Substituent Effect in the Chemical Reactivity and Selectivity of Substituted Cobalt Phthalocyanines

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We rationalize the chemical reactivity and selectivity for a set of substituted cobalt phthalocyanines (CoPc(X)$_n$) in terms of the global and local HSAB (hard soft acid base) principle. Electron donating and electron withdrawing groups were used as substituents. At a global level, we analyze the reactivity in terms of the molecular hardness that present each of the species. At a local level, the graphical maps of the Fukui function for identifying the selectivity of the different sites in the substituted cobalt phthalocyanines are obtained. It is shown that the reaction site in a *soft* CoPc(X)$_n$ is associated to a maximum value in the Fukui function. In contrast to this, for a *hard* CoPc(X)$_n$ the Fukui function focus seem not to be the adequate criterion to identify the reaction site. The results obtained at the PM3(tm) semiempirical level lead to conclude that the interactions with the CoPc(X)$_n$ species will be governed by *hard*−*hard* and *soft*−*soft* interactions.

1. Introduction

Many experimental studies are currently published on porphyrins and derivatives due to the characteristics of these compounds in relation to the attractive coordination chemistry that they present. These systems also are interesting due to the several applications which include such as dyes, sensors, medical therapy, etc. which are a consequence of their properties of high thermal and chemical stability, catalytic activity, high optical absorption in the visible range and electrical properties.[1−7] From a theoretical viewpoint, many studies have been published in porphyrins and aza derivatives. As an example, we may mention those studies covering aspects such as molecular structures and conformations.[8−14] electronic spectra,[15,16] ground-state electron distributions and configuration interaction,[17,18] ionization potentials, frontier molecular orbitals, molecular hardness, donor acceptor hardness, and Fukui function.[19−27]

Ab initio techniques (Hartree−Fock or density functional theory, DFT) applied to transition metal macrocycles constitute a complete challenge considering the large size of these molecules and in consequence the difficult to get an optimized structure to that level of calculation. However, semiempirical methods are a good alternative because present the advantage to be also based on a quantum mechanical framework. As these methods use a more approximate Hamiltonian and compensate with empirically fit parameters, they are much less costly than ab initio calculations. Thus, while ab initio methods can be applied very well to small molecules, semiempirical methods can be used to study relatively large molecules or collection of molecules. PM3(tm) semiempirical model, that is an extension of the standard PM3 method for transition metal (tm) elements, has proven to be quite successful for the calculation of equilibrium geometries, including the geometries of transition metal inorganic and organometallic compounds.[28−33]

Reactivity descriptors defined in the context of the density functional theory such as hardness and softness have been widely used to rationalize the reactivity in a chemical system.[34−38] Although in principle hardness and softness are global properties, there exist a permanent development in the construction of these properties from a local viewpoint. While the global hardness and softness give the chemical reactivity, the local softness predicts the site selectivity or site specificity in a chemical reaction. Another important local reactivity index is the Fukui function which was introduced on a first time by Parr and Yang.[39] This index has been used in the literature in order to analyze differents kind of chemical reactions.[40−43]

We have used previously DFT based reactivity descriptors to predict the reactivity of several substituted transition metal phthalocyanines and porphyrin when they interact with small molecules (2-mercaptoethanol (2ME), hydrazine, hydroxilamine, and molecular oxygen).[19−20,22−26] In these articles, the molecular hardness and donor acceptor hardness have been determined at PM3(tm) semiempirical level and at ab initio Hartree−Fock (CEP-31G and 6-31G) level. These reactivity indexes calculated have shown a good agreement in the reactivity trend calculated in comparison with the trend obtained by using experimental values of rate constants.[19−20,22−26] In relation to this, we also found a better agreement to the experimental values with PM3(tm) results than with ab initio Hartree−Fock results.[24] On the other hand, graphical maps of Fukui function and local hardness obtained with the PM3(tm) semiempirical method for the supermolecule CoPc···2ME along the reaction coordinate the distance Co···S(2ME) show to be very useful in the prediction of the preferred reaction site.[26]

In this article we propose the understanding of the chemical reactivity and the selectivity of a set of substituted cobalt phthalocyanines (CoPc(X)$_n$) in terms of the global and local HSAB (hard soft acid base) principle. In a first stage, we determine the molecular hardness of CoPc(X)$_n$ species in order to establish the global chemical reactivity that they present and to classify them in terms of the *soft* and *hard* concepts. Then the Fukui function is used to obtain the selectivity for each the molecules and to identify the corresponding reaction sites. Global and local indexes give a criterion to classify the species as *hard* or *soft*. It is important to mention that, as a first approximation we are interested in the obtention of the trend of reactivity that CoPc(X)$_n$ species present as a function of the

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kind of substituent by using some DFT-indexes and not in the accuracy of the level of calculation. Thus, in this article a PM3-(tm) calculation parameterized for transition metals is enough to get a good description of the systems studied here.

2. Theoretical and Computational Details

Global and local reactivity descriptors that were defined by the DFT such as molecular hardness (η) and Fukui function ($f(\vec{r})$), respectively, were used. Molecular hardness was determined by using the following approximation:[34−36]

$$\eta = \frac{1}{2}(I - A) \qquad (1)$$

where I (ionization potential) and A (electron affinity) are obtained of ΔSCF calculations, that is, $I = E^{+1} - E^{0}$ and $A = E^{0} - E^{-1}$. Here E^{+1} and E^{-1} correspond to the total energy of the cation and anion of the CoPc(X)$_n$, respectively, and E^0 correspond to the total energy associated to the neutral state of the CoPc(X)$_n$. Molecular hardness only provides information about the global reactivity of the CoPc(X)$_n$.

The Fukui function ($f(\vec{r})$) is a local reactivity descriptor and provides the reactivity site most probable where the reaction would occur. It is defined as[39]

$$f(\vec{r}) = \left(\frac{\delta\mu}{\delta\nu(\vec{r})}\right)_N = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_\nu \qquad (2)$$

where μ is the electronic chemical potential, ν is the external potential, ρ corresponds to the electronic density, and N is the total number of electrons of the system. The second formula for $f(\vec{r})$, written as $[\partial\rho(\vec{r})/\partial N]_\nu$, shows that it is a quantity involving the electron density of the atom or molecule in its frontier, that is the valence region. In other words, the Fukui function shows the site of highest reactivity because it gives the largest variation in the electronic density for a molecular system when it accepts or donates electrons. We may then assume that the preferred site is the one with largest value of $f(\vec{r})$ at the reaction site. Equation 2 as such provides three reaction indexes, because $\rho(\vec{r})$ as a function of N has slope discontinuities.[39] One therefore can define three different types of Fukui function:

$$f^{+}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{+}_{\nu(\vec{r})} = [\rho_{N+1}(\vec{r}) - \rho_{N}(\vec{r})] \approx \rho_{\mathrm{LUMO}}(\vec{r}) \qquad (3)$$

governing nucleophilic attack,

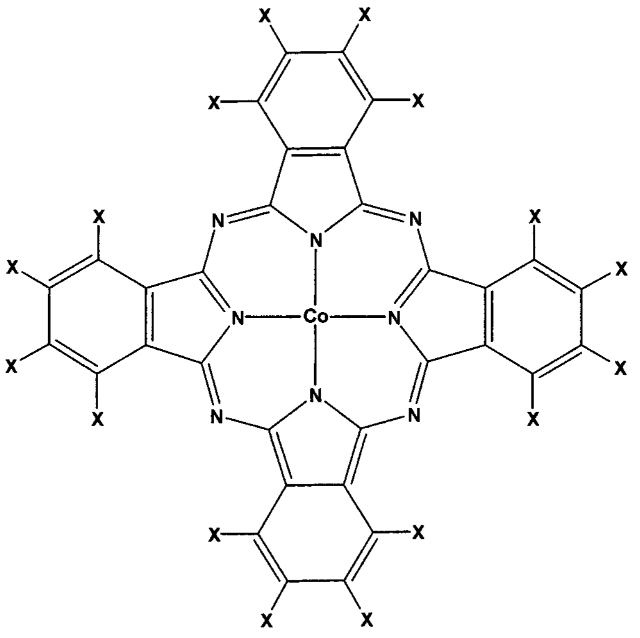
$$f^{-}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{-}_{\nu(\vec{r})} = [\rho_{N}(\vec{r}) - \rho_{N-1}(\vec{r})] \approx \rho_{\mathrm{HOMO}}(\vec{r}) \qquad (4)$$

governing electrophilic attack,

$$f^{0}(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)^{0}_{\nu(\vec{r})} = \frac{1}{2}[f^{+}(\vec{r}) + f^{-}(\vec{r})] \approx \frac{1}{2}[\rho_{\mathrm{LUMO}}(\vec{r}) + \rho_{\mathrm{HOMO}}(\vec{r})] \qquad (5)$$

governing radical attack.

If we adopt a molecular orbital viewpoint and use the "frozen core" assumption, where $d\rho = d\rho_{\mathrm{valence}}$, $f(\vec{r})$ can be identified with the electron density of the frontier molecular orbital involved.[39] Thus as an approximation the second right term appearing in eqs 3−5 is used for the Fukui function associated to the three different attacks. Here HOMO and LUMO are the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. These are just approximate rules for classical frontier orbital theory, as proposed by Fukui.[44−47] In a graphical way one may construct Fukui function maps by putting the FMO (frontier molecular orbital) on an isosurface of the electronic density.[26,48,49] It allows to identify the reactivity sites through which the reaction occurs. It is important to note that the Fukui function is a reactivity index based in the electronic density which has a physical meaning in contrast to the FMO which have not.



X = H, OH, SH, CH_3, CH_3O, COOH, NH_2, NO_2, SO_3H, $NHCH_3$, NCH_3CH_3, CN, OCH_2CH_3, F, Cl, $OCH(CH_2CH_3)_2$

Figure 1. Structure of the substituted cobalt phthalocyanine (CoPc-(X)$_n$) where X represents the substituent atom or group.

SCF/MO theoretical calculations were performed at PM3-(tm) semiempirical level for a set of 22 molecules of CoPc-(X)$_n$, where X represent the substituent, with the TITAN package.[50] A general view of the molecular structure and the kind of substituent used for CoPc(X)$_n$ is presented in Figure 1. Note that we have used a different number of substituents for each CoPc substituted. In particular, the 22 CoPc(X)$_n$ molecules that were studied correspond to a CoPc where X corresponds to H; a CoPc(X)$_{16}$ configuration which was applied to the F, Cl, and COOH substituents; a CoPc(X)$_8$ configuration which was used to the CH_3O, SH, CH_3, COOH, NO_2, NCH_3CH_3, F, CN, and OCH_2CH_3 groups; a CoPc(X)$_4$ configuration which was used to the CH_3O, SO_3H, OH, SH, ($OCH(CH_2CH_3)_2$), NH_2, CH_3, and $NHCH_3$; and finally a CoPc(X)$_2$ configuration which was only applied to the CH_3O group. Note that we have used two kind of substituent groups, electron donating or electron withdrawing groups, to discover the influence of the substituent on the global (molecular hardness) and local (Fukui function) reactivity. We performed a full optimization for each the species. Initially the structures were minimized by using the MMFF94 molecular mechanic method provided by TITAN[50] to get a good guess structure and then we use the PM3(tm) method relaxing all the structure. The multiplicity used for all the complexes is a doublet that is given by the presence of the cobalt atom which

TABLE 1: Values of Molecular Hardness (η) (eV), Cobalt Net Charge (q^{Co}) and Fukui Function for Cobalt f^-_{Co} Determined for the Set of CoPc(X)$_n$ at the PM3(tm) Semiempirical Level of Calculation

molecule	η	q^{Co}	f^-_{Co}
With A Substituent			
CoPc(CH_3O)$_2$	2.386	−0.295	0.019
CoPc(CH_3)$_8$	2.386	−0.290	0.019
CoPc(CH_3O)$_8$	2.384	−0.293	0.021
CoPc(CH_3O)$_4$	2.378	−0.291	0.019
CoPc(SH)$_4$	2.374	−0.289	0.014
CoPc(OCH_2CH_3)$_8$	2.374	−0.289	0.020
CoPc(NH_2)$_4$	2.364	−0.290	0.014
CoPc($NHCH_3$)$_4$	2.346	−0.290	0.014
CoPc(NCH_3CH_3)$_8$	2.344	−0.290	0.017
CoPc(OCH(CH_2CH_3)$_2$)$_4$	2.342	−0.290	0.020
CoPc(F)$_8$	2.341	−0.309	0.015
CoPc(COOH)$_8$	2.329	−0.298	0.023
CoPc	2.309	−0.313	0.015
CoPc(OH)$_4$	2.282	−0.325	0.014
CoPc(CH_3)$_4$	2.276	−0.324	0.015
CoPc(NO_2)$_8$	2.013	−0.318	0.016
With B Substituent			
CoPc(F)$_{16}$	4.342	−0.191	0.000
CoPc(Cl)$_{16}$	4.110	−0.193	0.000
CoPc(SH)$_8$	4.109	−0.195	0.000
CoPc(CN)$_8$	3.834	−0.170	0.000
CoPc(SO_3H)$_4$	3.782	−0.172	0.000
CoPc(COOH)$_{16}$	3.452	−0.173	0.001

present an unpaired electron in their HOMO molecular orbital. All of the structures were used with a zero total charge.

3. Results and Discussion

3.1. Global Property: Molecular Hardness. The substituent effect for a set of molecules may be studied in many chemical properties. In this article, we investigated the substituent effect on the reactivity of different substituted cobalt phthalocyanines. The reactivity has been studied from the determination of the molecular hardness which is obtained of PM3(tm) semiempirical calculations using eq 1. The results of η are shown in Table 1. In this article it has been used the A and B nomenclature for the substituents in order to classify the CoPc(X)$_n$ molecules in two groups, *soft* and *hard*. The classification in two groups is only based in the hardness values calculated in this work. We observe from this Table that the groups such as OR, OH, SH, CH_3, CH_3O, NH_2, NR_2, and NO_2 produce in the molecule of CoPc(X)$_n$ a decrease in the hardness value with respect to the respective value of CoPc(X)$_n$ with substituents such as F, SO_3H, CN, COOH, and Cl where the hardness present a highest value. Then we can establish that the A substituents produce a *soft* CoPc(X)$_n$ and the B substituents produce a *hard* CoPc(X)$_n$. Note that the number of substituents in a CoPc(X)$_n$ molecule also affect to the hardness value. For example, sixteen (16) fluor atoms as substituents giving CoPc(F)$_{16}$ produce a *hard* CoPc(X)$_n$, however eight (8) fluor atoms as substituents, that is, CoPc(F)$_8$, produce a *soft* CoPc(X)$_n$. The A substituents are being electron donating and the B substituents are being electron withdrawing indicating that in both cases a resonance effect is occurring between the substituent and the cobalt macrocycle. We may to mention that all of the CoPc(X)$_n$, which were fully optimized, are nearly planar structures although they are not completely planar, a C1 point group is obtained from the calculations. On the other hand, the reactivity of the CoPc(X)$_n$ is given by the frontier of the molecule, that is by the cobalt atom that contains *d* electrons. Therefore, the softness or the hardness of the CoPc(X)$_n$ determined by the A or B substituents, respectively, is widely connected with the properties of the cobalt atom. To rationalize in quantitative terms the substituent effect on the cobalt atom we correlated the molecular hardness of CoPc(X)$_n$ with the net charge of the cobalt atom (q^{Co}) derived from the natural atomic orbital approximation. The results obtained at PM3(tm) level of calculation are shown in Figure 2. We observe that a linear relationship is obtained between η and q^{Co} with a linear regression coefficient of ~0.9. In this figure we see clearly two regions well defined, one region presenting the lowest values of hardness is associated to values more negative of q^{Co}, the another region presenting the highest values of hardness is related to values less negative of q^{Co}. The kind of substituents in the CoPc(X)$_n$ molecule is determinant on their reactivity which is stated in a global property as the molecular hardness and in a local property as the net charge on the region of the cobalt atom. CoPc(X)$_n$ will be *soft* when the electronic density of the frontier of the molecule, given by the cobalt atom, increase which is stated in a q^{Co} more negative. Likewise, the CoPc(X)$_n$ will be *hard* when the electronic density of the frontier of the molecule, given by the cobalt atom, decrease, that is seen in a q^{Co} less negative. It is important to mention that in the comparison of the numerical values of the molecular hardness of the CoPc(X)$_n$, these should be seen in a relative way in order to classify them in two groups, *soft* or *hard*, and not in an absolute way. Finally, we can say that the information about of the reactivity of CoPc(X)$_n$ provided by the hardness can be very useful at an experimental level when the design of transition metal complexes with a high activity in charge-transfer processes is the main objective.

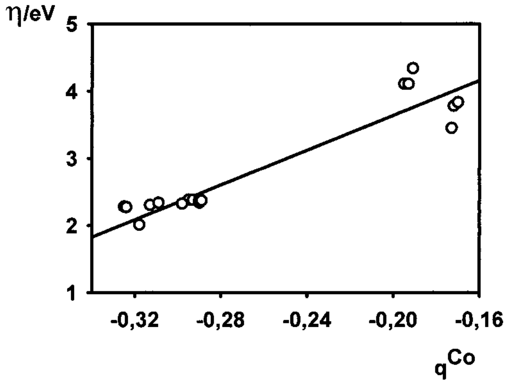


Figure 2. Theoretical correlation between the molecular hardness (η) (eV) of CoPc(X)$_n$ compounds and the net charge of the cobalt atom (q^{Co}).

It is clear that many other factors are important to consider in a chemical interaction, the symmetry of frontier molecular orbitals (FMO),[25] orbital overlap and donor acceptor hardness[23,24] being the latter determined by the energy of the FMO. However, we have shown that an analysis uniquely based in the molecular hardness is useful because it gives a trend of reactivity for the CoPc(X)$_n$ compounds. These results together to the HSAB principle will permit us to rationalize the major or minor affinity of a CoPc(X)$_n$ complexe with a species in a charge-transfer process. At theoretical level many compounds may be studied and their hardnesses calculated, which represent an advantage in order to take the best choice in an experimental study in relation to produce the highest activity for a charge-transfer reaction.

3.2. Local Property: Fukui Function. A local reactivity descriptor is useful not only to identify the selectivity sites in a molecule but also to show their range of application, that is that allow to explain a chemical behavior. We calculated at PM3(tm) level of calculation the Fukui function $f^-(\vec{r})$ for the

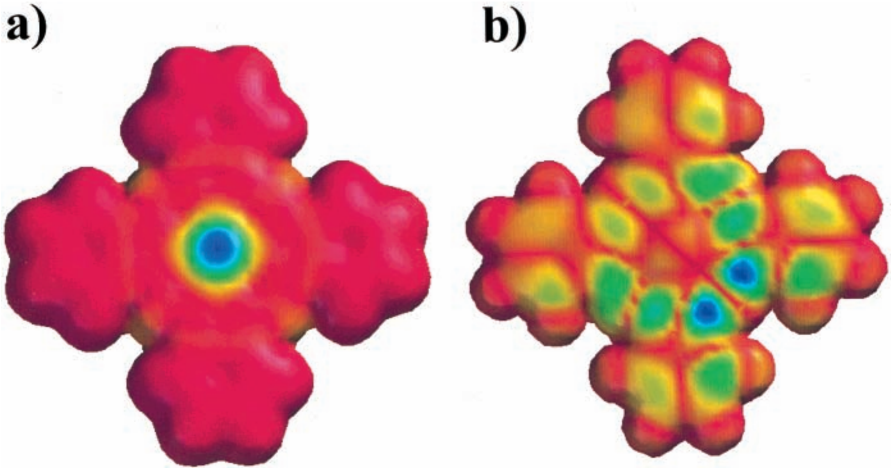


Figure 3. Graphical results of the Fukui function mapped into the charge density isosurface of 0.002 e/bohr^3 for one: (a) *soft* CoPc(X)$_n$, (b) *hard* CoPc(X)$_n$.

set of CoPc(X)$_n$. The results for $f^-(\vec{r})$ are obtained in terms of graphical maps and the numerical values for the cobalt atom are presented in Table 1. Since similar Fukui function maps are obtained for the group containing the A substituents, it has been chosen as an ilustration one of them to be present in Figure 3. The same is applied to the molecules containing the B substituents, one of the Fukui function maps obtained is presented in Figure 3. Thus, the $f^-(\vec{r})$ mapped in terms of a surface for one *soft* CoPc(X)$_n$ and for one *hard* CoPc(X)$_n$ is shown in Figure 3. We choose to analyze only one kind of Fukui function, that is $f^-(\vec{r})$, because the CoPc(X)$_n$ is an open shell molecule and their HOMO molecular orbital can act as a donor or an acceptor in a chemical reaction. In this Figure the extremum values correspond to the blue and red colors. So, the blue colors means the maximum value of $f^-(\vec{r})$ and the red color is associated to a minimum value of $f^-(\vec{r})$ such as zero. Intermedies values are given in yellow color. The highest values in these maps indicate the site more electrophilic and therefore where is concentrated the charge in the frontier of the molecule. The maps displayed in Figure 3 show that the maximum value of $f^-(\vec{r})$ for a *soft* CoPc(X)$_n$ is localized on the cobalt atom. In contrast, the maximum value of $f^-(\vec{r})$ for a *hard* CoPc(X)$_n$ is localized rather on the carbon atoms in the neighboring of the aza-nitrogen atoms or on the oxygen atoms than in the cobalt atom. In agreement with the HSAB principle, we may say that a *soft* CoPc(X)$_n$ will prefer to interact with a *soft* molecule. Likewise, a *hard* CoPc(X)$_n$ will prefer to interact with a *hard* molecule. We may conclude that for *hard*−*hard* interactions the Fukui function is not an adequate descriptor to identify the reaction site because does not show it. However, for *soft*−*soft* interactions the Fukui function is a good selectivity descriptor because it show exactly the reaction site that we would hope. Since the *hard*−*hard* interactions are *charge controlled reactions* and not *frontier controlled reactions* as the *soft*−*soft* interactions, Chattaraj says that the maximum net charge could be a good criterion instead of the Fukui function to identify the preferred site of the reaction.[42] We investigated the values of the net charge for the *hard* CoPc(X)$_n$ by using the natural atomic orbital approximation, that is for CoPc(F)$_{16}$, CoPc(SO$_3$H)$_4$, CoPc(SH)$_8$, CoPc(Cl)$_{16}$, CoPc(COOH)$_{16}$, and CoPc(CN)$_8$. We found that the maximum negative net charge occurs for the cobalt atom in the CoPc(F)$_{16}$, CoPc(SH)$_8$, CoPc(Cl)$_{16}$, and CoPc(CN)$_8$ molecules. In contrast to this, in the case of the CoPc(SO$_3$H)$_4$ and CoPc(COOH)$_{16}$ molecules we found that the maximum value of the negative net charge is obtained in the oxygen atoms instead of the cobalt atom. These results show that the SO$_3$H and COOH groups be behavior as electron withdrawing stronger than the another susbtituents leading to *hard* species due mainly to the presence of the oxygen atoms, which is in agreement with a resonance effect occurring between the susbtituent group and the cobalt macrocycle. In summary, the maximum net charge could be a good criterion in the identification of the preferred site of a reaction for a *hard* species. Note that if the criterion of net charge does not give enough information then an alternative criterion based in an electronic property must be considered.

4. Conclusions

We have shown that the molecular hardness, obtained from PM3(tm) calculations, is a good reactivity index to know the relative reactivity in a set of substituted cobalt phthalocyanines (CoPc(X)$_n$) by using electron donating and electron withdrawing substituents. We also explain the substituent effect on the cobalt phthalocyanines in terms of local electronic properties such as the cobalt net charge. From a local viewpoint, we determine the selectivity along the molecule CoPc(X)$_n$ by using the Fukui function ($f^-(\vec{r})$). We demonstrated that the Fukui function predicts very well the reaction site for the *soft* CoPc(X)$_n$. In contrast, $f^-(\vec{r})$ does not show the reaction site in the *hard* CoPc(X)$_n$. However, we shown that for the *hard* CoPc(X)$_n$, with the exception of those molecules containing oxygen atoms, an electronic property such as the net charge of the cobalt atom is useful to indicate the reaction preferred site. Hardness and Fukui function provides an important information to rationalize those charge transfer reactions that involve transition metal macrocycles. Further, these indexes together to the HSAB principle are convenient to use when the design of highly active species in these kind of reactions is the main objective.

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