

# Predicting the catalytic efficiency by quantum-chemical descriptors: Theoretical study of pincer metallic complexes involved in the catalytic Heck reaction

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## Abstract

A tool to predict the catalytic activity by interpolation was constructed, correlating a quantum chemical descriptor like absolute hardness with the catalytic activity experimentally measured in turnover numbers (TONs) for pincer metallic complexes. The linear relationship showed its usefulness reproducing correctly the magnitude order of TON for a catalyst reported in the literature. From the two quantum chemical descriptors considered in the present study, atomic charge on M and absolute hardness, the best correlation observed with the experimental catalytic activity corresponded to the case when the absolute hardness (calculated as  $(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2$ ) was involved, being this an evidence of the orbital-control present in these kind of complexes.

After systematic modifications to the general structure of a pincer complex, it was observed that the presence of P as heteroatom and Cl as leaving group gives a good compromise in terms of absolute hardness and charge on the metal center. The symmetry of the frontier orbitals is also an important issue to take into account: HOMOs with  $d_{z^2}$ -like orbital symmetry and LUMOs with  $d_{xy}$ -like orbital symmetry favor nucleophilic attacks and octahedral entrance of ligands.

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## 1. Introduction

One of the most operating reactions in catalytic processes is the oxidative addition, which is involved in a large number of important transformations to form new chemical bonds [1]. The oxidative addition usually entails the addition of a substrate to a transition metal complex with the subsequent oxidation of the metal center by two electrons. Commonly the reactions concerning an oxidative addition as the first step, also involve a reductive elimination, completing in this way a catalytic cycle. In this kind of reactions, the metallic complex works as a nucleophile, hence, all the known factors affecting the nucleophilicity

(or basicity) of the metallic center will have an influence on the efficiency of the catalytic process.

About catalytic efficiency, there has been a great investigation concerning the design of highly active catalytic compounds and different molecular constructions have been proposed. Among the molecular arrangements that have shown significant efficiency, the organometallic complexes formed by pincer ligands with different heteroatoms (N, O, P and S) and different transition metals with near-square planar geometries, appear as outstanding candidates. The general scheme of these complexes is shown in Fig. 1.

The arrangement of the tridentate pincer complexes has encouraged the examination of different manners to modulate the environment of the metal center, seeking for an increase in the catalytic activity. Thus, effects like electronic effects, and even steric effects are some of the issues that can

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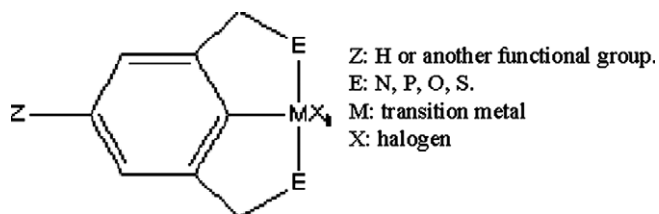


Fig. 1. General scheme of a pincer metallic complex.

be tuning to achieve an enhancement of the metal complexes performance.

Recently, the inductive effects on the metal center by the modification of the *para* substituents (Z in Fig. 1), was reported by van Koten et al. [2], obtaining a clear linear relationship between the natural charge on the metal center (Pt in this case) and the electronic nature of each substituent. Taking into account the possibilities of variation in such kind of structures, a systematic study modifying groups in the pincer complexes appears as an interesting idea. The computational chemistry represents a very useful tool to “play” with electronic and steric effects on the metal center, in order to ponder each effect in an specific process.

The well-known Heck reaction [3] is generally referred as the palladium-catalyzed C–C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base, with a high trans selectivity. The classical mechanism of this reaction involves an oxidative addition as the first step. Some facts already known about the oxidative addition and the Heck reaction are the following: (i) oxidative addition reactions are most facile when a stable two-electron redox couple is involved; (ii) the more reduced the metal center is, the greater the reactivity towards oxidative addition; and (iii) the oxidative addition of a specie A–B to a metal M will depend on the relative strengths of the A–B, M–A and M–B bonds.

According with their position in the periodic table, the transition metals usually used in catalytic complexes can be classified as follows: the lighter metals of a same subgroup are less nucleophilic than the heavier elements and those metals of the third transition series with low oxidative states are presumably the most propitious to carry out oxidative additions.

In the present study the transition metals Ni, Pd and Pt were considered as metal centers of catalytic systems based on pincer ligands and some electronic and steric effects were induced by specific modifications, focusing on the effect on the feasibility to carry out an oxidative addition in an hypothetical coupling reaction like the Heck reaction. To correlate the structure of metallic pincers with their catalytic activity, some experimental information was taken from the literature.

Recently, the group of Milstein [4] reported a set of PCP-type catalysts, based on Pd(II), highly efficient for the Heck reaction. Particularly the complex labeled as Milstein-2 showed in Fig. 2 exhibited the highest turnover numbers (TONs) [5], up to 500 000.

The authors attributed the efficiency of that catalyst to electronic factors, affirming that the metal center is more electron rich than in the other cases. The decrease of efficiency in the case of the catalyst labeled as Milstein-3 was attributed to steric effects due to the substituents (*t*-Bu) of the phosphine ligands.

In the meantime, Shibasaki and co-workers [6] reported the preparation in a one-pot reaction of a new catalyst illustrated in Fig. 3, very active, with turnover numbers up to 900 000 and apparently more versatile than those catalysts reported before, easier to prepare and surpassing the problem when aryl halides used as substrates have electron donating groups.

Considering, on the one hand, the experimental results reported for both, Milstein and Shibasaki and, on the other hand, the information about pincers and oxidative addition as the first event in reactions like the Heck coupling, the

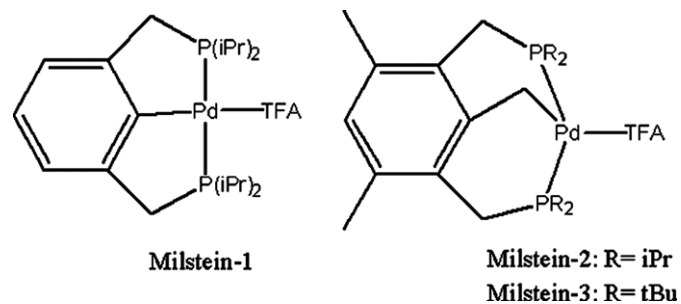


Fig. 2. Milstein's PCP catalysts.

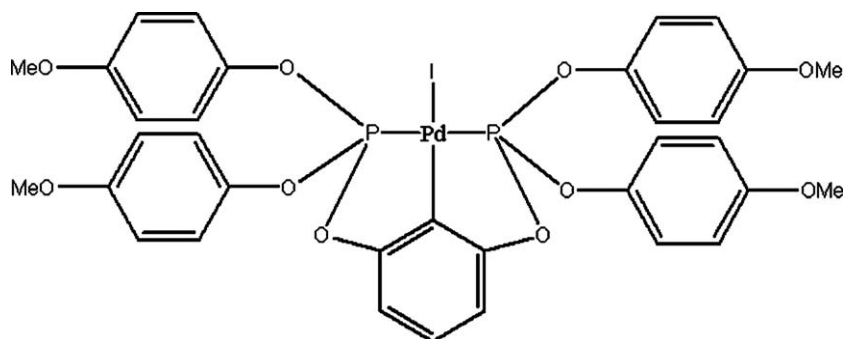


Fig. 3. Shibasaki's catalyst.

three structures from Figs. 2 and 3 were theoretically constructed together with other designed metallic pincers and their geometries were optimized. Molecular properties like natural charges, frontier orbitals HOMO–LUMO and absolute hardness were theoretically obtained, using density functional theory (DFT) as method. For its construction, the DFT model based on Hohenberg–Kohn theorems [7] and Kohn–Sham (KS) orbitals [8], has resulted in a very convenient and suitable way to relate quantum chemical results with chemical reactivity [9]. There are several chemical concepts that can be described by DFT (e.g. atomic charges, HOMO–LUMO gap energy, electronegativity, etc.) [10], some of them commonly used as quantum chemical descriptors.

The orbitals of Kohn and Sham, considering quasi-electrons, have some drawbacks like that coming from the definition of the coulomb potential ( $V_c$ ) where any electron, of all the  $N$  electrons, is considered to move in its own field, which is mathematically convenient but there is no physical sense involved. Within the Hartree–Fock approach this self-interaction is cancelled exactly by an equivalent term in the exchange interaction. In case of DFT methods, this self-interaction cancellation is not complete. Nevertheless, there is a correction known as self-interaction correction (SIC) which has been incorporated to remove this error. This correction has demonstrated its efficiency in the calculated single-particle eigenvalues and total energies [11]. Currently, particularly in the study of molecular structures including transition metals, DFT has demonstrated its applicability as theoretical method, being extensively used in the study of a variety of systems (biochemical systems, metal clusters, polyhydrides of transition metals, etc.) [12].

In the present study, some structure–activity relationships were found for pincer metallic complexes and a predictive tool was generated to estimate the catalytic activity by using only theoretical values of the absolute hardness.

## 2. Computational details

All initial structures were constructed and equilibrated (force field MMFF [13]) using the program Titan 1.0.5. The Geometry optimizations were carried out at DFT level of theory (B3LYP), using LACVP\*+ (included in Jaguar 5.0 program [14]) as basis set; incorporating polarization functions on all atoms not described by core potentials except H, as well as diffuse functions for heavy atoms. The used basis set is a 6-31G basis set which takes into account effective core potentials (ECPs) generated to replace the innermost core electrons for third-row (K–Cu), fourth-row (Rb–Ag) and fifth-row (Cs–Au), integrating relativistic effects (important for heavy atoms) and reducing in this way the computational efforts comparing with all-electron calculations [15]. Particularly the basis sets with initial letters LAC also include the outermost core orbitals (i.e. the  $ns$  and  $np$  orbitals). Natural charges were calculated by Natural Bond orbital analysis [16].

Frontier orbital surfaces and electrostatic potential surfaces were obtained by single point calculations, using Titan 1.0.5 program as interface.

## 3. Results and discussion

Twenty pincer metallic complexes were constructed and theoretically studied. First, 16 complexes were made according to Fig. 4, carrying out systematic modifications in order to evaluate steric and electronic effects. At the same time, four catalysts already prepared and reported in the literature were also constructed with the aim to confront results theoretically obtained with the experiment. In a first stage, taking into account the substituent; R, attached to the heteroatom; E, it was switched from Ph to *i*-Pr, maintaining constant E = nitrogen, X = C and Y = Cl and varying M: Ni, Pd or Pt (see Table 1).

From Table 1, independently of R, the negative charge on M increases as follows: Ni < Pd < Pt; however, when R = *i*-Pr, all the metal centers become less positives and the ionization potential energies are lower too. The ionization energy was obtained, by an approximation, as the negative values of the HOMOs, applying the Koopmans' theorem [17].

Under similar approximations it is possible to calculate the absolute hardness;  $\eta$ , involving the orbital HOMO/

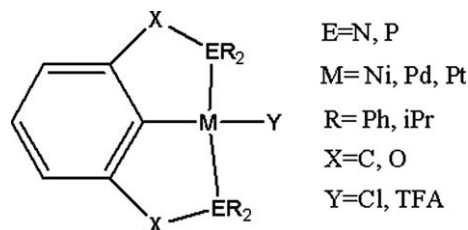


Fig. 4. Modification of pincer metallic complexes.

Table 1  
Quantum chemical descriptors for N-pincer complexes

	Ni–NCN–Ph	Pd–NCN–Ph	Pt–NCN–Ph
E = N, R = Ph			
Charge on M <sup>a</sup>	0.826	0.658	0.606
Ionization potential (eV) <sup>b</sup>	5.864	5.830	5.533
Absolute hardness (eV) <sup>c</sup>	1.986	1.892	2.116
Ni–NCN– <i>i</i> -Pr			
E = N, R = <i>i</i> -Pr			
Charge on M	0.816	0.633	0.569
Ionization potential (eV)	5.722	5.763	5.420
Absolute hardness (eV)	2.132	2.135	2.353

<sup>a</sup> Atomic charges obtained by Natural Bond Orbital analysis.

<sup>b</sup> Vertical values, within the validity of Koopmans' theorem.

<sup>c</sup> Absolute hardness =  $(E_{\text{LUMO}} - E_{\text{HOMO}})/2$ .

LUMO energies since the chemical hardness is related to the energy gap between occupied and unoccupied orbitals. There are several ways to calculate the absolute hardness [18] but the important issue is not mix the methods to obtain it. The common meaning of hardness is the resistance to deformation or change. In a real chemical process, the electronic density experiences a local perturbation, but the response is non-local, thus, second-order derivatives are more appropriate to describe the hardness since it is a non-local function. Using DFT it is possible to calculate:

$$(\partial\eta/\partial N)_v = (\partial^2 E/\partial N^2)_v = 2\eta$$

As it was mentioned above, the quantity  $\eta$  is defined as absolute or chemical hardness. From the method of finite differences [19] it is possible to obtain the next definition:

$$\eta \simeq (I - A)/2$$

where  $I$  and  $A$  are the ionization potential and the electron affinity, respectively. The units of  $\eta$  are usually in eV. Like it was mentioned before, the energies of frontier orbitals can be considered as:

$$-\varepsilon_{\text{HOMO}} = I \quad \text{and} \quad -\varepsilon_{\text{LUMO}} = A$$

therefore, the absolute hardness can be expressed as:

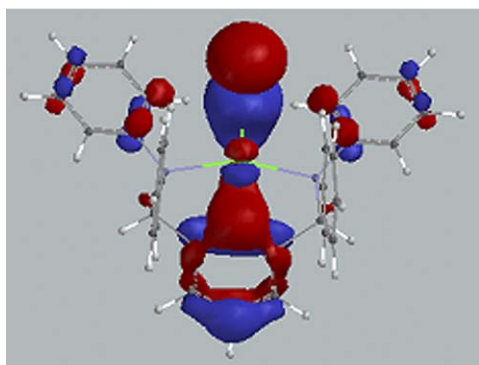
$$\eta = (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})/2$$

Chemically speaking, stable systems are related to high values of hardness, while reactive systems have small hardness values. Hence, according to Table 1, if is taken into account the sentence: “the more reduced the metal center is, the greater the reactivity towards oxidative addition”, the Pt–NCN-complex with R = *i*-Pr could be the best candidate but, if the concept of absolute hardness is considered, the Pd–NCN complex with R = Ph would be the most reactive complex since it has the lowest value of  $\eta$ .

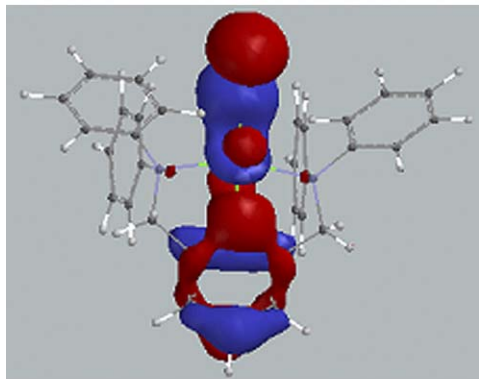
The HOMO–LUMO surfaces were calculated for both, Pd–NCN–Ph and Pt–NCN–*i*-Pr complexes (Fig. 5) by single point calculations at B3LYP/LACVP\* level of theory [20], and the natural atomic orbital occupancies were analyzed.

In case of Pt–NCN–*i*-Pr complex, the major occupancy on the metal d orbitals occurs in the  $d_{x^2-y^2}$ , actually observed in the frontier orbitals. If the crystalline field theory is invoked, the orbital symmetry observed could fit for

Pd–NCN–Ph



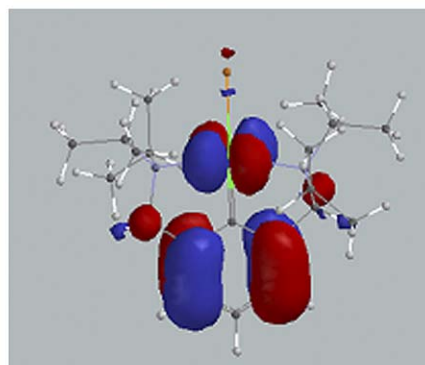
HOMO



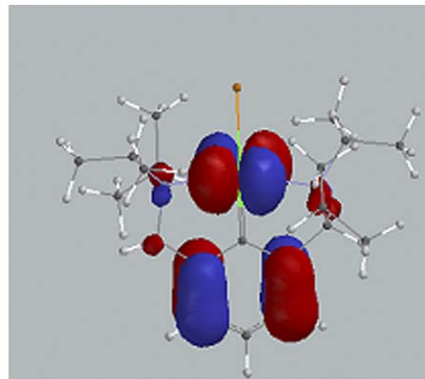
LUMO

$$\eta = 1.892$$

$$\text{Charge} = 0.658$$

Pt–NCN–*i*-Pr

HOMO



$$\eta = 2.353$$

$$\text{Charge} = 0.569$$

Fig. 5. Frontier orbitals for Pd–NCN–Ph and Pt–NCN–*i*-Pr complexes.

a tetrahedral access of external ligands. The halogen does not participate in the frontier orbitals.

On the other hand, the Pd–NCN–Ph complex with the lowest value of absolute hardness showed a very different orbital pattern. The  $d_{z^2}$  orbital predominates in the occupancy but the five d orbitals are mostly in the same level of energy. The HOMO  $d_{z^2}$  symmetry, with a concentrated electronic density along the z-axis, seems to be convenient, leading the metal center as a suitable site to carry out a nucleophilic attack by an antibonding  $\sigma$  interaction. Also an important participation is observed of the halogen in the frontier orbitals, which has sense in terms of reactivity of the complex.

Additionally, the electrostatic potential was mapped onto a surface of electron density to get a description of both, steric and electrostatic characteristics of the two complexes: Pd–NCN–Ph and Pt–NCN–*i*-Pr (Fig. 6). The colors toward blue and red represent positive and negative regions, respectively. Practically the same electrostatic environment is observed in both cases. When the *i*-Pr groups are present there is a slight flattening in front of the reaction site but generally both groups have similar bulky properties.

Thus, the orbital occupancy, the symmetry of the d orbitals and the frontier orbitals gap (directly related to the absolute hardness), are the issues which in fact distinguish both complexes; the electrostatic environment and the atomic charges, although they should contribute in processes like an oxidative addition, apparently they are not preponderant.

Next, according to Fig. 4, E was modified, placing P instead of N, upholding constant X = C and Y = Cl. The results are shown in Table 2.

With E = P the tendency of natural charge on the metal center is preserved: Pt has the less positive charge but remarkably, in this case the positive charge is almost three times fewer than that obtained with E = N.

Again, similar to that obtained before with E = N, the complex with less negative charge on the metal (0.469 for Ni–PCP–Ph in this case), has the lowest value of  $\eta$  and the complex with the highest negative charge on M

Table 2

Quantum chemical descriptors for P-pincer complexes

	Ni–PCP–Ph	Pd–PCP–Ph	Pt–PCP–Ph
E = P, R = Ph			
Charge on M	0.469	0.286	0.214
Ionization potential (eV)	5.800	5.886	5.584
Absolute hardness (eV)	2.131	2.152	2.196
Ni–PCP– <i>i</i> -Pr Pd–PCP– <i>i</i> -Pr Pt–PCP– <i>i</i> -Pr			
E = P, R = <i>i</i> -Pr			
Charge on M	0.465	0.278	0.212
Ionization potential (eV)	5.667	5.774	5.504
Absolute hardness (eV)	2.332	2.379	2.493

(0.212 for Pt–PCP–*i*-Pr) shows a relative low value of  $\eta$ ; thus, an opposite behavior is observed for charge on M and  $\eta$ .

The frontier orbitals for these two complexes were calculated with the same level of theory used before. They are shown in Fig. 7.

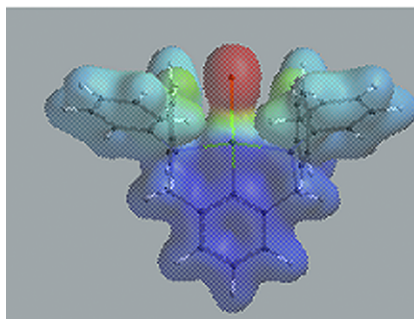
In this case there are coincidences in the symmetry of the d orbitals. The LUMOs have major contribution of the  $d_{xy}$  orbital suitable to accept ligands in an octahedral fashion. The HOMOs have important contribution by occupancy of the  $d_{z^2}$ -like orbitals, already discuss as convenient in terms of nucleophilic attacks. The general observation when P is present as heteroatom is that there is a good compromise between the charge on the metal, the symmetry of the frontier orbitals and the reactivity, estimated by the absolute hardness theoretically obtained.

When the electrostatic potential surfaces were obtained for these complexes with E = P, a clear difference was observed, not between them but between the complexes with E = N (see Fig. 8).

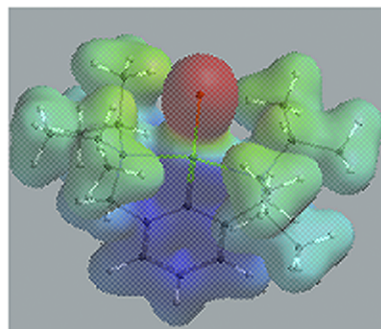
Well defined red zones are observed on the P atoms attached to the metal center, which are totally absent when E = N, so there is an increment of the electron density onto the surroundings of the metal.

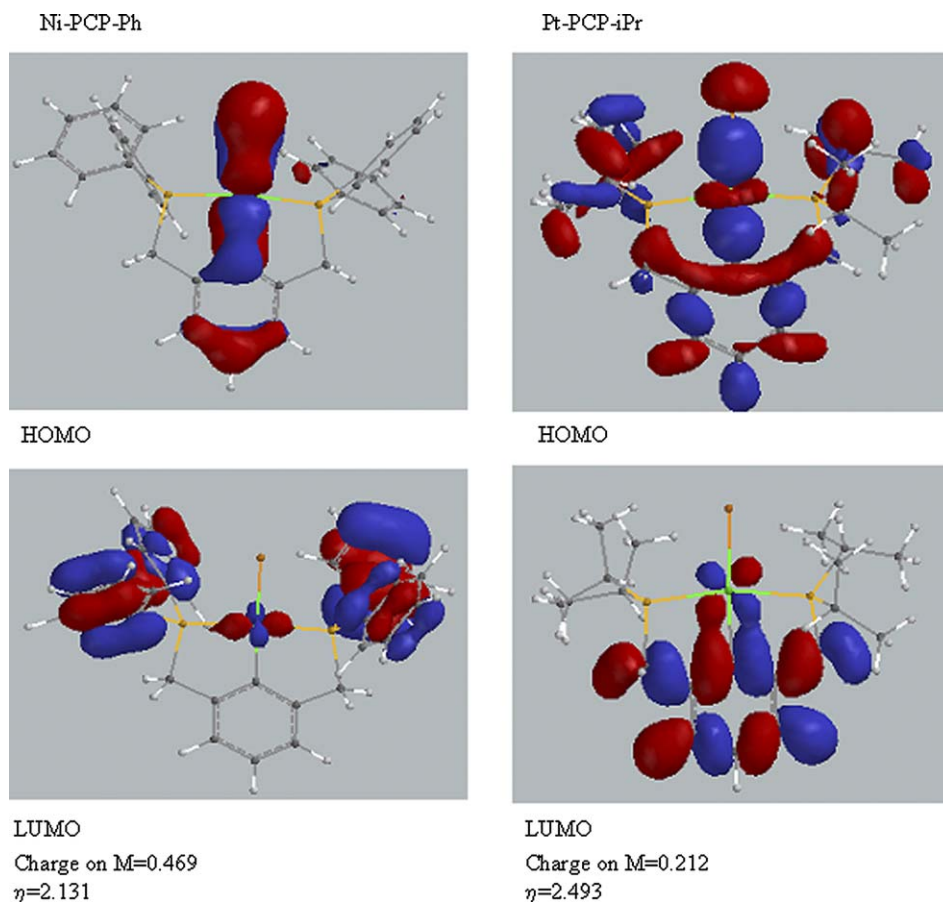
Back to Fig. 4, the next modification made was the change of Y: TFA (–OCOCF<sub>3</sub>) instead of Cl. Considering the complexes with E = P and R = *i*-Pr (in general with less

#### Electrostatic Potential Surfaces (isovalue=0.02)

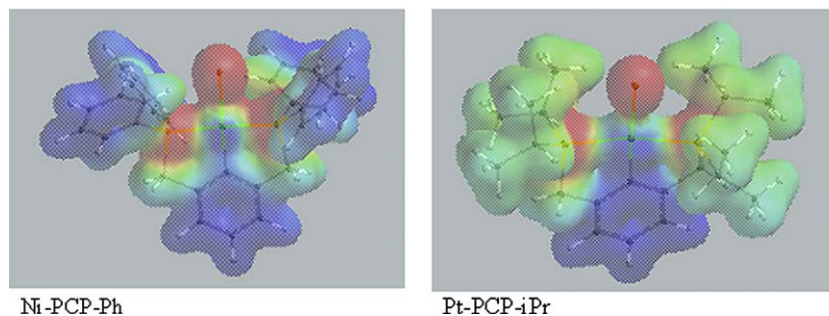


Pd–NCN–Ph

Pt–NCN–*i*-PrFig. 6. Electrostatic potential surfaces for Pd–NCN–Ph and Pt–NCN–*i*-Pr complexes.

Fig. 7. Frontier orbitals for Ni-PCP-Ph and Pt-PCP-*i*Pr complexes.

Electrostatic potential  
(isovalue=0.02)

Fig. 8. Electrostatic potential surfaces for Ni-PCP-Ph and Pt-PCP-*i*Pr complexes.

participation than Ph), the same parameters, charge on M, ionization potential and absolute hardness, were calculated. The results are shown in Table 3.

Under the same analysis done before, this leaving group leads worse conditions in terms of charge on the metal and ionization potentials, comparing with Cl as leaving group.

The calculated frontier orbitals (Fig. 9) show a significant reduction in atomic participation, mainly in the center of the complex. Both, the charge on the metal and the absolute hardness are inferior, according with the criteria

Table 3

Quantum chemical descriptors for P-pincer complexes, with TFA as leaving group

	Ni	Pd	Pt
E = P, R = <i>i</i> -Pr, Y = TFA			
Charge on M	0.536	0.339	0.298
Ionization potential (eV)	6.083	6.244	5.958
Absolute hardness (eV)	2.431	2.503	2.622

considered before for the analysis. Comparing the electrostatic potential surface, the TFA group produce a region toward blue; i.e. positive values of electrostatic potential.

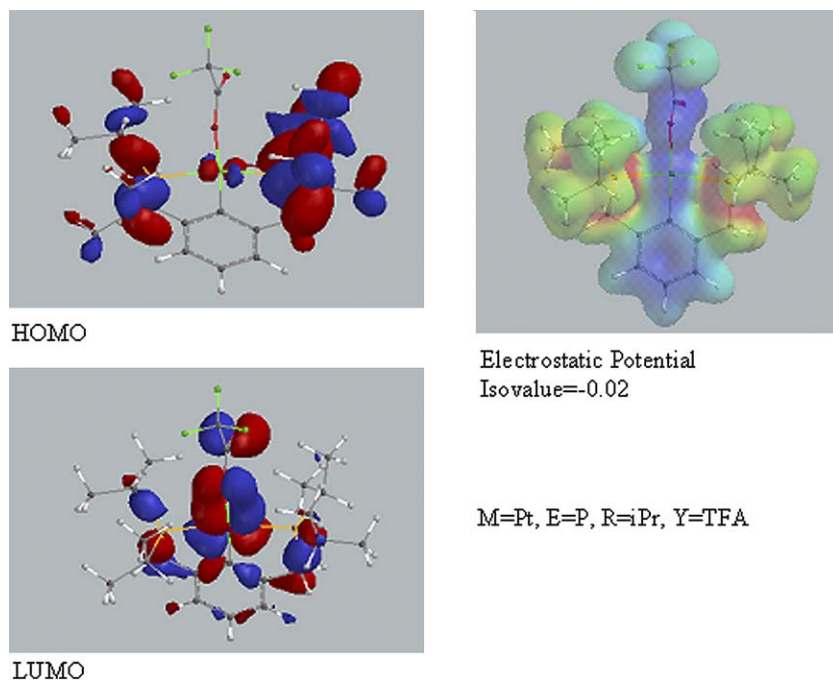


Fig. 9. Change of leaving group: TFA instead of Cl.

According to the theoretical results, Cl is better than TFA as leaving group.

The final modification according to Fig. 4 was the change of X: O instead of C.

The comparison was done only for the Pt-pincer complex with E = P, R = *i*-Pr and Y = Cl. Table 4 shows such comparison between **A** and **B** from Fig. 10.

The expected inductive effects due to the oxygen atoms resulted in a slight increase in negative charge on M and also in a small reduction of the absolute hardness, both favorable effects; but not highly significant.

Thus, from the first part of the study, the presence of P and Cl as part of the pincer complexes seems to provide a good compromise between absolute hardness and charge. On the other hand, among the metal series Ni, Pd, Pt, the Pt pincer complex with R = *i*-Pr, E = P and Y = Cl showed the most negative charge while the Pd pincer complex with R = Ph, E = N and Y = Cl showed the lowest chemical hardness.

From the literature two groups of catalysts were taken: the Milstein's and the Shibasaki catalyst (Figs. 2 and 3, respectively). Using the same level of theory, they were constructed and their quantum-chemical descriptors were calculated (Table 5).

The fourth line of Table 5 corresponds to data of turnover numbers (see Ref. [5]) experimentally obtained for the Heck reaction between PhI and CH<sub>2</sub>=CHCOOR (R = Me, *t*-Bu) at 140 °C.

The same quantum chemical descriptors were calculated for these complexes and their catalytic activity was independently correlated to charge on M and to the absolute hardness, both quantum chemical descriptors, with the aim to construct tools to predict the catalytic activity, only

Table 4  
Quantum chemical descriptors for P-pincer complexes, with and without oxygen in the pincer chain (**B** and **A** respectively)

	<b>A</b>	<b>B</b>
Charge on Pt	0.212	0.204
Ionization potential (eV)	5.504	5.677
Absolute hardness (eV)	2.493	2.413

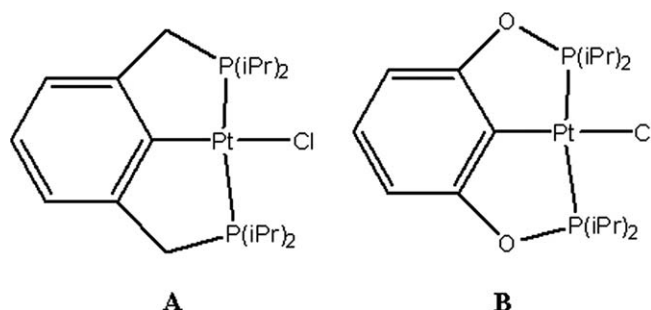


Fig. 10. Evaluation of inductive effects by the presence of oxygen.

Table 5  
Calculated quantum chemical descriptors and turnover numbers (TON) experimentally obtained for pincer complexes taken from the literature

	Milstein-1	Milstein-2	Milstein-3	Shibasaki
Charge on M	0.339	0.378	0.437	0.169
Ionization potential (eV)	6.244	5.576	5.613	5.726
Absolute hardness (eV)	2.503	2.058	1.993	1.809
Turnover number (TON)	267 600	528 700	–	650 000

by the interpolation of one of those descriptors, theoretically obtained.

Two correlations were obtained but the only one showed is that one between the absolute hardness with the TONs with a very good correlation (see Fig. 11). When the natural charges on the metal centers were plotted against TONs, the correlation obtained was of 0.95, being not too much reliable as a predictive tool. This result can be taken as an indication of the orbital-controlled reactivity of these pincer complexes.

To corroborate the applicability of this plot, a different catalyst involved in the same Heck reaction (the same substrates) was considered from the literature. The catalyst is a dimer (Fig. 12) and it was catalogued as highly efficient for the Heck reaction [21].

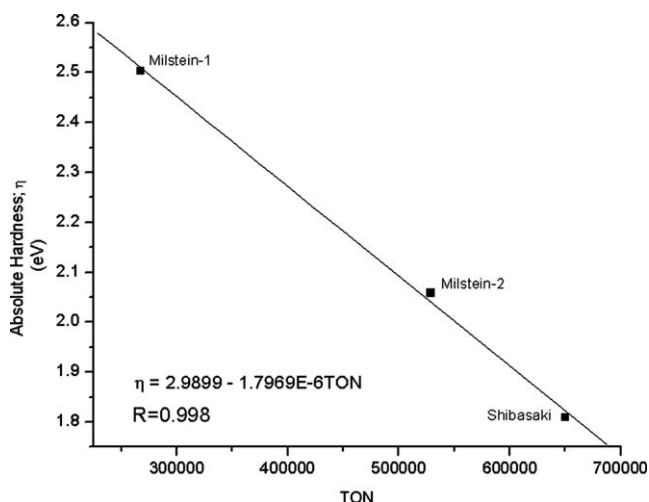


Fig. 11. Absolute hardness vs. experimental turnover numbers. Interpolation tool.

After the same theoretical treatment, the energy of the frontier orbitals was calculated, and the absolute hardness was obtained:

$$E_{\text{HOMO}} = -5.4341 \text{ eV}$$

$$E_{\text{LUMO}} = -3.13784 \text{ eV}$$

$$\eta = 1.14815 \text{ eV}$$

By interpolation, using the expression:  $\text{TON} = (2.9899 - \eta)/1.7969\text{E} - 6$ , a theoretical turnover number value (TON) of 1024959.65 was obtained for this catalyst, predicting correctly the magnitude order observed experimentally since the reported TON experimental value is 1087000. Thus, using quantum chemical descriptors like the absolute hardness it is possible to “assign” reactivity indexes when similar experimental conditions are involved.

Finally, keeping in mind the catalytic process (Fig. 13), only the circled part of the cycle was studied, hence there is more to explore in terms of quantum chemical descriptors.

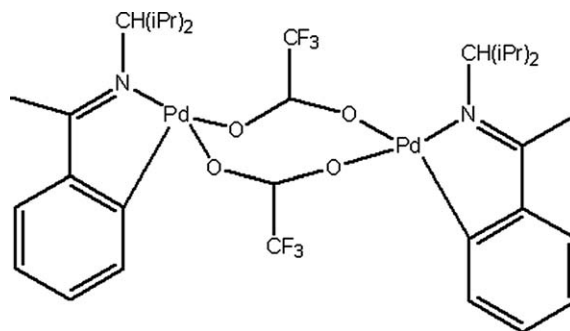


Fig. 12. Milstein's dimeric catalysts.

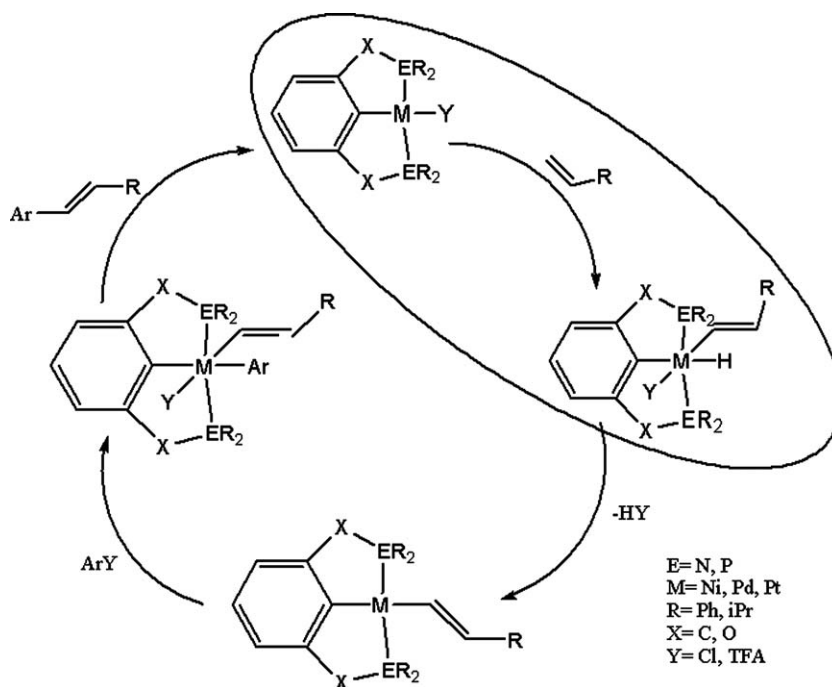


Fig. 13. Catalytic cycle involving pincer metallic complexes.



Further work also will be the theoretical study of the mechanism involved in these kind of catalytic cycles with pincer metallic complexes, in view of the fact that M(II)/M(IV) species could be the catalytically active ones.

#### 4. Conclusions

Twenty pincer metallic complexes were constructed and theoretically studied. Sixteen of them were systematically modified in order to evaluate some electronic and sterical effects, focus on the feasibility to carry out an hypothetical oxidative addition. The last four were taken from the literature with the aim to confront experimental information with quantum chemical descriptors theoretically obtained. The best correlation observed between quantum chemical descriptor and catalytic activity (measured in turnover numbers; TON) was that obtained when the absolute hardness is involved (0.998), allows us to use this linear correlation as predictive tool of the catalytic activity when the same experimental conditions are using.

Lower correlation was observed when the atomic charges were considered, thus suggesting that the reactivity of these pincer complexes is mainly orbital-controlled. The resulting analysis after several modification to the pincer complex structure showed that generally the presence of P as heteroatom and Cl as leaving group gives a good compromise in terms of absolute hardness and charge on the metal center. The symmetry of the frontier orbitals is also an important issue to take into account: HOMOs with  $d_{z^2}$ -like orbital symmetry and LUMOs with  $d_{xy}$ -like orbital symmetry seem to be convenient.

As a final comment, DFT resulted in a good quantum method to calculate these organometallic compounds and the further work, using again the DFT tools, will be the study of the catalytic mechanism when species M(II)/M(IV) are considered.

#### References

- [1] J. March, *Advanced Organic Chemistry*, Wiley, New York, 1992.
- [2] M.Q. Slagt, G. Rodriguez, M.M.P. Grutters, R.J.M. Klein-Gebbink, W. Klopper, L.W. Jenneskens, M. Lutz, A.L. Spek, G. van Koten, *Chem. Eur. J.* 10 (2004) 1331.
- [3] (a) P.A. Patel, C.B. Ziegler, N.A. Cortese, J.E. Plevyak, T.C. Zebovitz, M. Terpko, R.F. Heck, *J. Org. Chem.* 42 (1977) 3903; (b) N.A. Cortese, C.B. Ziegler, B.J. Hrnjez, R.F. Heck, *J. Org. Chem.* 43 (1978) 2952; (c) R.F. Heck, *Org. React.* 27 (1982) 345.
- [4] M. Ohff, A. Ohff, M.E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* 119 (1997) 11687.
- [5] Turnover number (TON) is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the % yield of product.
- [6] F. Miyazaki, K. Yamaguchi, M. Shibasaki, *Tetrahedron Lett.* 40 (1999) 7379.
- [7] P. Hohenberg, W. Khon, *Phys. Rev. A* 136 (1964) 864.
- [8] W. Kohn, L. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [9] H. Chermette, *J. Comput. Chem.* 20 (1999) 129.
- [10] R.G. Pearson, *Chemical Hardness: Applications from Molecules to Solids*, Wiley-VCH, Germany, 1997.
- [11] J.P. Perdew, A. Zunger, *Phys. Rev. B* 23 (1981) 5048.
- [12] E.R. Davidson (Ed.), *Chem. Rev.* 100 (2000) 351–818.
- [13] T.A. Halgren, *J. Comput. Chem.* 17 (1996) 490.
- [14] Jaguar 5.0, Schrodinger, LLC Portland, OR, 2000.
- [15] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [16] E.D. Glendening, J.K. Badenhoop, A.E. Reed, J.E. Carpenter, J.A. Bohmann, C.M. Morales, F. Weinhold, NBO 5.0. Theoretical Chemical Institute, Madison, WI, 2001.
- [17] T.A. Koopmans, *Physica* 1 (1933) 104.
- [18] P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* 103 (2003) 1793.
- [19] Given a sequence, the *method of finite differences* can be used to try to find a polynomial function that either fits or approximately fits the data.
- [20] To chose the level of theory to calculate frontier orbitals, previous calculations were made, attempting DFT and HF methods, considering the experimental ionization potential value for Pt atom as a reference. The  $-$ energy of the HOMO was taken as ionization potential in both cases. DFT gave a 1.6% of error while HF gave a 10.7% of error.
- [21] M. Ohff, A. Ohff, D. Milstein, *Chem. Commun.* (1999) 357.