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Molecular models of monometallic-phenazine sandwich complexes $M(phz)_2$ (M=Ti, Cr, Fe and Ni; phz=$C_{12}H_8N_2$): A DFT investigation.

M. Merzoug[a] and B. Zouchoune[a,b]

[a] *Laboratory of Applied Chemistry and Materials Technology, Larbi Ben M'Hidi University (04000) Oum El Bouaghi, Algeria.*
[b] *Research Unit for Environmental and Molecular Structural Chemistry, University-Constantine1, Algeria.*

merzoug.meriem@yahoo.fr & bzouchoune@gmail.com

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Abstract

This work deals with the calculations of the energy stability of mononuclear sandwiches compounds of transition elements based on a density functional theory DFT. In this paper, the structure and electronic properties of a series of organometallic compounds $M(C_{12}H_8N_2)_2$ (M= Ti, Cr, Fe and Ni) have been systematically studied by using a functional BP86 based on the density functional theory. Calculations indicate that the phenazine ligand can bind to the metals involving its C6 or C4N2 rings through η^6, η^4, η^3 and η^2 coordination modes for $[M(phz)_2]$ complexes. The calculated spin contamination $<S^2>$ is comparable to the expected value of 2.00. The energy decomposition analysis was used to characterize the geometry distortion and the steric interaction (electrostatic and Pauli) and orbital interaction in the total bonding energy. The results showed that the interactions in the studied compounds are governed by covalent character than ionic.

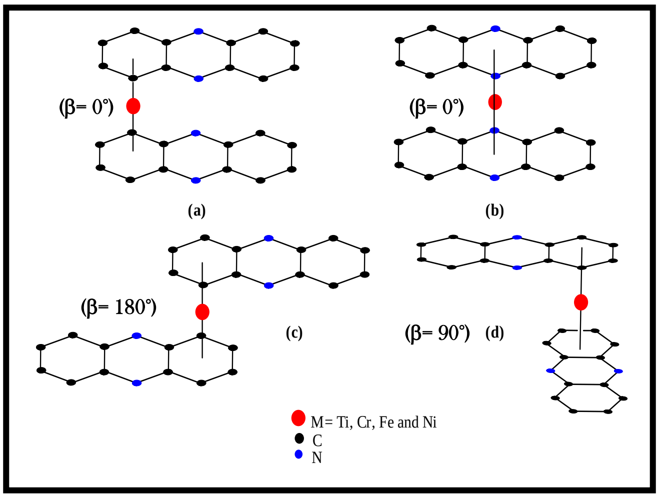
Keywords: phenazine, Transition metals, Density functional theory, electronic structure, decomposition bonding analysis.

1. Introduction

Transition-metal sandwich complexes play a major role in modern organometallic chemistry, since the breakthrough of the ferrocene [1]. They correspond to a metal atom or more sandwiched between two aromatic ligands through metal-ligand bonding. Structurally similar species to ferrocene, with different metals or coordinating ligands, are generally termed metallocenes. Fischer made sandwich compounds with Cr and benzene molecules, a great surprise for chemists at that time [2].In this work we are interested in one metal atom sandwiched by two phenazine (phz) ligands. Phz molecule is an aromatic electron donating system (14 π-electrons) which is isoelectronic with acridine and anthracene presenting a delocalized scheme in accordance with a formal bond order of 1.5[3]. Assuming that a mononuclear complexation occurs either with one terminal C6 ring or with the C4N2 of each phenazine, it appears from Scheme 1[4], that the phenazine can provide only a maximum of 6 π-electrons among 14 to the metal center. The main purpose of this work is the studying by means of DFT method the predicted low-lying states obtained by the interactions between the two phenazine ligands in their various forms and the transition metals of the first row Ti, Cr, Fe and Ni having an even number of valence electrons in their singlet and triplet spin states.

2. Molecular structures

The studied molecular structures of $[M(phz)_2]$ compounds are composed of two phenazine ligand and a transition metal. Depending on the disposition of the two phenazine ligands and the position of the metal, four structures are possible for $[M(phz)_2]$ complexes, as shown in **Scheme 1**. When the two (phz) ligands are totally eclipsed, two conformations (a) and (b) are possible. For the conformation (a) the metal coordinated to C6 ring of each phenazine giving C_{2v} symmetry, while for (b) the metal is linked to C4N2 cycle of each phenazine corresponding to a D_{2h} symmetry. The conformation (c) corresponds to the fully staggered arrangement (C_{2h} symmetry). The intermediate conformation (d) where both (phz) ligands are oriented to each other by an angle **0°<β≤90°** (gauche) corresponds to C_2 symmetry. The geometries of the $[M(phz)_2]$ complexes were optimized in their lowest energy structure. The parameters computed data are gathered in table 1 and the selected parameters are reported in supporting information. The molecular structures for M= Ti, Cr, Fe and Ni are shown in figures 1-4 (only the most stable structure of each conformation are represented) and the remaining structures are schematized in figures S1-S4 in supporting information.



Scheme 1. Projection sketches of the $M(Phz)_2$: eclipsed (C_{2v}) (a) and D_{2h} (b), (c) staggered (C_{2h}) and gauche (C_2) (d)

3. Results and discussion

3.1. Geometric structures of [Ti(Phz)$_2$] and [Ni(Phz)$_2$] (Ti=3d^4, Ni=3d^{10})

The hypothetical [Ti(phz)$_2$] and [Ni(Phz)$_2$] complexes are firstly analyzed. The geometric optimization of these complexes was accomplished by means of BP86 with TZP basis set (see computational methods). The DFT calculations gave four conformations for [Ti(Phz)$_2$] species; C_{2v}, C_{2h}, C_2 and D_{2h} and five for [Ni(Phz)$_2$] complex; C_{2v}, C_{2h}, C_2, D_{2h}, C_s derived from that of C_{2v} and C_{2h}. All structures are shown in Figure 1 and Figure 2 and the main computed data is grouped in table 1 and Table S1 and S4. In the all Ti complexes; each (phz) ligand donate its 6-π electrons to the metal and therefore is hexacoordinated while the Ni atom is tetracoordinated. These optimizations shows that the Titanium and Nickel complexes favored the gauche structure (d), in which both phenazine are partially eclipsed by angle of **(β=87°)** and **(β=84°)**, respectively. The triplet [Ti(η^6-Phz)$_2$] structure is calculated most stable in energy than all isomers, that is confirmed by a short Ti-C bond lengths which are ranging between 2.360 and 2.477Å, giving an average one of 2.403 Å(see Table 1), this average is similar to finding in [Ti(phz)]$_2$ [4] and [Ti(ant)]$_2$ complex [5], signifying strong interactions between the metal and the carbon atoms. In this global minimum structure the metal atom coordinated by a perfect coordination mode of η^6 in accordance with a weak slippage of δ=4% defined as (average longer M-C bond - average M-C shorter/ average longer M-C bond) (see Figures) accompanied by distortion angle of θ=3°calculated as (N-C6-C5-C4). In this structure the calculated spin contamination $<S^2>$ of 2.02 is comparable to the expected value $<S^2>$ of 2.00. The singlet [Ni(η^4–phz)$_2$] isomer is calculated as a global minimum displaying an important energetic gap of 1.48 eV between HOMO (35b) and the LUMO (36b) indicative of a very good thermodynamically stability (see figure 5). This global minimum exhibits a relatively long Ni–C bond distances ranging from 2.096 to 2.364 Å, in which the Ni metal atom displays a symmetric η^4 coordination mode fully consistent with the relatively important slippage δ= 18% of Ni metal center toward the external C(2)–C(3) and C'(2)–C'(3) bonds. In this case, we consider the Ni metal atom as 18-MVE center. The Titanium complexes isomers are favored in the triplet state than the singlet ones. The homolog of global minimum [Ti(η^6-phz)$_2$] is higher in energy by 6.6 kcal/mol. This isomer exhibits a significant gap of 0.91 eV between the HOMO (34a) and the LUMO (35a). The passage from the global minimum to singlet state C_{2v} structure leads to a structural modifications that consistent of shortening of Ti-C bond distances within the range of 2.283-2.380 Å and the decrease of energetic gap to 0.14 eV. Indeed, this isomer is modeled less stable than the global minimum by 12.5kcal/mol. The calculation of the vibration frequencies gave no imaginary value, with the exception of the singlet eclipsed structure (b) which has an imaginary frequency of 81i. The stability order of theses complexes increases according to the following order (according to the spin state and the symmetry): $D_{2h}(S=0)<C_{2v}(S=0)<C_{2h}(S=0)<C_2(S=0)<D_{2h}(S=1)<C_{2v}(S=1)<C_{2h}(S=1)<C_2(S=1)$.

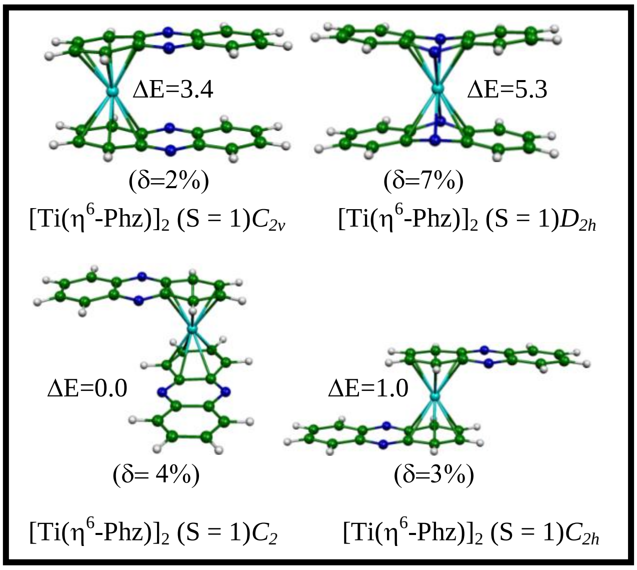


Figure 1. Optimized geometries for [Ti(phz)$_2$].

The remaining of [Ni(phz)$_2$] isomers as depicted in Figure 2. Inversely to the [Ti(phz)$_2$] C_{2h} structure, the singlet isomers are more stable than those of triplet ones. Really, the [Ni(η^4–phz)$_2$] isomer with C_2 symmetry is calculated as a global minimum. The singlet [Ni(η^2-phz)$_2$] and triplet [Ni(η^4-phz)$_2$] structures corresponding to the totally eclipsed arrangement are computed higher in energy than the global minimum by 8.4 and 17.1 kcal/mol, respectively. This weak instability is due to repulsions π–π occurred between the two uncoordinated C6 cycle of both phenazine highlighted by the long distance d=4.563 and

4.267 Å, respectively. The average Ni–C (2.241 Å) calculated for the [Ni(η^4-phz)$_2$] C_{2v} (S=1) isomer are longer than those obtained for its homolog Ni–C (2.080 Å), this tallest leads to the rupture of four Ni-C bond, this singlet isomer displaying a low η^2 hapticity giving rise to deficient 14-MVE configuration for Ni center. The lowering of symmetry from C_{2v} to C_s leads to slight geometric modifications consistent with the shortening of Ni-C but the coordination mode does not change, therefore, the Ni-C length bond ranging from 2.078 to 2.080 Å for singlet structure and 2.135 to 2.350 Å for its homolog triplet. The second modification, that consistent the π–π repulsions, these are more important in structure (b) than those in structure (a). These repulsions are shown by the distance of d=4.709 **(b)** and 4.304 Å **(a)** between the uncoordinated C6 rings. The geometric modifications lead to the instability of these isomers making it calculated less stable than the global minimum by 9.1 and 17.3kcal/mol. The singlet [Ni(η^2-phz)$_2$] and triplet [Ni(η^4-phz)$_2$] structures corresponding to the staggered arrangement (c) and C_s derived from that of C_{2h} are higher in energy by 22.6, 16, 10 and 12.4 kcal/mol than the global minimum with η^2, η^4, $\eta^{2/4}$ and $\eta^{4/2}$ coordination modes, respectively in accordance with Ni-C bond length giving rise to metal 14, 18, 16, 16-MVE configurations, respectively. These isomers structures are marked by a slippage of 4, 15, 29 and 20%, respectively.

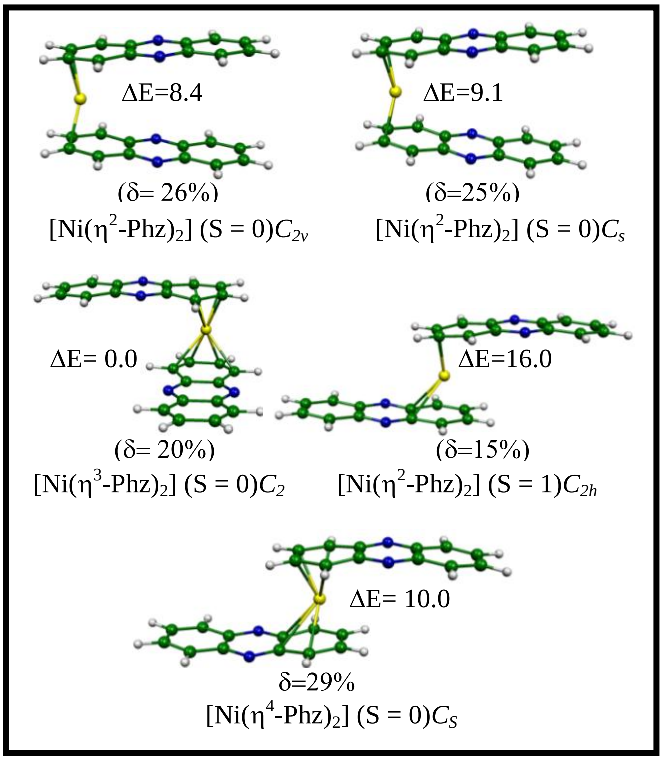


Figure 2. Optimized geometries for [Ni(phz)$_2$].

3.2. Geometric structures of [Cr(phz)$_2$] and [Fe(phz)$_2$]: Cr=3d^6 and Fe=3d^8

The optimized energy minima calculated for [Cr(phz)$_2$] (d^6) and [Fe(phz)$_2$] (d^8) complexes are shown in Figure 3 and Figure 4 and the computed data are reported in Table S2, S3, respectively. The most stable, chromium and iron species adopts totally eclipsed conformations (a), which are 18-MVE and 16-MVE, respectively. The calculated [Cr(phz)$_2$] sandwich model exhibits a similar coordination mode to the [Ti(phz)$_2$] species. Eight [Cr(η^6-phz)$_2$](4 singlet states and 4 triplet) characterized energy minima of C_{2v}, C_{2h}, C_2 and D_{2h} symmetries were found in the range 1.0 to 23.0 kcal/mol. In this case, the most stable conformation is a triplet, is calculated lower in energy than its homolog (singlet state) by 4.0kcal/mol. For this global minimum, the chromium atom is linked to one C6 cycle of each phenazine ligand by η^6, this obtained coordination mode is in agreement with the Cr-C bond distances in the range 2.156-2.390Å, giving an average of 2.225Å, this distances are comparable to the Cr$_2$(phz)$_2$ complex with C_s symmetry derived from that of C_{2v} [5]. All the rest isomers are less stable than the global minimum by 1.5, 1.1, 3.6, 4.8, 28.5 and 23.1 kcal/mol for the C_2(S=0), C_2(S=1), C_{2h}(S=0), C_{2h}(S=1), D_{2h}(S=0) and triplet D_{2h} structures, respectively. The optimized structures of all isomers are schematized in Figure 3 and the all selected parameters are reported in table S2.

The passage from **M** = Cr to **M** = Fe corresponds to two more electrons in the LUMO of Cr complex. Partial decoordination should result. The global minimum of iron complexes [Fe(phz)$_2$] displays a relatively important gap of 0.95eV separating the occupied orbital (19b$_1$) and the unoccupied orbital (21a$_1$) (see figure 5). In this structure, the iron atom is tetracoordinated to one C6 ring of each phenazine ligand by coordination mode of η^4 (each **phz** is a 4-π electrons donor), in which the Fe-C bond length in the range 2.080-2.143 Å, giving an average bond distance of 2.111Å (see Table 1). This stability is compatible with a slippage δ=16% of the Iron atom toward C2-C3 and C'2-C'3 bonds. This structure represented a slightly distortion of the **phz** ligands evidenced by weak folding angle of θ=9°. All optimized structures for these complexes are sketched in figure 4 and the geometric parameters are reported in Table S3. The passage from global minimum to its homolog shown a stretching of Fe-C(1), Fe-C(2), Fe-C(3) and Fe-C(4) distances bond to 2.301, 2.187, 2.187 and 2.301 Å, respectively and a shortening of Fe-C(5) and Fe-C(6) from 2.506 to 2.415 Å (see Table S3), that leads to the increasing of coordination mode from η^4 to η^6. This homolog is modeled less stable than the global minimum by18.7 kcal/mol. The isomers with C_2(S=0), C_2(S=1), C_{2h}(S=0) and C_{2h}(S=1) symmetry are modeled less stable than global minimum by 11.3, 6.0, 4.5 and 8.6 kcal/mol, respectively. The singlet and triplet isomers of D_{2h} symmetry are less stable than the global minimum by 59.0 and 39.4 kcal / mol, respectively. This singlet structure was not characterized as energy minimum showing large imaginary frequency of 553.6i.

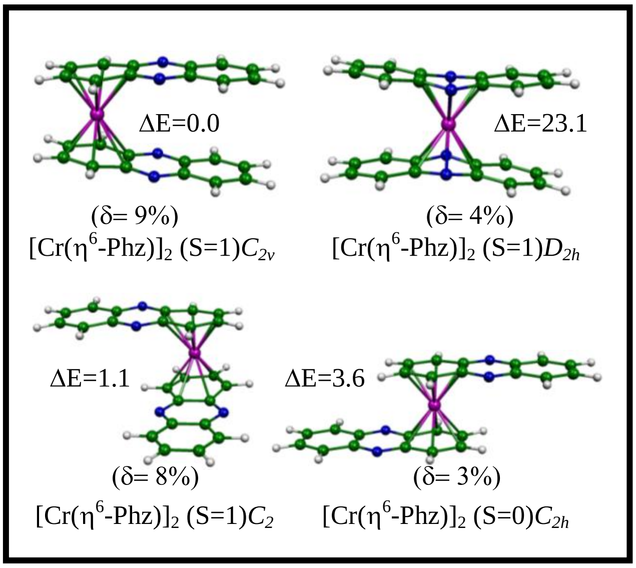


Figure 3. Optimized geometries for $[Cr(phz)_2]$.

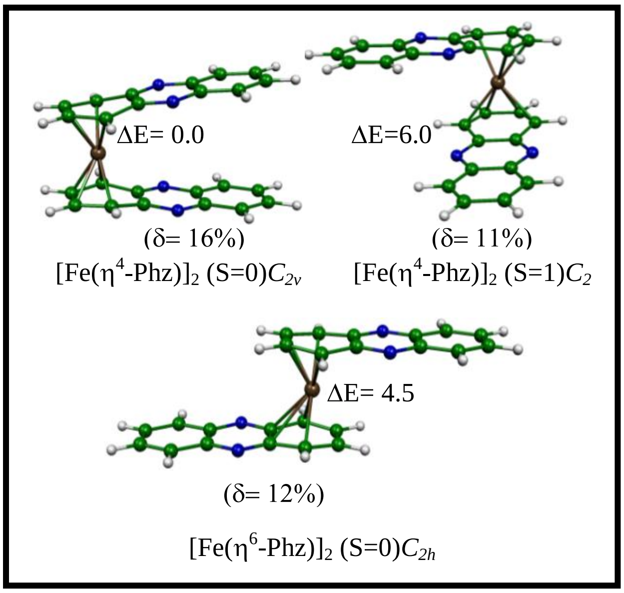


Figure 4. Optimized geometries for $[Fe(phz)_2]$.

Table1: The selected parameters of the most stable structure of each complex.

Complex	Symmetry	S	ΔE	H-L	M_{M-C}	S^2
$[Ti(Phz)_2]$	C_2	1	0.0	-	2.403	2.02
$[Ni(Phz)_2]$	C_2	0	0.0	1.48	2.358	0.00
$[Cr(Phz)_2]$	C_{2V}	1	0.0	-	2.255	2.08
$[Fe(Phz)_2]$	C_{2V}	0	0.0	0.95	2.243	0.00

4. Decomposition bonding analysis

The molecular interaction defined by ADF program as the energy between the M and the $[phz]_2$ fragments, which are usually computed as spin restricted. Table 2, shows the results of the interaction ΔE_{int} energies composed of three components as follows: $\Delta E_{int} = \Delta E_{pauli} + \Delta V_{elstat} + \Delta E_{orb}$ (In parentheses, total attractive interactions ΔE_{elstat} and ΔE_{orb}). The first term ΔE_{Pauli} refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with same spin cannot occupy the same region in space. The second term ΔE_{elstat} accounts of the electrostatic interaction energy between the fragments, which are calculated using the frozen electron density distribution of the fragments. The last term ΔE_{orb} orbital interaction energy is the stabilizing orbital interaction tem: it is calculated in the final step of the bond decomposition energy (BDE) method [6, 7] when the Kohne-Sham orbitals relax to their optimal form, it accounts for electron pair bonding, charge transfer as exemplified by HOMO-LUMO interactions and polarization (empty/occupied orbital mixing on one fragment due to the presence of another fragment). It has been believed that the relative values of the two attractive terms ΔE_{elstat} and ΔE_{orb} may be used to characterize the nature of the chemical bonding [8, 9].

For all complexes, the results gathered in **Table 2** show clearly that the bonding energies are stabilizing for all cases but can be ordered as function of the Metal. As reported in **Table 2**, the most stable isomer of Cr, Fe and Ni complexes corresponds to the minimal ΔE_{int} between the M and **$[phz]_2$** fragments. The decomposition energies show that the ΔE_{elstat} and ΔE_{orb} are comparable for the same metal; whereas, the ΔE_{orb} corresponds to contributions varying from 64% to 65% for Cr and from 58 to 60% for Fe, while for Ti and Ni are 62 and 69%, respectively whatever the symmetry was. These results show that the difference between ΔE_{orb} and ΔE_{elstat} exceed 24% of the total attractive interactions ΔE_{orb} and ΔE_{elstat}. Overall, the studied compounds are governed by covalent interactions evidenced by important covalent character than ionic character.

5. Computational details

All the structures were fully optimized at the Bp86, where B denotes Becke's 1988 exchange functional (usually abbreviated as B88 or just B) [10] and P86 denotes Perdew's 1986 correlation functional [11]. Geometries were optimized without including non local corrections. Frequency analysis calculations were performed to characterize the structures to be the minima or transition states this theoretical frequencies were scaled with the factor recommended by Scott and Radom [12]. The application of approximate density functional theory to organometallic chemistry has been reviewed recently [13]. All calculations were performed with the ADF 2007.01, ADF 2012 and ADF 2014 program [14] developed by Baerends and coworkers [15-19]. Representation of the molecular structures and molecular orbitals were done using ADF-GUI [14] and MOLEKEL4.1 [20], respectively.

Table 2: Results of the energy decomposition analysis obtained between M and (Phz)$_2$ fragments (M= Ti, Cr, Fe and Ni) at BP86 for singlet structures. Energies are given in kcal/mol.

	Symmetry	**E**$_{int}$	E$_{Pauli}$	**E**$_{Orb}$	**E**$_{elect}$
[Ti(Phz)$_2$]	C_{2v}	-138.1	1009.4	-712.5 (62.0)	-434.9 (38.0)
	C_2	-135.3	996.0	-702.1 (62.0)	-429.2 (38.0)
	C_{2h}	-143.0	860.0	-622.6 (62.0)	-380.3 (38.0)
[Cr(Phz)$_2$]	C_{2v}	-233.0	628.0	-551.4 (64.0)	-309.6 (36.0)
	C_2	-228.3	617.5	-539.2 (64.0)	-306.7 (36.0)
	C_{2h}	-232.7	617.8	-543.7 (64.0)	-306.7 (36.0)
	D_{2h}	-210.2	595.6	-521.3 (65.0)	-284.5 (35.0)
[Fe(Phz)$_2$]	C_{2v}	-213.0	465.2	-410.9 (59.0)	-276.3 (41.0)
	C_2	-198.4	479.2	-395.5 (58.0)	-282.1 (42.0)
[Ni(Phz)$_2$]	C_{2v}	-133.7	544.2	-399.0 (59.0)	-278.8 (41.0)
	C_2	-147.3	627.7	-456.3 (59.0)	-318.7 (41.0)

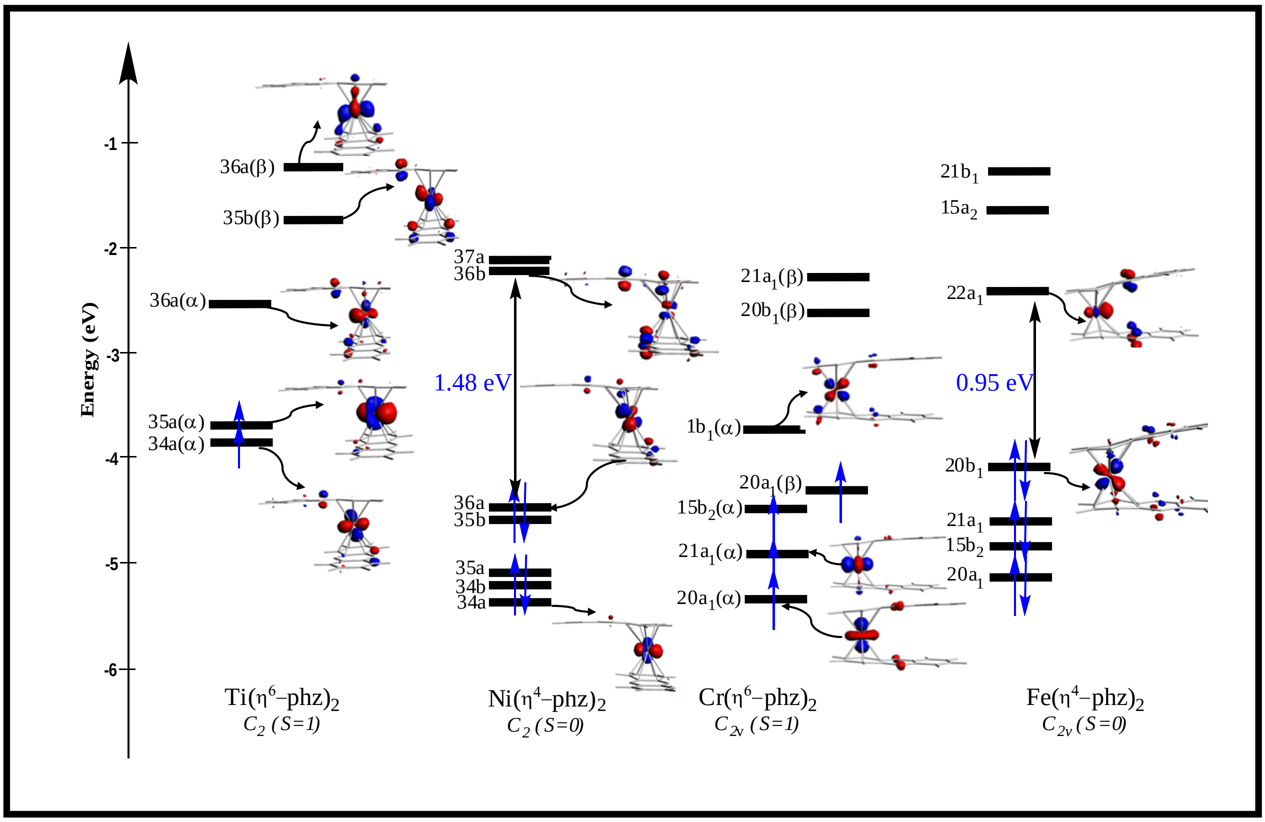


Figure 5. MOs diagrams obtained for [Ti(η^6-phz)$_2$], [Ni(η^4-phz)$_2$], [Cr(η^6-phz)$_2$] and [Fe(η^4-phz)$_2$]. Contour values of MO plots are ±0.06 (e/bohr^3)

6. Conclusion

In this work we have focused the our attention on the electronic communication and the molecular structure of [M(phz)$_2$] complexes for Ti, Cr, Fe and Ni metal atoms coordinated to the phenazine ligand in their C_{2v},C_2, C_{2h}, D_{2h} and C_s configurations. The geometries obtained by BP86 method are consistent with each other giving the same stability orders between isomers of the studied metal complexes. In the investigated complexes, the gauche conformation lie at lower energy than the totally eclipsed and staggered in [Ti(phz)$_2$] and [Ni(phz)$_2$] counter to the [Cr(phz)$_2$] and [Fe(phz)$_2$] species where the totally eclipsed are most stable. In this work the most favored closed-shell count is 18-MVE for Cr and Ni, inversely to Ti and Fe complexes which prefer 16-MVE configuration. The electronic π–π repulsions defined as the distance between the centers of uncoordinated cycles are weak in Ti and Ni complexes but it important in the Cr and Fe are presenting by distance d= 4.015 and 4.362 Å, respectively between the uncoordinated cycle of each phenazine. The results of the interactions energies for the studied compounds are governed by covalent interaction than ionic character. This theoretical study allows us to recognize the sandwich complexes and motivates us to synthesize these new complexes.

Supporting information:

Figure S1-S4: The remaining optimized structures for [Ti(phz)$_2$], [Cr(phz)$_2$], [Fe(phz)$_2$] and [Ni(phz)$_2$] complexes.

Table S1-S4: Selected calculated parameters for [M(phz)$_2$] (M = Ti, Cr, Fe and Ni) complexes. Bond distances are given (in Å).

Acknowledgments

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Supporting information

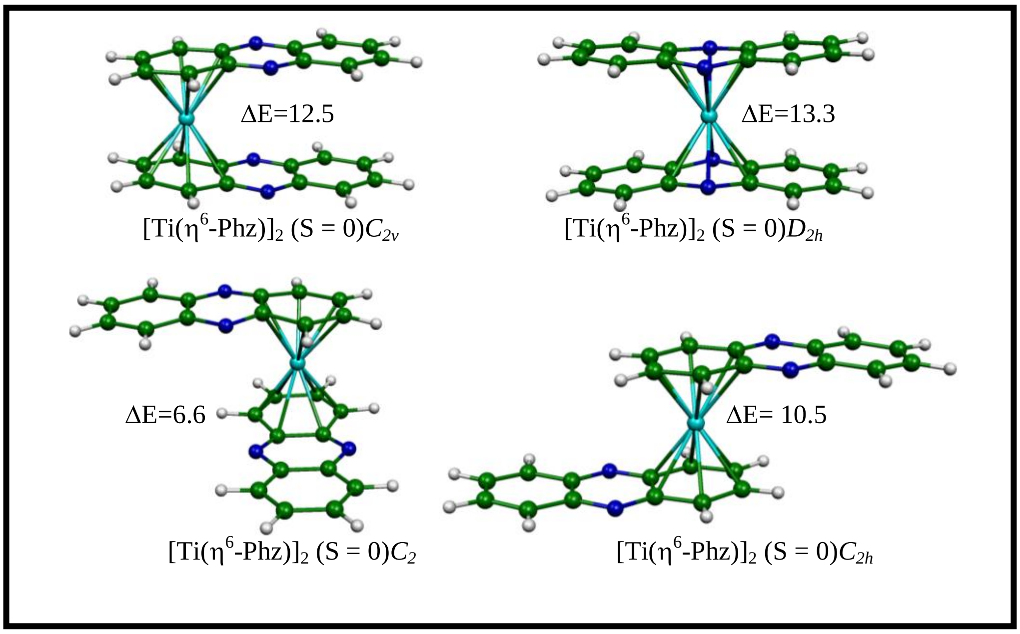

Figure S1: Optimized geometries for [Ti(phz)$_2$]. The relative energies between isomers are given in kcal/mol.

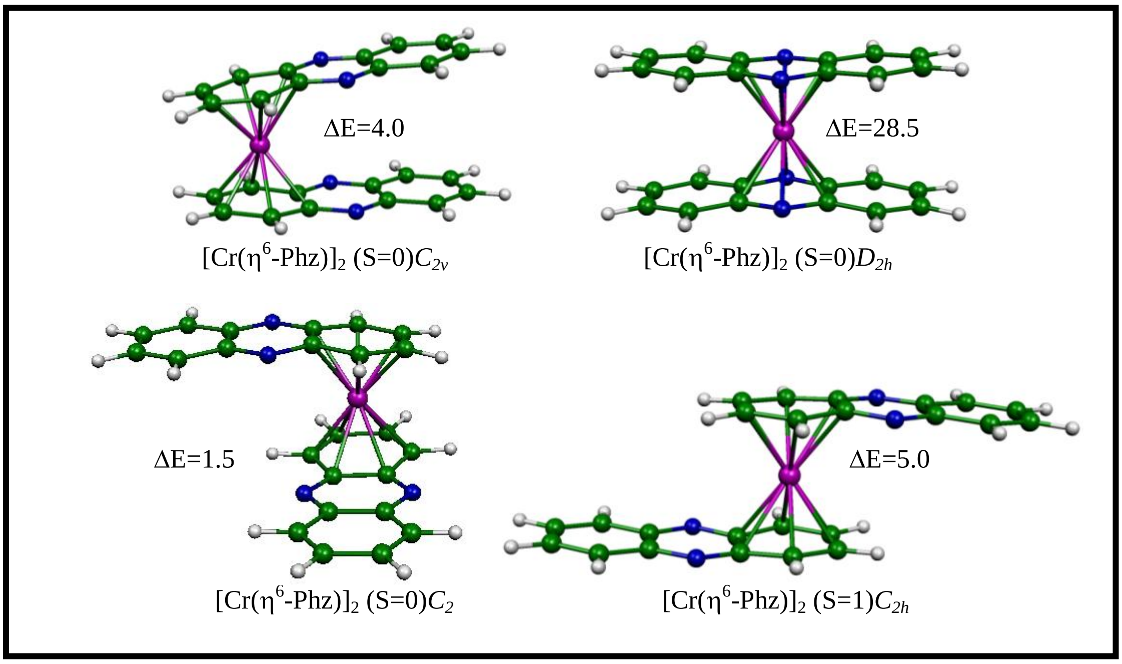

Figure S2: Optimized geometries for [Cr(phz)$_2$]. The relative energies between isomers are given in kcal/mol.

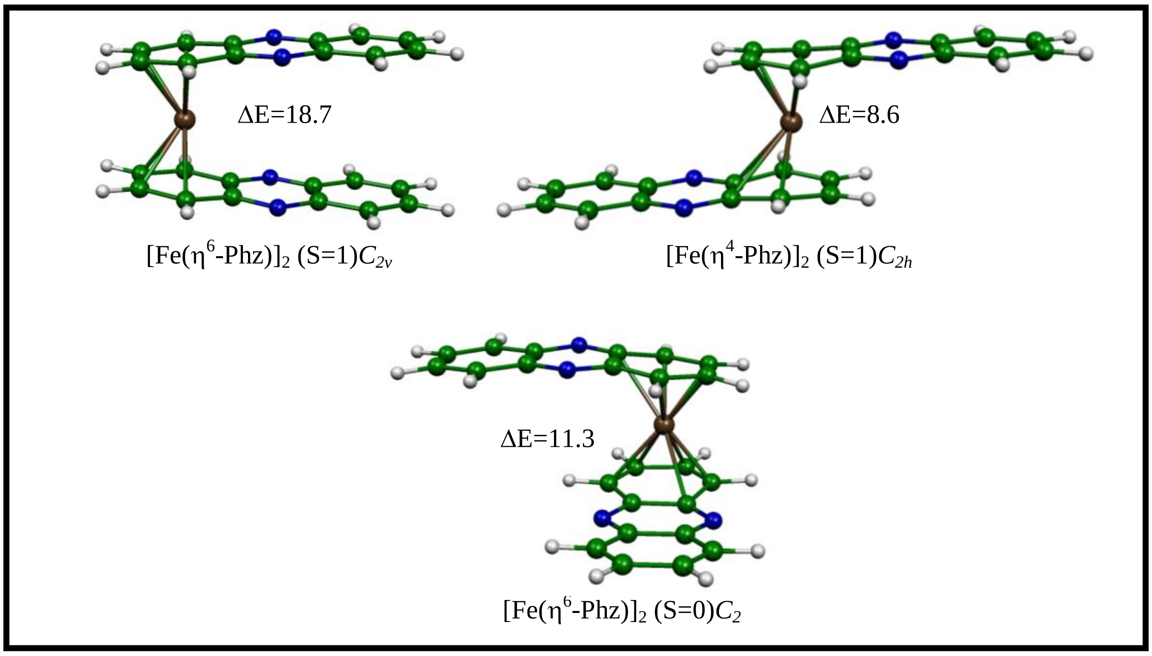

Figure S3: Optimized geometries for [Fe(phz)$_2$]. The relative energies between isomers are given in kcal/mol.

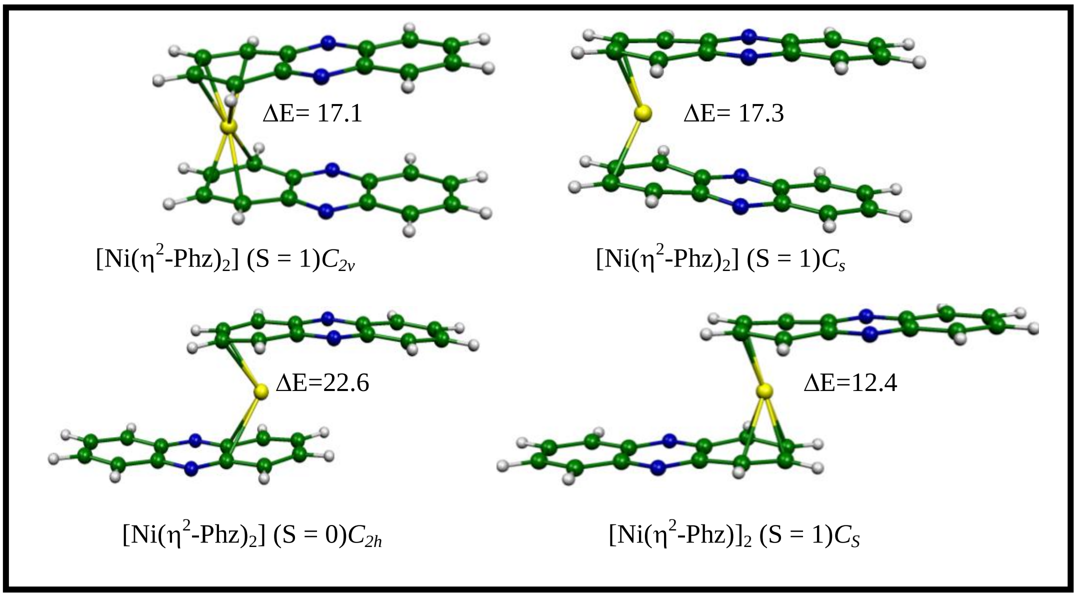

Figure S4: Optimized geometries for [Ni(phz)$_2$]. The relative energies between isomers are given in kcal/mol.

Table S1. Selected parameters for $[Ti(Phz)_2]$ isomers.

complex	$[Ti(Phz)_2]$							
symmetry	C_{2v}		C_2		C_{2h}		D_{2h}	
Spin state	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1
Gap H-L (eV)	0.14	-	0.91	-	0.14	-	0.08	-
Relative energies ΔE (kcal/mol)	12.5	3.4	6.6	0.0	10.5	0.9	13.3	5.3
Ti-C(1)	2.331	2.387	2.359	2.360	2.342	2.392	-	-
Ti-C(2)	2.283	2.401	2.423	2.375	2.290	2.388	-	-
Ti-C(3)	2.283	2.401	2.411	2.375	2.290	2.388	-	-
Ti-C(4)	2.331	2.387	2.345	2.392	2.342	2.392	-	-
Ti-C(5)	2.380	2.437	2.426	2.477	2.383	2.474	2.302	2.395
Ti-C(6)	2.380	2.437	2.425	2.444	2.383	2.474	2.302	2.395
Ti-C'(1)	2.331	2.387	2.345	2.392	2.342	2.392	-	-
Ti-C'(2)	2.283	2.401	2.411	2.375	2.383	2.474	-	-
Ti-C'(3)	2.283	2.401	2.423	2.375	2.383	2.474	-	-
Ti-C'(4)	2.331	2.387	2.359	2.360	2.342	2.392	-	-
Ti-C'(5)	2.380	2.437	2.425	2.444	2.290	2.388	2.302	2.395
Ti-C'(6)	2.380	2.437	2.426	2.477	2.290	2.388	2.302	2.395
Ti-C(7)	-	-	-	-	-	-	2.302	2.395
Ti-C(8)	-	-	-	-	-	-	2.302	2.395
Ti-N(1)	-	-	-	-	-	-	2.253	2.219
Ti-N(2)	-	-	-	-	-	-	2.253	2.219
Ti-C'(7)	-	-	-	-	-	-	2.302	2.395
Ti-C'(8)	-	-	-	-	-	-	2.302	2.395
Ti-N'(1)	-	-	-	-	-	-	2.253	2.219
Ti-N'(2)	-	-	-	-	-	-	2.253	2.219

Table S2. Selected parameters for [Cr(Phz)$_2$] isomers

complex	[Cr(Phz)$_2$]							
symmetry	C_{2v}		C_2		C_{2h}		D_{2h}	
Spin state	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1
Gap H-L (eV)	0.16	-	0.52	-	0.20	-	0.25	-
Relative energies ΔE (kcal/mol)	4.0	0.0	1.5	1.1	3.6	4.8	28.5	23.1
Cr-C(1)	2.205	2.219	2.208	2.249	2.209	2.242	-	-
Cr-C(2)	2.172	2.156	2.185	2.204	2.191	2.257	-	-
Cr-C(3)	2.172	2.156	2.172	2.147	2.191	2.257	-	-
Cr-C(4)	2.205	2.219	2.217	2.174	2.209	2.242	-	-
Cr-C(5)	2.275	2.390	2.283	2.399	2.266	2.348	2.213	2.243
Cr-C(6)	2.275	2.390	2.271	2.379	2.266	2.348	2.213	2.243
Cr-C'(1)	2.205	2.219	2.217	2.174	2.209	2.242	-	-
Cr-C'(2)	2.172	2.156	2.172	2.147	2.666	2.348	-	-
Cr-C'(3)	2.172	2.156	2.185	2.204	2.666	2.348	-	-
Cr-C'(4)	2.205	2.219	2.208	2.249	2.209	2.242	-	-
Cr-C'(5)	2.275	2.390	2.271	2.379	2.191	2.257	2.213	2.243
Cr-C'(6)	2.275	2.390	2.283	2.399	2.191	2.257	2.213	2.243
Cr-C(7)	-	-	-	-	-	-	2.213	2.243
Cr-C(8)	-	-	-	-	-	-	2.213	2.243
Cr-N(1)	-	-	-	-	-	-	2.227	2.156
Cr-N(2)	-	-	-	-	-	-	2.227	2.156
Cr-C'(7)	-	-	-	-	-	-	2.213	2.243
Cr-C'(8)	-	-	-	-	-	-	2.213	2.243
Cr-N'(1)	-	-	-	-	-	-	2.227	2.156
Cr-N'(2)	-	-	-	-	-	-	2.227	2.156

Table S3. Selected parameters for [Fe(Phz)$_2$] isomers.

complex	[Fe(Phz)$_2$]							
symmetry	C_{2v}		C_2		C_{2h}		D_{2h}	
Spin state	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1
Gap H-L (eV)	0.95	-	0.25	-	0.40	-	0.30	-
Relative energies ΔE (kcal/mol)	0.0	18.7	11.3	6.0	4.5	8.6	59.0	39.4
Fe-C(1)	2.143	2.301	2.265	2.231	2.150	2.160	-	-
Fe-C(2)	2.080	2.187	2.142	2.136	2.099	2.106	-	-
Fe-C(3)	2.080	2.187	2.047	2.136	2.099	2.106	-	-
Fe-C(4)	2.143	2.301	2.078	2.181	2.150	2.160	-	-
Fe-C(5)	2.506	2.415	2.343	2.446	2.401	2.474	2.275	2.323
Fe-C(6)	2.506	2.415	2.384	2.471	2.401	2.474	2.275	2.323
Fe-C'(1)	2.143	2.301	2.078	2.181	2.150	2.160	-	-
Fe-C'(2)	2.080	2.187	2.047	2.136	2.401	2.474	-	-
Fe-C'(3)	2.080	2.187	2.142	2.136	2.401	2.474	-	-
Fe-C'(4)	2.143	2.301	2.265	2.231	2.150	2.160	-	-
Fe-C'(5)	2.506	2.415	2.384	2.471	2.099	2.106	2.275	2.323
Fe-C'(6)	2.506	2.415	2.343	2.446	2.099	2.106	2.275	2.323
Fe-C(7)	-	-	-	-	-	-	2.275	2.323
Fe-C(8)	-	-	-	-	-	-	2.275	2.323
Fe-N(1)	-	-	-	-	-	-	2.180	2.350
Fe-N(2)	-	-	-	-	-	-	2.180	2.350
Fe-C'(7)	-	-	-	-	-	-	2.275	2.323
Fe-C'(8)	-	-	-	-	-	-	2.275	2.323
Fe-N'(1)	-	-	-	-	-	-	2.180	2.350
Fe-N'(2)	-	-	-	-	-	-	2.180	2.350

Table S4. Selected parameters for $[Ni(Phz)_2]$ isomers.

complex	$[Ni(Phz)_2]$											
symmetry	C_{2v}		$C_S(C_{2V})$		C_2		C_{2h}		$C_S(C_{2h})$		C_S (D_{2h})	
Spin state	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1	S=0	S=1
Gap H-L (eV)	0.73	-	0.72	-	1.48	-	0.02	-	0.41	-	0.93	-
Relative energies ΔE (kcal/mol)	8.4	17.1	9.1	17.3	0.0	30.8	22.6	15.9	10.0	12.4	31.2	49.4
Ni-C(1)	2.570	2.348	2.540	2.347	2.364	2.367	2.377	2.333	2.681	2.369	-	-
Ni-C(2)	2.080	2.135	2.080	2.147	2.108	2.226	2.283	2.136	2.071	2.111	-	-
Ni-C(3)	2.080	2.135	2.080	2.147	2.096	2.168	2.283	2.136	2.074	2.110	-	-
Ni-C(4)	2.570	2.348	2.540	2.347	2.108	2.323	2.377	2.333	2.684	2.362	-	-
Ni-C(5)	3.024	2.731	2.970	2.724	2.724	2.580	2.383	2.636	3.145	2.779	2.905	2.642
Ni-C(6)	3.024	2.731	2.970	2.724	2.751	2.606	2.383	2.636	3.145	2.783	2.905	2.642
Ni-C'(1)	2.570	2.348	2.608	2.350	2.108	2.323	2.377	2.333	2.280	2.352	-	-
Ni-C'(2)	2.080	2.135	2.078	2.135	2.096	2.168	2.383	2.636	2.382	2.751	-	-
Ni-C'(3)	2.080	2.135	2.078	2.135	2.108	2.226	2.383	2.636	2.390	2.744	-	-
Ni-C'(4)	2.570	2.348	2.608	2.350	2.364	2.367	2.377	2.333	2.295	2.336	-	-
Ni-C'(5)	3.024	2.731	3.071	2.746	2.751	2.606	2.283	2.136	2.204	2.101	2.950	2.670
Ni-C'(6)	3.024	2.731	3.071	2.746	2.724	2.580	2.283	2.136	2.196	2.110	2.950	2.670
Ni-C(7)	-	-	-	-	-	-	-	-	-	-	2.109	2.188
Ni-C(8)	-	-	-	-	-	-	-	-	-	-	2.109	2.188
Ni-N(1)	-	-	-	-	-	-	-	-	-	-	2.551	2.313
Ni-N(2)	-	-	-	-	-	-	-	-	-	-	2.551	2.313
Ni-C'(7)	-	-	-	-	-	-	-	-	-	-	2.102	2.197
Ni-C'(8)	-	-	-	-	-	-	-	-	-	-	2.102	2.197
Ni-N'(1)	-	-	-	-	-	-	-	-	-	-	2.572	2.340
Ni-N'(2)	-	-	-	-	-	-	-	-	-	-	2.572	2.340