# Orbital Splitting and Pairing Energy in Open-Shell Organometallics: A Study of Two Families of 16-Electron Complexes [$Cp_2M$] (M = Cr, Mo, W) and [$CpM(PH_3)$] (M = Co, Rh, Ir)

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The singlet–triplet gap for two families of 16-electron organometallic complexes has been examined in detail by DFT calculations at the B3LYP level with polarized basis sets on both metal and ligands. For the first family, the group 6 metallocenes ($Cp_2M$ with Cp = $\eta^5$-$C_5H_5$ and M = Cr, Mo, W), the singlet–triplet gap ($E_S - E_T$) is always positive and decreases continuously on going from Cr to Mo to W. For the family of group 9 $CpM(PH_3)$, on the other hand, there is a decrease on going from Co to Rh, followed by a slight increase on going further to Ir. These trends have been analyzed in qualitative monoelectronic terms as a function of the competition between the pairing energy and the orbital gap. While the pairing energy decreases as expected in the order 3d >> 4d > 5d, the orbital gap varies in a different way for the two families and, though quantitatively less important, is responsible for the different trends. It is argued that changes in orbital gap are system-dependent for open-shell organometallic systems, thus it is not possible to establish a universal trend of singlet–triplet gaps for a homologous series of complexes with a group of transition metals.

## Introduction

Reaction selectivities and catalytic activities can be tuned by the relative stabilization of the reaction intermediates and transition states. The most typical situation encountered in organometallic chemistry involves reaction intermediates that are less electronically saturated than the reagents and products; for instance a saturated, 18-electron compound may generate a 16-electron intermediate by a ligand dissociation, or reductive elimination, or migratory insertion, etc. Although most organometallic reactions involve reagents, products and intermediates having a diamagnetic ground state, it is now well appreciated that compounds with fewer than 18-electrons and a paramagnetic ground state are also involved in all sorts of stoichiometric and catalytic transformations.[1,2] Even when the reagents and the products are saturated, diamagnetic systems, it is possible that a reaction takes place via more than one potential energy surface, through open-shell intermediates in a different spin state.[3–7]

Three distinct factors are recognized to play a role in the energetic stabilization of open-shell compounds, relative to more saturated ones. Steric pressure, enforced by encumbering ligands, destabilizes higher coordination numbers and therefore stabilizes less saturated intermediates in a relative sense. Ligands possessing inactive electron pairs for the saturated systems (e.g. π-symmetry lone pairs), may stabilize the less saturated intermediates by becoming engaged in bonding with the metal orbital associated with the open coordination site. Finally, a third factor is present when the system undergoes a changes of spin state on going from the reagent to the intermediate. The binding energy lost during the formation of the open coordination site can be partially recovered by unpairing two electrons. In the qualitative, single-electron framework, the promotion of one electron to a higher-energy orbital may be more than compensated by the lower electron–electron coulombic repulsion ($J$) and by a gain in exchange energy ($K$). The combination of these factors is known by the general term “pairing energy”.

The concept of pairing energy has a solid place in the chemistry of Werner-type coordination compounds to understand the preference of a low- vs. high-spin configuration for octahedral or tetrahedral complexes, as a function of the orbital splitting between the $t_{2g}$ and $e_g$ orbitals ($\Delta_O$) or between the $e$ and $t_2$ orbitals ($\Delta_T$), respectively. In particular, it is widely appreciated that, whereas this separation increases down a series of transition metals (e.g. $3d \leqslant 4d \leqslant 5d$ for elements within the same group), the pairing energy correspondingly decreases.[8] Therefore, both factors concur for the stabilization of the low-spin state relative to the high-spin one on going from the lighter to the heavier element.

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However, the same trend does not appear to be valid in general for open-shell organometallic compounds. Few families of $ML_n$ complexes within the same group of transition metals have been studied in terms of high spin–low spin energy gap at the same level of theory. The trend of the Werner complexes seems reproduced for the organometallic group 8 $M(CO)_4$ systems, the energy difference ($E_S - E_T$, in kcal mol$^{-1}$) being 1.7 for Fe, –13.1 for Ru, and –16.2 for Os at a nonlocal DFT level.[9] On the other hand, a nonmonotonous variation of the same quantity results for the group 9 CpM(CO) series at various computational levels, for instance 11.2 for Co, –5.9 for Rh, and 0.3 for Ir using a CI calculation combined with a couple pair functional to correct the lack of size consistency.[10] It is generally known that the pairing energy decreases on going from the lighter to the heavier element, because of the cloud expansion (nephelauxetic) effect on going from lower (e.g. 3d) to higher (e.g. 5d) valence shells. It is also known that this effect is particularly strong on going from the 3d to the 4d element.[8] This trend is common to the Werner-type octahedral and tetrahedral complexes mentioned above. On the other hand, it is not clear how the orbital splitting should change along a homologous series of open-shell organometallic compounds.

There is an important difference between Werner-type complexes and open-shell organometallic compounds. For the Werner-type systems, the higher-energy orbitals whose occupation increases in the higher spin state have metal-ligand antibonding character (strong for the octahedral $e_g$ orbitals, weaker for the tetrahedral $t_2$ orbitals), while those losing electrons in the same process are nonbonding (or π-bonding in the presence of π-acceptor ligands). Thus, the well-known increase of metal–ligand binding energy on going from the lighter to the heavier metal[11,12] results in an energy increase for the higher-energy orbitals and possibly in an energy decrease for the lower-energy ones, both effects contributing to raise the orbital gap. On the other hand, both the high energy and the low energy orbitals involved in the spin transition for open-shell organometallic compounds generally have similar characteristics with respect to metal-ligand bonding (essentially σ nonbonding; possibly π bonding), thus the variation of this orbital gap along a group of transition metals cannot be easily predicted a priori.

For this reason, we set out to study two representative families of homologous 16-electron complexes, the group 6 metallocenes $Cp_2M$ (M = Cr; Mo, W) and the Group 9 "one-legged piano stools" $CpM(PH_3)$ (M = Co, Rh, Ir), that are models of the more widely studied $PMe_3$ complexes. A variety of calculations at different levels of theory[13–19] have already shown that these complexes, or at least some of them, adopt a spin-triplet ground state configuration. In this contribution, we examine for the first time the details of how orbital gap and pairing energy vary along the two homologous series, and compare these findings with the computed singlet–triplet gaps. It will be shown that the trends of the singlet–triplet energy difference are qualitatively reproduced by the approximate one-electron formula, which expresses the energy difference as a combination of orbital energy gap and a pairing energy term. Thus, the qualitative thinking that is often applied to Werner-type coordination compounds can be successfully extended to open-shell organometallics. However, although the pairing energies trends are as expected, the trends of orbital gaps are found to be family-dependent. Therefore, a universal trend for the singlet–triplet gap upon descending a group of transition metals cannot be established.

## Results and Discussion

### DFT Calculations: Electronic and Molecular Structures

Our investigation makes use of the DFT approach, using the B3LYP functional and polarized basis sets, which has proven effective for the computation of several other cases of spin-state dichotomy in coordination and organometallic chemistry.[7,10,20,21] The optimized geometries for all systems are shown in Figure 1 for the group 6 metallocenes and Figure 2 for the group 9 $CpM(PH_3)$ systems.

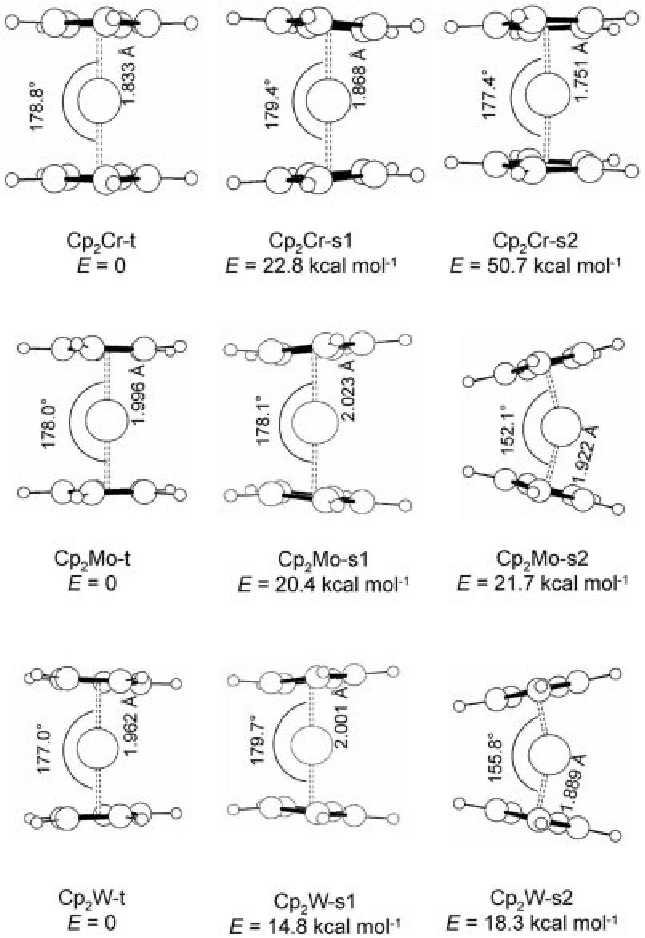

Figure 1. Views of the optimized geometries, relative energies, and selected bonding parameters for the $Cp_2M$ systems (M = Cr, Mo, W; s = singlet, t = triplet). The distance of the metal from the Cp ring is calculated from the ring centroid (CNT).

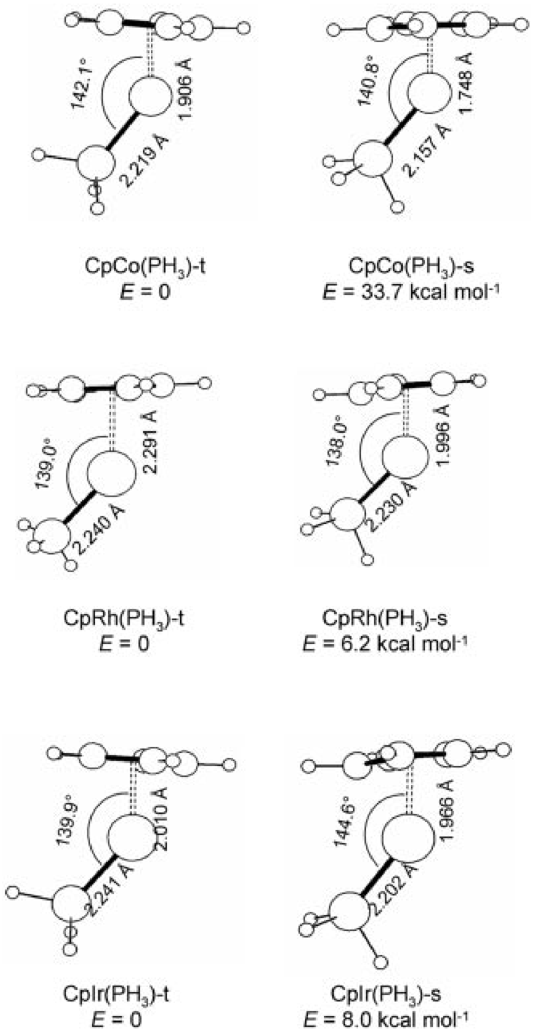

Figure 2. Views of the optimized geometries, relative energies, and selected bonding parameters for the CpM($PH_3$) systems (M = Co, Rh, Ir; s = singlet, t = triplet). The distance of the metal from the Cp ring is calculated from the ring centroid (CNT).

The energies obtained at the chosen level of theory favor a triplet ground state for all systems. From the experimental point of view, chromocene is a stable triplet compound[22] whereas molybdenocene and tungstenocene cannot be isolated. However, a magnetic circular dichroism study demonstrates their triplet ground state.[23,24] The calculated Cr–Cp (center) distance of 1.833 Å for triplet $Cp_2Cr$ is in relatively good agreement with the experimentally determined one of 1.791(4) Å.[25] There is no experimental information on any 16-electron CpM($PR_3$) system, to the best of our knowledge.

All metallocene molecules yielded two different stable minima (termed s1 and s2 in Figure 1) that differ by their orbital occupation, as shown in Figure 3. It is noteworthy that, with only one exception for chromocene,[21] all previously published computational studies on the group 6 metallocenes report only one energy minimum for both the singlet and the triplet state.[15,26] The recent report by Reiher et al.,[21] which probed the effect of the exact exchange admixture parameter $c_3$ on the singlet–triplet gap for various first row metallocenes, mentions the location of a second singlet minimum for chromocene at low $c_3$ values. However, neither the energy difference between these two minima, nor the optimized geometry of either minimum, were reported.

It is curious that the two chromocene minima s1 and s2 were obtained starting with the same input geometry and guess orbitals, at the same computational level, and using the closely related Gaussian98 and Gaussian03 programs, respectively. With particular care in the choice of alternative input geometries, or by artificially altering the list of filled and empty guess orbitals, both energy minima were eventually obtained with both program packages. The molybdenocene and tungstenocene molecules only yielded the s2 minima initially. They provided the lower-energy s1 minima only by artificially altering the list of filled and empty guess orbitals, and, in particular, by substituting the LUMO for the HOMO in the guess density of the self-consistent procedure. This example serves to illustrate that one has to be very careful about checking all considered states in close-to-degeneracy situations.

The origin of the double-singlet minimum can be related to the observed geometrical distortions as follows. In an ideal symmetric top geometry ($D_{5x}$ with $x = h$ or $d$ or nothing, depending on the dihedral angle), the metallocene electronic structure is well known.[27] The metal frontier orbitals ($z^2$, $xy$ and $x^2 - y^2$) are partitioned into a singly degenerate ($z^2$, $a_1$-type) orbital and a doubly degenerate ($xy$, $x^2 - y^2$, $e$-type) set, their complete symmetry label depending on the point group (e.g. $a_1'$ or $a_{1g}$ for $z^2$ in $D_{5h}$ and $D_{5d}$, respectively). However, a molecular distortion that lowers the symmetry to $C_{2v}$ splits the $e$-set into an $a_1$ and a $b_2$ orbital.[28] This symmetry lowering allows orbital mixing with a consequent energy lowering, a phenomenon known as the pseudo-Jahn–Teller effect (or second-order Jahn–Teller effect).[29] Different levels of mixing lead to different orbital energies and consequently to different geometries and orbital occupations. The s1 minimum corresponds to the configuration $(x^2 - y^2)^2(z^2)^2$, whereas the s2 minimum has the configuration $(x^2 - y^2)^2(xy)^2$ (we maintain the same orientation of the principal axes as in the higher-symmetry molecule). The same double-minimum phenomenon has been described previously for several other 16-electron organometallic complexes such as a variety of $d^6$ $ML_5$ complexes,[30,31] $[(\text{arene})Nb(CO)_3]^+$,[32] and $[CpMo(L)_2X]$ (L = CO, $PH_3$; X = H, $CH_3$, Cl, Br, I, etc.).[33,34] For the latter two systems in particular, Hasanayn was able to show that the second-order Jahn–Teller distortion generates two different symmetry states for both the singlet and the triplet electronic configurations. In principle, more than one triplet minimum could also exist for the metallocenes. However, only a single minimum with the same relative orbital ordering as the s1 singlet could be located, yielding the $(x^2 - y^2)^2(z^2)^1(xy)^1$ configuration ($^3B_2$). Numerous attempts, starting with differently populated guess geometries, either linear or bent, led to the same optimized minimum.

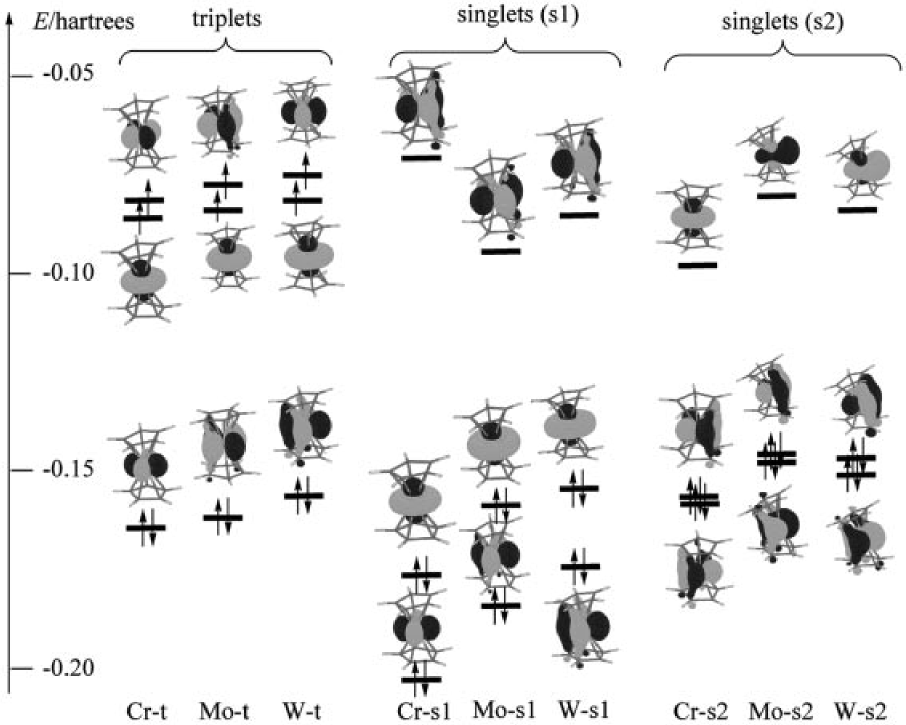

Figure 3. Electronic structure (frontier orbital region) of the singlet and triplet metallocenes. The orbital energies shown for the triplet states were obtained at the ROB3LYP level.

The metal orbital mixing, resulting from the geometrical distortion, is only very slight for all triplets and also for the s1 singlets. The Mo and W metallocenes of s2 type show a significant participation of the p orbital that points along the symmetry $C_2$ axis ($a_1$ type) in the LUMO (see Figure 3). There is no significant mixing of this kind, on the other hand, for the chromocene s2 minimum. This orbital mixing is reflected in the molecular geometry, which is severely bent (CNT-M-CNT $<<$ 180°) for the molybdenocene and tungstenocene s2 minima (see Figure 1).

On the other hand, all triplets and s1 singlets, as well as the chromocene s2 minimum, are very close to linear. The different orbital occupancy reflects very strongly on the Cp–M distance: the double occupation of the $z^2$ orbital, which has a slight Cp-M σ* character, considerably lengthens the M–CNT distance in $Cp_2M$-s1 relative to $Cp_2M$-s2. This distance is, in fact, even longer in $Cp_2M$-s1 than in $Cp_2M$-t.

A second interesting effect is that the Cp rings are differently tilted from the ideal arrangement, with equivalent M–C distances, in which the metal lies on the $C_5$ symmetry axis of the Cp moiety. The s2 singlets do not display any significant tilting, the angle between the M–CNT vector and the Cp least-squares plane being 90.0° for all three metals. On the other hand, the distortion is significant for the triplets (85.4°, 85.9°, and 85.9° for Cr, Mo, and W, respectively) and even more so for the s1 singlets (76.4°, 84.3°, and 81.1° for Cr, Mo, and W, respectively). This effect can be attributed to δ-type M–Cp back-bonding interactions, as previously highlighted by Hoffmann et al.[35] These interactions can be established by the $x^2 - y^2$ and $xy$ orbitals. When both orbitals are filled, as in the s2 singlets, the δ back-bonding has cylindrical symmetry and no major distortion occurs. This cylindrical symmetry is broken by the molecular distortion to $C_{2v}$ symmetry for the molybdenocene and tungstenocene, resulting in a slight ring tilting, but both back-bonding interactions are still present, as can be appreciated from Figure 3. The triplets and the s1 singlets, on the other hand, have a reduced population of the $xy$ orbitals, thus the prevalence of the back-bonding interaction from the $x^2 - y^2$ orbital causes the ring tilting. It is noteworthy that neither $Cp_2Cr$-s1 nor $Cp_2Cr$-s2 correspond to the optimized geometry obtained by the previous calculation reported by Green and Jardine,[26] which is bent like those of the Mo and W analogs, with an inter-ring angle of 26.8°. Our s1 and s2 minima have inter-ring angles of 10.1° and 2.7°, respectively.

It should be noted that the higher-energy s2 singlets for molybdenocene and tungstenocene are better pre-organized than the corresponding s1 singlets for the interaction with molecules of L or X–Y type, leading to L addition or X–Y oxidative addition to generate saturated $Cp_2M(L)$ or $Cp_2M(X)(Y)$ products. The metallocene is bent as in the final products and the LUMO is geometrically well disposed to receive electron density from the L or X–Y donating orbital. Thus, a reaction coordinate leading from the free $Cp_2M$ triplet molecule to the above singlet products should involve crossing of the reagent triplet surface with the higher-energy s2 singlet surface, rather than with the lower-energy one. A similar situation has been described for the addition of CO and $N_2$ to triplet $[CpMo(PH_3)_2Cl]$,[33] which is isoelectronic with the metallocenes studied here.

The energy of the frontier orbitals for the $Cp_2M$ triplet systems increases regularly on going from the 3d to the 5d metal (see Figure 3), following the analogous trend of the atomic orbitals which contribute almost totally to their composition. On the other hand, the orbital energies for the singlet systems show a different and more complex trend, which is probably related to the different degree of orbital mixing and geometrical distortions discussed above. The chromocene s1 system is anomalous for having a higher-energy LUMO than the heavier congeners. Within the s2 series, on the other hand, tungstenocene unexpectedly shows lower energies for all frontier orbitals relative to molybdenocene.

For each member of the group 9 $CpM(PH_3)$ series, we located only one singlet and one triplet minimum. We did not exhaustively explore the possibility of other minima in any of the two spin-states. Since the geometry of these molecules is much farther from a pseudo-symmetry situation than for the metallocenes, less complications of this kind are anticipated. The optimized geometries (Figure 2) are very close to those obtained for the same systems at other levels of theory. All metal–ligand bonds shorten slightly on going from the triplet to the singlet, as expected. The main structural changes observed upon changing spin state have been amply discussed previously.[16] The electronic and molecular structures of the $CpM(PH_3)$ systems do not deserve any further discussion. The orbital energies, shapes, and occupations in both spin states are shown in Figure 4. The electronic structure remains unchanged along the series for both triplets and singlets. The orbital analysis agrees with that already reported by Ziegler et al.[16] for $CpRh(PH_3)$, although in this paper we find a somewhat larger mixing between the metal and the Cp orbitals. Notice, however, that in that work a reverse order was found for the singlet–triplet energy gap: the singlet was found to be the most stable state. The rationalization of the orbital energies is found in the interaction of the metal orbitals with different types of Cp orbitals, with minor effects of the σ- and σ*-orbitals of $PH_3$. For instance, the HOMO in the singlet state shows a small antibonding metal-Cp character, indicating a destabilization due to the interaction with the occupied π-orbitals of Cp. On the contrary, metal-Cp bonding character, due to interaction with the empty π*-orbitals, is observed for the low-lying, metal-based molecular orbitals. The most notable change in the series is the stabilization of the LUMO for the singlet system on going from Co to Ir, whereas the HOMO remains approximately at the same energy. Consequently, the HOMO–LUMO gap decreases.

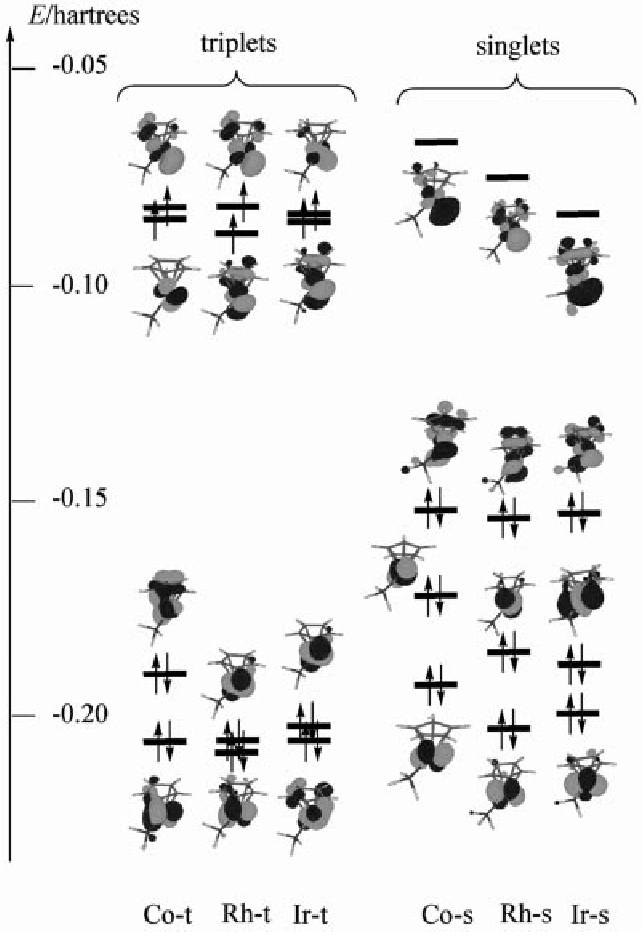

Figure 4. Electronic structure (frontier orbital region) of the singlet and triplet $CpM(PH_3)$ systems (M = Co, Rh, Ir). The orbital energies shown for the triplet states were obtained at the ROB3LYP level.

## DFT Calculations: Singlet–Triplet Gaps

As far as we are aware, experimental determinations of the singlet–triplet gap are unavailable for any of the compounds examined here. As anticipated in the introduction, there is no clear monotonous trend of singlet–triplet gap on going from the 3d through the 4d to the 5d system within each family. The gap is larger for the 3d system, relative to the heavier congeners, within each family of complexes. On going from the 4d to the 5d system, on the other hand, the calculations predict a slight decrease for the metallocene series and a slight increase for the $CpM(PH_3)$ series. In previous computational work on the same systems, the singlet state was found to be higher than the triplet for all $Cp_2M$ systems (M = Cr, 34.8; Mo, 16.4; W, 17.9 kcal mol$^{-1}$).[26] Our own previous calculations on $Cp_2M$ (M = Mo, W) gave a lower-energy triplet by 24.1 and 19.1 kcal mol$^{-1}$ at the B3LYP/LANL2DZ level, or by 23.0 and 19.6 kcal mol$^{-1}$ at the same level used here, except that polarization functions on the metal atoms were not used (those calculations dealt only with the singlet structure that corresponds to the s2 minimum reported herein).[15] For the $CpM(PH_3)$ series, the Co system was found as a ground-state triplet, 33.0 kcal mol$^{-1}$ more stable than the singlet at the B3LYP/LANL2DZ level.[13] For the Rh and Ir systems, the triplet was reported to be more stable by 8.17 and 20.1 kcal mol$^{-1}$ at the MP2/LANL1DZ level,[18] and by 13.2 and 16.9 kcal mol$^{-1}$ at the B3LYP/LANL2DZ level,[19] respectively. However, another report on the Ir system gives a relative stability for the triplet of 6.4 or 8.4 kcal mol$^{-1}$ by using B3LYP and the LANL2DZ or TZV basis sets.[14] In all reported cases, except one,[26] the stability of the triplet state relative to the singlet on going from the 4d to the 5d metal *decreases* for the $Cp_2M$ system and *increases* for the $CpM(PH_3)$ system.

### Analysis of the Orbital Gaps and Pairing-Energy Factors

Using the qualitative concepts of orbital splitting and pairing energy, the singlet–triplet gap for the neutral system can be approximately expressed as in Equation (1), where the relevant orbital energies, $\varepsilon$, and the two-electron coulombic ($J$) and exchange ($K$) integrals appear.

$$\Delta E_{ST} = E_S - E_T = (J_{11} - J_{12} + K_{12}) - (\varepsilon_2 - \varepsilon_1) \quad (1)$$

In this simple expression the pairing energy ($J_{11} - J_{12} + K_{12}$) is defined as the change of electrostatic energy in going from a $\varphi_1\alpha\varphi_2\alpha$ (triplet) to a $\varphi_1\alpha\varphi_1\beta$ (singlet) configuration irrespective of the one-electron potential arising from the nuclei and from the other electrons (core electrons). The latter is accounted for by the orbital energy gap ($\varepsilon_1 - \varepsilon_2$), which includes also the kinetic energy of the orbitals entering Equation (1). This equation is, of course, a rather drastic approximation because both the orbital relaxation and the electronic correlation between the two active electrons, which may be of crucial importance for low singlet–triplet energy gaps, are completely neglected. In addition, the core electrons are considered frozen, i.e. their distribution is assumed to be independent of the configuration of the two active electrons. Nevertheless, this simple picture has a great appeal, and in several cases can furnish a fashioned model to rationalize a number of results, the best known application in coordination chemistry being the rationalization and prediction of high-spin vs. low-spin magnetic properties for octahedral complexes of $d^4$–$d^7$ metal ions.[8] Assuming $\varepsilon_1 < \varepsilon_2$, it is apparent that high orbital energy gaps favor the singlet state, i.e. the one-electron terms stabilize the singlet state. Conversely, the pairing energy expression contains the $J_{11} - J_{12}$ term, which is generally positive and accounts for the larger electron–electron repulsion energy of the singlet, as well as the $K_{12}$ exchange term, which further stabilizes the triplet state; greater values for $J$ and $K$ integrals therefore lead to a stronger preference for the higher spin state.

Once the model has been well characterized, a second important problem arises. How can the active orbitals to be used in Equation (1) be determined? One possibility was originally suggested and implemented by Hall et al.[36] in order to analyze nephelauxetic effects in the series of compounds $[Ti(dmpe)_2X_2]$ (X = Cl, OPh),[36] and later applied by us to a family of [CpCr(NO)XY] compounds (X, Y = Cl, alkyl, amido).[37] In this approach, the active orbitals are the LUMO and LUMO+1 of a simple HF calculation with $n - 2$ electrons (dication in our case). As pointed out by the authors,[36] this choice provides an unbiased determination of the active orbitals, which proved to predict qualitatively correct singlet–triplet splittings. One other possibility that we suggest here is based on the DFT approach which, in the Kohn–Sham (KS) scheme, furnishes a set of orbitals and a set of orbital energies which can be recognized to have a physical meaning. For instance, in Slater's transition state method,[38] the basic Equation (2) shows that the change in the total energy, $E$, due to an infinitesimal increase of charge in the KS orbital $\varphi_i$, corresponds to its eigenvalue $\varepsilon_i$. This equation gives a real physical meaning to the KS orbitals and recognizes the orbital energies of the occupied orbitals as true ionization potentials.[39–41] The extension to unoccupied orbitals is trivial and HOMO and LUMO KS orbital energies are currently used to estimate a number of molecular properties. Therefore, the B3LYP KS eigenvalues and the corresponding orbitals obtained for the dication can be inserted in Equation (1) in order to look for some rationale for the energy splittings. This choice, while preserving the simplicity of such an expression, has the clear advantage, with respect to the previous choice based on HF results, of using orbitals that represent a more accurate density function and are thus expected to give more reliable estimates of the quantities entering Equation (1). As a matter of fact, we found that the KS orbitals are generally a bit more contracted than the HF ones and lead to slightly higher values of the Coulomb and exchange integrals. This finding can be rationalized as the effect of the electronic correlation, which optimizes the inter-electronic repulsion energy and allows the density to better accumulate in the wells of the nuclear potential.

$$\frac{\delta E}{\delta n_i} = \varepsilon_i \quad (2)$$

In view of the approximations contained in Equation (1), only general and clear trends may be physically meaningful; conversely, some caution must be used in order to draw conclusions based on strongly method-dependent quantities. For instance, the comparison between the results for the different systems can be meaningful only if the active orbitals in the dication systems (LUMO and LUMO+1) have the same nature, i.e. show similar lobes along each series. In addition, these orbitals should be pure metal orbitals, in order for the resulting $J$ and $K$ values to have a stronger significance. The only cases where we found this set of conditions to be satisfied, for the $Cp_2M$ systems, are for the B3LYP calculations of the dication using either the s1 optimized structures or the optimized triplet structures of the neutral complexes. This is probably because the three geometries follow a regular trend in these cases. The orbital order found in the dications is the same as that observed for the neutral triplets and s1 singlets (Figure 3), with $z^2$ below $xy$. For the $CpMPH_3$ systems, the best trend was observed for the singlet optimized geometries and these were then used for the dication calculations. The results are shown in Table 1. The results obtained with the triplet geometries for the metallocene series (not reported) are nearly identical to those obtained with the s1 geometries.

Despite the approximations just described, it is possible to analyze trends of orbital gap and pairing energy along both series of isoelectronic complexes and draw some reasonable conclusions. As stated in the introduction, conventional wisdom tells us that the $J$ values should decrease on

Table 1. Orbital energies and relevant $J$ and $K$ integrals (in kcal mol$^{-1}$) for the $Cp_2M$ (M = Cr, Mo, W) and $CpM(PH_3)$ complexes. The reported quantities arise from B3LYP calculation of the 2+ ion at the geometries of the neutral complex.

| | $Cp_2M$[a] | | | $CpM(PH_3)$[b] | | |
|---|---|---|---|---|---|---|
| M | Cr | Mo | W | Co | Rh | Ir |
| $\varepsilon_2$ | –318.5 | –328.3 | –321.2 | –316.3 | –303.7 | –299.0 |
| $\varepsilon_1$ | –330.6 | –329.9 | –326.1 | –333.1 | –330.6 | –323.7 |
| $J_{11}$ | 435.5 | 289.7 | 264.1 | 275.4 | 208.3 | 194.2 |
| $J_{12}$ | 383.3 | 271.1 | 252.9 | 249.9 | 188.6 | 176.8 |
| $K_{12}$ | 16.8 | 17.1 | 18.8 | 9.6 | 9.2 | 10.0 |
| $(\varepsilon_2 - \varepsilon_1)$ | 12.1 | 1.5 | 4.9 | 16.7 | 26.9 | 24.7 |
| PE[c] | 69.0 | 35.7 | 30.0 | 35.1 | 29.0 | 27.5 |
| $\Delta E_{ST}$[d] | 56.9 | 34.2 | 25.1 | 18.4 | 2.1 | 2.8 |

[a] Using the singlet (s1) optimized geometries. [b] Using the singlet optimized geometries. [c] PE = Pairing energy = $J_{11} - J_{12} + K_{12}$. [d] Estimated singlet–triplet energy gap from Equation (1).

going from the 3d to the 4d element, and then again (though by a smaller extent) on going from the 4d to the 5d element. This is indeed what our calculations reveal (see Table 1). It can also be seen that, as expected, $J_{11}$ is greater than $J_{12}$ for all systems and that the $J$ values are much greater than the $K$ values.

It is apparent from the data of Table 1 that the simple Equation (1) is able to reproduce the correct energy trends for both systems: the triplet is always the most stable state (see Figures 1 and 2). For the metallocene systems, the $\Delta E_{ST}$ values from Table 1 must be compared with the gap between the triplet state and the s1 state, because that is the state having the same orbital ordering as the triplet state, used for the $\Delta E_{ST}$ calculation by Equation (1).

For the $Cp_2M$ series, $\Delta E_{ST}$ is dominated by the pairing energy whose decrease is mainly due to the difference between $J_{11}$ and $J_{12}$, since $K_{12}$ is almost constant. Notice that the orbital gap is of the same order as those of the RO-B3LYP triplet calculations on the neutral molecule (3–4 kcal mol$^{-1}$) and is much smaller than the HOMO–LUMO gap of the singlet s1, which involves the same orbitals. This can be expected because the two involved orbitals have the same occupancy in the triplet and in the dication (1 and 0, respectively). Thus, unlike the neutral singlets, their near degeneracy is preserved.

For the $CpM(PH_3)$ systems, the PE decreases whereas the orbital energy gap increases on going from 3d to 4d and changes little from 4d to 5d. It is somewhat surprising that the trend of this gap is in contrast with the HOMO–LUMO gap of the neutral singlet calculation, which shows a monotonic decrease. However, the different meaning of the orbital energies in the dication (empty orbitals include interactions with $n - 2$ core orbitals only) and of the neutral singlet system (empty and occupied orbitals feel the effect of $n$ and $n - 1$ electrons, respectively, for Self Interaction free methods) do not allow a significant comparison. Differently from the $Cp_2M$ systems, the orbital energy gaps are greater than the (HOMO – 1)–HOMO gaps of the neutral triplet state: this is possibly related to the geometry used for the dication (neutral singlet) which can remove the near degeneracy. Calculations of the dications at the neutral triplet geometry indeed show generally lower energy gaps. All in all we do not see any systematic trend in the orbitals leading to a rationale for the variation of the energy splitting along the $CpM(PH_3)$ series.

The different trend of the PE and orbital energy gap for $CpM(PH_3)$ generates a nonmonotonic behavior of $\Delta E_{ST}$ along the series. Whereas for Co the PE dominates and favors the triplet state, for Rh and Ir complexes the two terms practically cancel each other out, leading to near degenerate triplet and single states. This feature agrees with the DFT calculations of the neutral systems, whose relative energies are reported in Figure 2: 33.7, 6.2, and 8.0 kcal mol$^{-1}$ for Co, Rh, and Ir, respectively.

## Conclusions

This contribution reports the first analysis of the electronic structure of families of open-shell organometallic complexes in terms of the variations of the pairing energy and the orbital gap. On one side, there is always a monotonous decrease of the pairing energy on going from the 3d to the 4d and further to the 5d orbitals, the biggest change occurring between 3d and 4d. On the other side, the variations of the orbital gap are smaller upon descending the group and may occur, in principle, in either direction (increase or decrease). As a result, a very different trend of the low-spin–high-spin energy gap, relative to the Werner-type octahedral and tetrahedral complexes, may result on going from the 3d to the 5d element within a group of transition metals. In some cases, like the group 9 $CpM(PH_3)$ complexes examined here, a nonmonotonous change may result. While the pairing-energy effect seems to dominate the situation on going from the 3d to the 4d complex, such that the lighter complex seems to always favor the higher-spin ground state to a greater extent, the low-spin–high-spin energy gap may decrease or increase on going from the 4d to the 5d metal, depending on the system under consideration. A universal model allowing us to predict this trend for any structure is not available at the moment, thus one must examine this problem on a case-by-case basis.

## Computational Details

All geometry optimizations were performed using the B3LYP three-parameter hybrid density functional method of Becke,[42] as implemented in the Gaussian03 suite of programs.[43] However, many calculations were also carried out with the previous version (Gaussian98) of the program. With one exception (see Results section), both programs gave the same optimized geometry and energy, within insignificant fractions of 1 kcal mol$^{-1}$. All calculations were performed with no symmetry restrictions and all optimized geometries were characterized as local minima of the potential energy surface (PES) by verifying that all second derivatives of the energy were positive. The unrestricted formulation was used for the triplet states, whereas singlet states were obtained within the restricted formulation. For the purpose of computing and visualizing the shape of the Kohn–Sham orbitals, the calculations for all triplet states were also carried out by the Restricted Open (RO) method at the fixed unrestricted optimized geometry (these energies were generally 1–2 kcal mol$^{-1}$ higher than the unrestricted ones). All reported relative energies are relative to the unrestricted computations. Numerical integrations were performed using the "ultrafine" grid of Gaussian98 and Gaussian03, consisting of 99 radial shells and 590 angular points per shell, and the default values were chosen both for the self consistency and for the geometry optimization convergence criteria. The basis sets used for the geometry optimizations are the standard 6-31G** for C, H, and P atoms, and the standard LANL2DZ basis set, which includes the Hay and Wadt effective core potentials (ECP),[44] for the metal atoms. To the latter, however, was added a single *f*-type polarization function ($\alpha = 0.8$) in order to obtain a balanced basis set and to improve the angular flexibility of the metal functions. In the model calculations for the study of the trends in the metal series a newly coded program (SPINETTA) was used to read the results of the DFT calculations, to sort the relevant orbitals, and to compute the one- and two-electron necessary integrals.

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