necessary to reduce the steric repulsion leads to the opposite variation. For these compounds, both the steric and the orbital terms lead to a diminution of the bonding energy with respect to **1**.

The energy difference between s-*cis* and s-*trans* conformers can also be partitioned, using the same scheme, into preparation, steric and orbital contributions [Eq. (2)]. Table 6 presents the results obtained in this analysis. We observe a

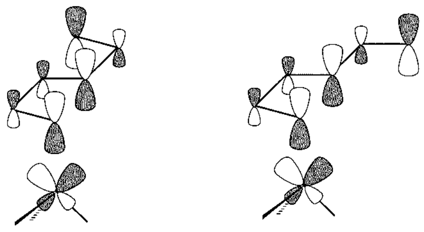
$$\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{st}} + \Delta E_{\text{orb}} \qquad (2)$$

different behavior for carbonylic and olefinic derivatives. For **2a** and **2b**, the main contribution to the energy difference comes from the orbital term. When going from the s-*cis* to the s-*trans* conformer, the back-donation contribution to the interaction energy decreases by 2–3 kcal mol^{-1}. This difference in the back-donation term can be understood from a more efficient overlap between the HOMO of $Fe(CO)_3$ and the LUMO of the diene in the s-*cis* conformation (see Scheme 3). Therefore, the interaction with the metal fragment has an important role in the control of the conformational equilibrium.

Table 6. Analysis of the energy difference[a] between the less stable conformation of [(η^4-butadiene)$Fe(CO)_3$] complexes and the most stable one.

		2a-*trans*	**2b**-*trans*	**5a**-*cis*	**5b**-*cis*	**5c**-*cis*	**5d**-*cis*
ΔE_{prep}	$Fe(CO)_3$	−0.3	−0.3	0.3	−0.2	0.3	−0.4
	diene	−0.2	−0.7	2.9	2.7	2.8	3.6
	Total	−0.5	−1.0	3.2	2.5	3.1	3.2
ΔE_{st}	Pauli	−1.7	−4.5	−2.2	1.4	−2.6	2.0
	Elstat	1.0	3.7	0.9	−0.6	1.1	−1.1
	Total	−0.7	−0.8	−1.3	0.8	−1.5	0.9
ΔE_{orb}	don	0.3	2.2	1.2	0.6	1.3	0.8
	back	2.1	3.1	−0.3	−0.3	−0.1	−0.3
	syn	−0.7	−0.5	−0.5	−0.1	−0.6	−0.1
	Total	1.7	4.8	0.4	0.2	0.6	0.4
ΔE		0.5	3.0	2.3	3.5	2.2	4.5

[a] Values in kcal mol^{-1}. See text for definitions.


s-*cis* s-*trans*

Scheme 3. Scheme showing the overlap between the HOMO of $Fe(CO)_3$ and the LUMO of the diene in the s-*cis* and s-*trans* conformations.

On the other hand, for the olefinic derivatives the preference for the s-*trans* conformation is determined by the preparation of the diene, so that the role played by the metal is not crucial. However, we can observe qualitative differences between **5a** and **5c** on one side and **5b** and **5d** on the other side. For the first two compounds, the steric interaction energy is less destabilizing in the s-*cis* conformation, while for **5b** and **5d** there is more repulsion. This fact is related to the presence of a methyl group in *cis* position.

From the preceding discussion we have seen that, in the carbonylic derivatives, the complexation with the metal leads to a higher preference for the s-*cis* conformation than in the isolated ligand. This preference is due to a more favorable back donation when the carbonylic moiety of the diene ligand adopts an s-*cis* arrangement. The presence of an electron-withdrawing substituent in the C_1 position of the diene ligand would increase the back donation, while an electron-donor group would reduce it. We have optimized the geometries of complexes **2c** (R = CN) and **2d** (R = OMe). For **2c** the s-*cis* conformation is 0.9 kcal mol^{-1} more stable than the s-*trans* one, so that the energy difference has increased with respect to **2a** (see Table 2). On the other hand, for **2d** the energy difference between the s-*cis* and the s-*trans* conformations decreases to 0.3 kcal mol^{-1}. According to these results, we would predict that electron-withdrawing groups in the position C_4 of the diene ligand would enhance the diastereoselectivity for nucleophilic attack, while electron-donor groups would lead to less selective reactions.

Conclusions

The energy profiles corresponding to the C–C rotation in substituted derivatives of [(η^4-butadiene)$Fe(CO)_3$] have been studied. For the carbonylic derivatives **2a** and **2b** the s-*cis* conformer is more stable than the s-*trans* one, while in the olefinic derivatives **5a**, **5b**, **5c**, and **5d** the s-*trans* conformer is the preferred one. The computed energy differences between s-*cis* and s-*trans* structures predict relative equilibrium populations of s-*cis* and s-*trans* conformers in qualitative agreement with the diastereoselectivities observed in several reactions. The analysis of the Fe–butadiene bonding energy shows in all complexes that the bond is dominated by the Fe →butadiene back donation. For the carbonylic derivatives this interaction plays an important role in the relative stabilities of s-*cis* and s-*trans* conformations. In contrast, for the olefinic derivatives the role of the metal in the conformational equilibrium is not so crucial.

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