

Density Functional Studies on the Catalytic Activity of Core-Functionalized Dendrimers

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This paper presents a theoretical approach to the prediction of the relative catalytic power of structurally related core-functionalized dendritic catalysts. Using this approach, we have studied two palladium complexes integrating dendronized alkylsilyl chains linked to the *p*-carbon atoms of the phenyl groups of the arylphosphine ligands, which are of general formula $[\text{PdCl}_2(\text{L})_2]$ and named with 3a and 3b, respectively ($\text{L} = [\text{P}(\text{C}_6\text{H}_5)_n((\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SiEtMe}_2)_3-n)]$, n equals 2 for 3a and 1 for 3b, respectively). The computational results rationalize the experimental finding that better catalytic efficiency was observed for 3b in a selected Heck coupling reaction in supercritical carbon dioxide (scCO_2) compared with that of 3a.

1. Introduction

From the beginning, catalysis has been recognized as one of the main potential applications of dendritic molecules.¹ There are two general strategies for the design of dendritic catalysts. One strategy is to locate multiple catalytic sites in the surface of the dendrimer.² The other is based upon the installation of one single catalytic site at the core of the dendrimer. Several groups have reported core-functionalized dendrimers as examples of the second strategy.^{3,4} A molecular dynamic research on dendritic architectures of this kind has been published.⁵ According to the conclusion drawn in the article, for the structurally related dendritic catalysts with one single active site at the core, the efficiency of the catalytic process decreases with the size and/or the degree of ramification of the dendrimer provided that the dendritic regions do not participate in the chemical transformation.

However, there exists a departure from the behavior of catalysts predicted by the conclusion. A very recent paper described the employment of palladium compounds as precatalysts in a homogeneous Heck coupling reaction between iodobenzene and methyl acrylate in supercritical carbon dioxide (scCO_2).⁴ These metal complexes were constructed by appending carbosilane dendrons to the arylphosphine ligands coordinated to palladium. To compare the catalytic power of these complexes, the corresponding experiments have been carried out in scCO_2 with triethylamine present as a base and palladium complexes as precatalysts.⁴ It was reported that when 3b was applied, the homogeneous palladium-catalyzed Heck reaction yielded more of the product under the same reaction conditions with a large excess of methyl acrylate (conversion of 38 or 42% to the coupled product was found using 3a or 3b as precatalysts, respectively. The reaction temperature is 373 K). To gain a deeper insight in this respect, we have developed an improved method combining density functional calculation with the hard-sphere collision theory.⁶ We hope our work can motivate the development of dendritic systems research.

2. Method

According to the hard-sphere collision theory,⁶ the kinetic constant k_{coll} associated with the collision of two reagents to

give a chemical transformation is given by

$$k_{\text{coll}} = \sigma^* (8kT/\pi\mu)^{1/2} N_A \exp(-\Delta E_a/RT) \quad (1)$$

where σ^* is the reactive collision cross section which can be expressed as

$$\sigma^* = P\sigma \quad (2)$$

with P being the steric factor and σ the spheric collision cross section.

In eq 1, μ is the reduced mass of the reactants described by eq 3

$$\mu = (1/m_1 + 1/m_2)^{-1} \quad (3)$$

and ΔE_a is the activation energy, the remaining symbols of eq 1 having their usual meaning.

It is assumed that σ is linearly related to the solvent accessible surface S_{AS} . In addition, for a given family of structurally related catalyst, P can be taken as inversely proportional to the molecular weight M_w of the catalyst. Therefore, for the dendrimers described above, the reactive collision cross section σ^* can be approximated as

$$\sigma^* = \alpha S_{\text{AS}}/M_w \quad (4)$$

where α is a proportionality constant.⁵

So a plot of k_{coll} versus $\mu^{-1/2} S_{\text{AS}}/M_w$ will be linear with a slope of $\alpha(8kT/\pi)^{1/2} N_A \exp(-\Delta E_a/RT)$.

It is easy to see from eq 1 that the activation energy ΔE_a plays a dominant role in deciding the kinetic constant k_{coll} . However, the theoretical calculation of activation energy ΔE_a involving macromolecules is very difficult. Alternatively, we propose a new strategy to make a qualitative analysis. This strategy is based on the correlation between the reactivity of chemical species and their intrinsic electronic properties. It has been suggested by Olive and Olive that the larger the amount of positive charges the central metal bears, the lower the activity of organometallic catalyst will be detected.⁷ The frontier orbital theory of Fukui must also be mentioned. Relating the reactivity of a molecule with respect to electrophilic and nucleophilic attack to the charge density, the Fukui theory is one of the most successful and best-known methods to assess the reactivity of

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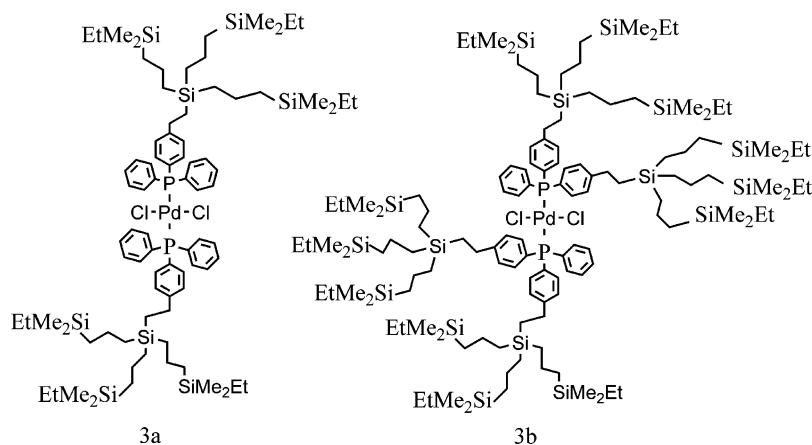
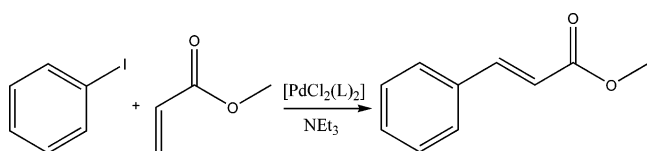


Figure 1. Palladium Complexes of 3a and 3b.

SCHEME 1: Heck Coupling Reaction of Iodobenzene in scCO_2 

regions of a molecule.⁸ The Fukui functions measure the sensitivity of the charge density $\rho(r)$ with respect to the loss or gain of electrons via the expressions

$$f^+(r) = (\rho_{N+\Delta}(r) - \rho_N(r))/\Delta N \quad (5)$$

$$f^-(r) = (\rho_N(r) - \rho_{N-\Delta}(r))/\Delta N \quad (6)$$

where ΔN denotes the number of electrons removed or added for the calculation of the charge density of the ions. In conventional computations, a value of 1.0 is used for ΔN .

The $f^+(r)$ Fukui function measures changes in the charge density when the molecule gains electrons and, hence, corresponds to reactivity with respect to nucleophilic attack. Conversely, the $f^-(r)$ function corresponds to reactivity with respect to electrophilic attack (loss of electrons). Being the average of $f^+(r)$ and $f^-(r)$, the $f^0(r)$ function reflects susceptibility to attack by radicals. In each case, greater values reflect a greater susceptibility to attack. Quantitative predications can be obtained for any atom of a molecule from the Fukui functions assigned to the specific atom. If the catalytic centers of the dendrimers have greater susceptibility to attack, the activation energy would be smaller.

As stated above, we can estimate the catalytic power of core-functionalized dendrimer with resort to the value of $\mu^{-1/2} S_{AS}/M_w$ and the intrinsic electronic properties of the active center.

The details of the work are as follows.

First, the density functional method implemented in the DMol3 module of the *MS Modeling* package⁹ was utilized to optimize the initial geometries of palladium complexes. A generalized gradient-corrected exchange-correlation functional PW91¹⁰ in combination with DND basis set was adopted in all density functional theory (DFT) calculations. The size of the DND basis is comparable to Gaussian 6-31G* basis sets. However, the numerical basis set is much more accurate than a Gaussian basis set of the same size. The specified geometry optimization convergence tolerance for the displacement vector was 0.005 Å. The threshold for energy convergence during

TABLE 1: Structural Parameters of 3a and 3b

entry	Pd precatalyst	formula	M_w (g/mol)	S_{AS}^a (Å ²)
1	3a	$\text{C}_{82}\text{H}_{138}\text{Cl}_2\text{P}_2\text{PdSi}_8$	1587.93	1817.39
2	3b	$\text{C}_{128}\text{H}_{246}\text{Cl}_2\text{P}_2\text{PdSi}_{16}$	2473.96	2951.69

^a Computed with a probe radius of 1.1 Å.

geometry optimization was 2.0×10^{-5} hartree. The gradient convergence criterion for geometry optimization was 0.004 hartree per angstrom. The geometry was considered optimized when the gradient convergence criterion was satisfied and either the displacement convergence or energy convergence criteria were satisfied. Considering the existence of apolar branches located at the periphery of the palladium complex, we think that the charge distribution of the solute molecule will not polarize a low-polarity dielectric medium significantly and induce strong electrostatic interaction that has great impact on molecular conformation. Hence, the molecular systems studied were treated as in the gas phase, which may represent the most apolar medium condition.

The subsequent processes of computation were performed on the basis of the optimized structures. The solvent accessible surfaces (S_{AS}) of the dendritic molecules were obtained by use of *Cerius 2* package. The average C–H distance of 1.10 Å is selected as the probe radius to measure S_{AS} , since this is the bond to be broken as a consequence of the effective collision of methyl acrylate and the catalysts. Population analysis and the computation of Fukui function were processed with the DMol3 module of the *MS Modeling* package.

3. Evaluation of the Catalytic Power of Palladium Complexes. The DFT studies suggest that for molecules of palladium complexes the chemical reactivity of central Pd and the value of $\mu^{-1/2} S_{AS}/M_w$ increase from 3a to 3b with the increasing number of dendronized alkylsilyl chains linked to phosphine ligands, as can be used to explicate the better catalytic efficiency of 3b.

The structural parameters of 3a and 3b are collected in Table 1, and the results of the population analysis and computation of Fukui function are listed in Table 2.

Corresponding to 3a and 3b, the values of $\mu^{-1/2} S_{AS}/M_w$ are 0.1267 and 0.1309, respectively (μ is the reduced mass of the catalyst and methyl acrylate). The fact that the value of $\mu^{-1/2} S_{AS}/M_w$ of 3b is a little bigger than that of 3a illustrates the higher catalytic power of 3b.

It is reasonable to presume that the palladium atom in a 3b molecule is more active than the same atom in a 3a molecule.

TABLE 2: Results of Population Analysis and Computation of Fukui Function

entry	central metal	charge (1) ^a	charge (2) ^b	$f^+_{\text{Pd}}^c$	$f^-_{\text{Pd}}^d$	$f^0_{\text{Pd}}^e$
1	Pd in 3a	0.334	0.2958	0.025	0.074	0.050
2	Pd in 3b	0.313	0.2909	0.030	0.077	0.053

^a ESP charges. ^b Hirshfeld atomic charges. ^c Fukui indices for nucleophilic attack obtained by Mulliken method. ^d Fukui indices for electrophilic attack obtained by Mulliken method. ^e Fukui indices for radical attack obtained by Mulliken method.

As can be seen in Table 2, the values of the Fukui indices of 3b are relative bigger than those of 3a and the amount of positive charge for 3b is relative smaller than that of 3a. For the calculation of different systems with similar structures by a specified theoretical method, the dynamic disorders are approximate. So we think the result of the comparison between 3a and 3b is reliable.

The higher conversion for the Heck coupling reaction using 3b as catalyst precursor thus may be attributed to the increased chemical reactivity of the palladium in a 3b molecule and the relative greater value of $\mu^{-1/2} S_{\text{AS}}/M_{\text{w}}$ of 3b, which make it possible that 3b exhibits higher catalytic power than 3a.

From the results reported above, this method to compare the relative catalytic power among structurally related dendrimers with one active site at the core proved to be feasible.

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