

Theoretical Analysis on Mechanisms Implied in Hybrid Integrated Circuit Building

Giacomo Giorgi¹, Filippo De Angelis¹, Nazzareno Re², and Antonio Sgamellotti¹

¹ Dipartimento di Chimica e Istituto CNR di Scienze e Tecnologie Molecolari, Università di Perugia, via Elce di Sotto 8, I-06123 Perugia, Italy
giac@thch.unipg.it

² Facoltà di Farmacia, Università G. D'Annunzio, I-66100 Chieti, Italy

Abstract. Nowadays the relevance of silicon chemistry is increasing due to the applications of Si, in particular in semiconductors, in order to obtain an increasing number of performing materials. A theoretical investigation based on the Density Functional Theory has been done on the reaction paths implied in the Pt-catalysed alkene hydrosilylation, a process through which the selective grafting of organic molecules to silicon can be obtained. We studied the Si-H oxidative addition of SiH₄ to a diphosphine molecule, the C₂H₄ insertion on Pt-H and Pt-SiH₃ bonds, the isomerisation of the product of the C₂H₄ insertion, and the two following Si-C and C-H reductive eliminations. The set of these processes are known as the Chalk-Harrod mechanism and the modified Chalk-Harrod mechanism, respectively. The goal of this work has been to identify the rate determining step of both mechanisms. The dynamics of the oxidative addition step has been simulated.

1 Introduction

A theoretical investigation has been performed on the reaction pathways involved in the Pt(PH₃)₂-catalysed ethylene hydrosilylation by SiH₄. We have studied both mechanisms proposed to explain the formation of the vinyl-silane product. First of all we have analysed the Chalk-Harrod mechanism. It consists of three processes: (I) the Si-H oxidative addition of SiH₄ to Pt(PH₃)₂, (II) the C₂H₄ insertion into the Pt-H bond, (III) the Si-C reductive elimination. Next we analysed the modified Chalk-Harrod mechanism. It consists of the same preliminary oxidative addition of SiH₄ to the Pt(PH₃)₂, followed by the C₂H₄ insertion into the Pt-Si bond and, finally, by the C-H reductive elimination. We have investigated each step participating in both mechanisms by gradient-corrected DFT methods, and then performed *ab initio* molecular dynamics simulations on the initial oxidative addition step. One of the best known catalysts for hydrosilylation process is chloroplatinic acid (H₂PtCl₆, Speier's catalysts)[1], for which Chalk and Harrod have suggested the two reaction mechanisms [2] previously described in order to obtain the final organosilicon compound. (See Fig.1) Considering the ambiguous behavior of the Speier's catalyst, we used a model Pt(0)

diphosphine complex which has been demonstrated to be the active species in the well characterised homogeneous catalysis by $\text{Pt}(\text{PR}_3)_4$ [3]. Sakaki and coworkers

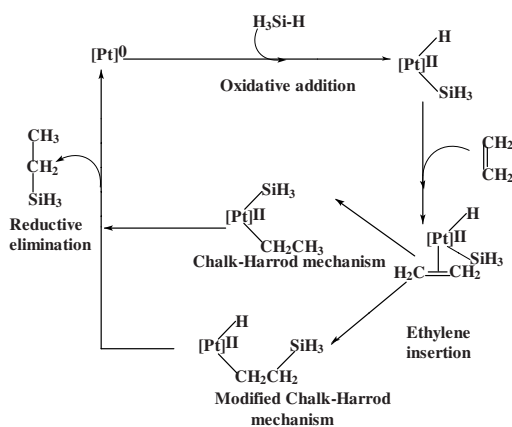


Fig. 1

Fig. 1. Chalk-Harrod and modified Chalk-Harrod mechanisms scheme

have theoretically investigated the Chalk-Harrod and modified Chalk-Harrod mechanisms at HF and post-HF level[4, 5], while Coussens et al.[6] have done a DFT analysis on the C_2H_4 insertion in the cationic systems $(\text{H})\text{Pt}(\text{P}\text{X}_3)_2^+$. Since in the works by Sakaki the geometry optimisation of the C_2H_4 insertion step was done at the uncorrelated Hartree-Fock level, in our work we have investigated both hydrosilylation mechanisms performing geometry optimisation of each step at a correlated level of theory. It means that both the Chalk-Harrod and modified Chalk-Harrod mechanisms were treated by gradient-corrected DFT methods. Furthermore, *ab initio* molecular dynamics (AIMD) simulations were carried out by means of the Car- Parrinello method, to study the dynamical features of the initial Si-H oxidative addition to $\text{Pt}(\text{PH}_3)_2$, the initial step that is shared by both mechanisms.

2 Computational Details

All the static calculations have been performed using the Gaussian 98[7] program package. Reactants, transition states (TS) and products geometries of the two mechanisms analysed have been fully optimised using Density Functional Theory. A preliminary study on the oxidative addition process has been recently done [8] using the “pure” BPW91 [7] exchange-correlation functional to provide consistency between static and dynamic analyses. In this paper, we have used both the “pure” BPW91 and hybrid B3LYP[7] functionals, comparing the results achieved with the two different approaches for the activation barrier (E_a)

of the Rate Determining Step of the whole mechanism. We have made geometry optimisation using the relativistic pseudopotential LANL2DZ[7] for the Pt atom, the 6-31G**[7] basis set for Si, C and the reacting H atom, and the 6-31G[7] for P and for the remaining H atoms: we summarise these basis set as BSa. The optimised geometries have been subsequently employed to perform single-point calculations. Here we have still used the relativistic pseudopotential LANL2DZ for the Pt atom, while for all other atoms we have employed the 6-311++G(3df,3pd)[7] basis set: we summarise these basis set as BSb. Every TS structure for the key reaction steps has been checked by doing an Intrinsic Reaction Coordinate (IRC) analysis[7]. We have found an excellent agreement between the “pure” BPW91 and the hybrid B3LYP functionals. In fact, considering BSa, the activation energy for the Chalk-Harrod RDS is 32.2 kcal/mol and 32.1 kcal/mol for BPW91 and B3LYP, respectively. For the Car-Parrinello calculations gradient corrected AIMD simulations have been performed using the parallel version developed by F.De Angelis of the Car-Parrinello code [9] implementing Vanderbilt pseudopotentials[10–12]. The Perdew-Zunger[13] parameterisation has been employed for the LDA exchange-correlation functional, while the gradient-corrected functional is taken from Ref.[14]. Core states are projected out using pseudopotentials. For Pt atom “ultra-soft” pseudopotentials were generated following the Vanderbilt scheme, while the Hamann-Schluter-Chang (HSC) pseudopotential[15] has been used for P and Si atoms. The wavefunctions were expanded in plane waves up to an energy cutoff of 25 Ry. Periodic boundary conditions were used by placing the model molecule in a cubic box of 10.6Å, to avoid coupling between periodic images. The equations of motion were integrated using a time step of 6 a.u. (0.145 fs) with an electronic fictitious mass $\mu=500$ a.u.. Constrained dynamics simulations were performed by means of the SHAKE algorithm[16], employing the slow-growth method[17]. The thermal equilibrium was maintained checking the temperature of the nuclei by a Nosé thermostat[18,19], which creates a canonical ensemble (NVT). All simulations were performed at 300 K.

3 Results and Discussion

3.1 Oxidative Addition

In Figure 2 we show the oxidative reduction reaction mechanism. Our results achieved at the BPW91/BSa level, show a structure for the TS ($TS_{R \rightarrow 1}$ where the Si-H bond does not lie in the P-Pt-P plane. Moreover, we have that the Si-H bond approaches the Pt atom in an out- of-plane fashion. This can justify the presence of a *trans*-Pt(PH₃)(H)(SiH₃) product that is not obtainable through an in-plane approach.

The AIMD simulations we performed confirm the reaction mechanism of the oxidative addition process. Constrained dynamics simulations were made by varying the Si-Pt distance in the range 4.6-2.3Å (see Fig.3), the former value corresponding to the unbound free reactants, the latter being close to the Si-Pt distance in the oxidative addition product. Dynamics simulations were initialised

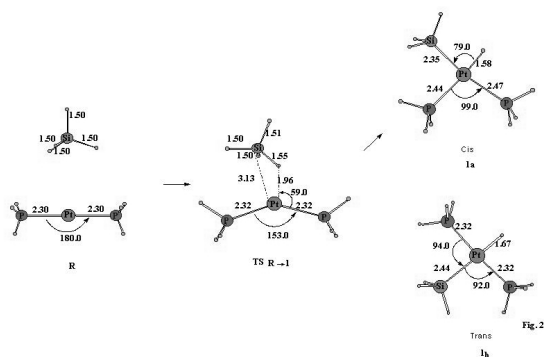


Fig. 2. Oxidative addition process: reactants, TS and products (1a and 1b). 1a is the most stable product (cis). (Å, degrees)

by fixing the distance Si-Pt at 4.6 Å, minimising the corresponding structure, and thermalising the resulting system at 300 K for 1.4 ps. Subsequently, we decreased the Si-Pt distance in the cited range during a time span of 5.8 ps.

3.2 Chalk-Harrod Mechanism

We have considered the four-coordinated $\text{PtH}(\text{SiH}_3)(\text{PH}_3)(\text{C}_2\text{H}_4)$ complex. This species is the product of a reaction that involves the loss of a PH_3 group followed by an C_2H_4 coordination on the Pt-H bond (endothermic by 43.7 kcal/mol compared to free reactants R in Fig.2). We will hereafter refer to C_α and C_β as the C_2H_4 carbons in complex 2 facing the H and the PH_3 groups, respectively. We find a point of inflection instead of the minimum we should expected for the insertion products and, to clarify this point, we have done a linear transit calculation constraining the bond distance between C_β and H atom bound to Pt to vary in the range 2.5-1.0 Å. A “true” TS has been found for the isomerisation step; the geometry optimisation of $\text{TS}_{2 \rightarrow 4}$ (see Fig.4), has led to an $E_a = 25.1$ kcal/mol. We then have calculated that the more stable product is 4b because of the *trans*-effect given by the bulky group SiH_3 . In fact, in the product 4a we have an agostic interaction between an hydrogen bound to C_α and the Pt atom that, being in the trans site to the SiH_3 , does not allow the stabilising *trans*-effect. The 4a and 4b products were found 3.7 and 4.7 kcal/mol below 2.

3.3 Modified Chalk-Harrod Mechanism

Contrary to the “simple” Chalk-Harrod mechanism, in the modified mechanism we have distinguished an insertion process and an isomerisation step. The main

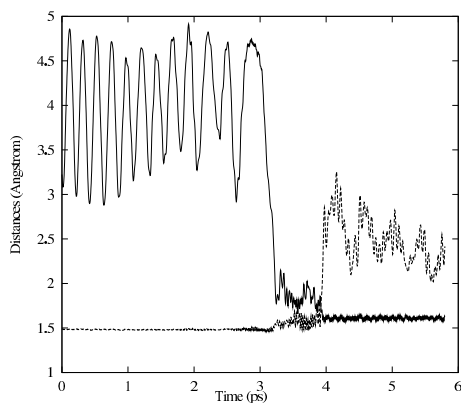


Fig. 3. Time evolution of the Pt-H (solid line) and Si-H (dashed line) distances for the time span going from 3 to 4 ps, corresponding to a Pt-Si distance decrease from 3.20 to 2.74 Å. Time in ps, distances in Å.

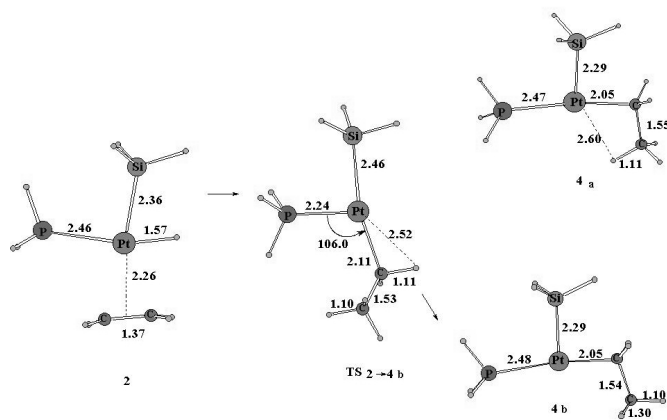


Fig. 4. Chalk-Harrod mechanism: Insertion plus Isomerisation step. Reactants, TS and products (4a and 4b). 4b is the most stable product.

difference between the Chalk-Harrod mechanism and its modified version is observable in the insertion process. In fact, while in the Chalk-Harrod mechanism the C_2H_4 insertion takes place on the Pt-H bond, in the modified version it takes place on the Pt-Si bond (see Fig. 5). We have obtained an insertion product ($3'$) characterised by an agostic interaction between an hydrogen atom bound to the Si and the Pt. $3'$ can simply isomerise and give the products $4'a$ and $4'b$ (see Fig. 6). Here we have, contrary to the Chalk-Harrod mechanism, that the $4'a$ is the more stable product because in the product $4'b$ H group is too small to give *trans*-effect and the agostic interaction between an H bound to Si and the Pt atom stabilises slightly $4'a$.

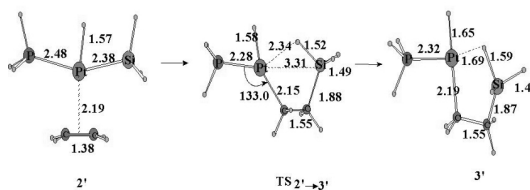


Fig. 5. Modified Chalk-Harrod mechanism: Insertion step. Reactants, TS, and product.

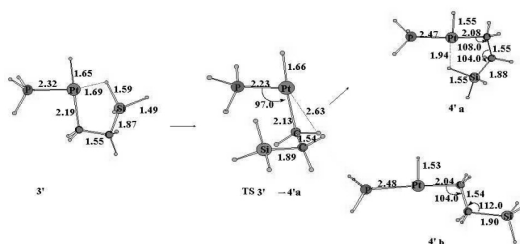


Fig. 6. Modified Chalk-Harrod mechanism: Isomerisation step. Reactant, TS and products ($4'a$ and $4'b$). $4'a$ is the most stable product.

3.4 Reductive Elimination

In the Chalk-Harrod mechanism, the C_2H_4 insertion and the isomerisation is followed by coordination of a PH_3 group, before of the Si-C reductive elimination. The 4b product has been considered as the starting reactant because of its bigger stability (see Fig.7). The energy gain of PH_3 coordination is computed to be 45.4 kcal/mol. The resulting diphosphinic complex 5 then undergoes the Si-C reductive elimination leading to the final $SiH_3CH_2CH_3$ reaction product P, restoring the initial catalyst. The main characteristic of this reaction is to find in the TS non-planar structure, contrary to the C-H reductive elimination. For this step we have computed an activation energy of 24.1 kcal/mol (referred to 5), with a small exothermicity of 3.7 kcal/mol.

In the modified Chalk-Harrod mechanism the C-H reductive elimination (see Fig.8) is again preceded by the coordination of a PH_3 group to the 4'a species leading to 5'. The TS connecting 5' to the final products P ($TS_{5' \rightarrow P}$) shows the concerted breaking of the Pt-C $_{\alpha}$ bond and the formation of the H-C $_{\alpha}$ bond. This process is kinetically favored over the Si-C reductive elimination. In fact, here we have an E_a for the C-H reductive elimination 5.2 kcal/mol lower than that for Si-C (18.9 vs. 24.1 kcal/mol) reflecting the directionality of the sp^3 valence orbital of SiH_3 . Also thermodynamics confirms this trend: we have found the C-H reductive elimination favored over the Si-C one by 10.7 kcal/mol (-14.4 vs. -3.7 kcal/mol), reflecting the lower stability of 5' with respect to 5 (see Figs.9 and 10, respectively).

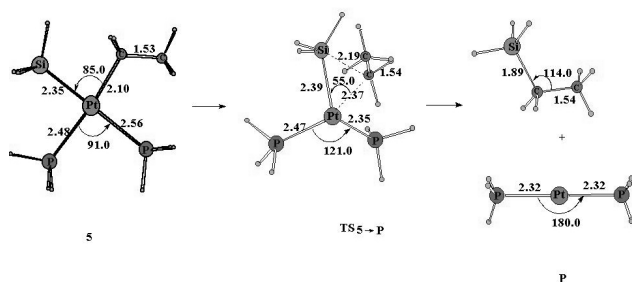


Fig. 7. Si-C Reductive Elimination: Reactant, TS, and Products

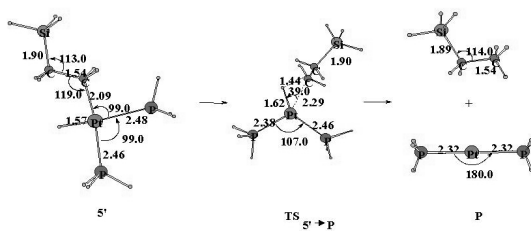


Fig. 8. C-H Reductive Elimination: Reactant, TS, and Products

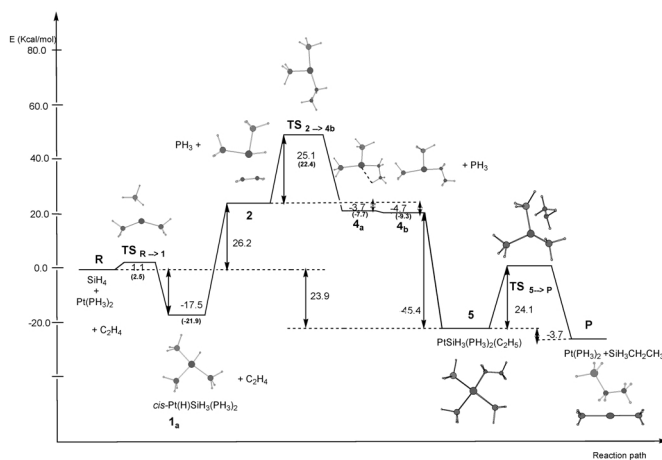


Fig. 9. Energy changes in the Chalk-Harrod mechanism (kcal/mol). In parentheses Sakaki's values

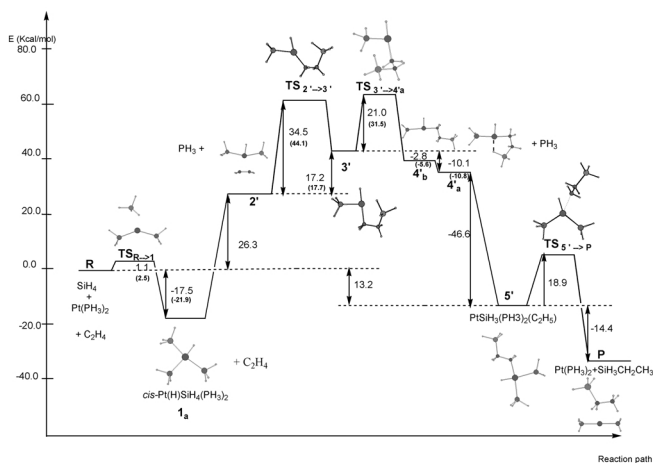


Fig. 10. Energy changes in the modified Chalk-Harrod mechanism (kcal/mol). In parentheses Sakaki's values

4 Conclusion

In this work we have analysed the mechanisms implicated in the Pt-catalysed hydrosilylation of C_2H_4 by combining static and dynamic calculations. The Chalk-Harrod mechanism and the modified Chalk-Harrod mechanism have been investigated by a DFT approach, checking the effect of different exchange-correlation functionals and basis set expansion on the energetics of both mechanisms; furthermore, dynamics simulations, by means of Car-Parrinello method, have been performed on the preliminary oxidative addition step. This analysis have revealed that the formation of the preliminary Pt-H bond takes place before that the Si-H bond breaks, going directly to the more stable *cis* isomer through a non planar TS.

In agreement with previous theoretical works, we compute a maximum energy barrier of 25.1 kcal/mol and 38.2 kcal/mol in correspondence of the C_2H_4 insertion and isomerisation step, for the Chalk-Harrod and modified Chalk-Harrod mechanisms, respectively.

References

1. Speier, J.L., Webster, J.A., Barnes, G.H.: The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. Use of Group VIII Metal Catalysts. *J. Am. Chem. Soc.* **79**, (1957), 974–979
2. Harrod, J.F., Chalk, A.J.,: Wender, I., Pino, P.(Eds.), *Organic Synthesis via Metal Carbonyls*, vol.2, Wiley, New York, 1977, p.673.
3. Prignano, A.L., Troglor, W.C.,: Silica-supported bis(trialkylphosphine)platinum oxalates. Photogenerated catalysts for hydrosilylation of olefins. *J. Am. Chem. Soc.* **109**, 1987, 3586–3595

4. Sakaki, S., Mizoe, N., Sugimoto, M.: Theoretical Study of Platinum(0)-catalyzed Hydrosilylation of Ethylene. Chalk-Harrod Mechanism or Modified Chalk-Harrod Mechanism. *Organometallics*, **17**, 1998, 2510–2523
5. Sakaki, S., Ieki, M.: Oxidative addition reactions of saturated Si-X bonds (X=H, F, C, or Si) to Pt(PH₃)₂. An ab initio MO/MP4 study. *J. Am. Chem. Soc.*, **115**, 1993, 2373–2381
6. Coussens, B.B., Buda, F., Oevering, H., Meier, R.J.: Simulations of Ethylene Insertion in the Pt^{II} Bond of (H)Pt(PX₃)₂⁺. *Organometallics* **17**, 1998, 795–801
7. Frisch, M.J., Trucks, G.W., *et al.*: Gaussian, Inc., Pittsburgh PA, 1998 and references therein.
8. Giorgi, G., De Angelis, F., Re, N., Sgamellotti, A.: Oxidative addition of SiH₄ to Pt(PH₃)₂: a dynamical density functional study. *Chem. Phys. Lett.*, **364**, 2002, 87–92
9. F. De Angelis, PhD thesis, University of Perugia, (1999).
10. The implementation that we use is described in: Pasquarello, A., Laasonen, K., Car, R., Lee, C., Vanderbilt, D.: Ab initio Molecular Dynamics for d-Electron Systems: Liquid Copper at 1500 K. *Phys. Rev. Lett.*, **69**, 1992, 1982–1985
11. The implementation that we use is described in: Pasquarello, A., Laasonen, K., Car, R., Lee, C., Vanderbilt, D.: Car-Parrinello molecular dynamics with Vanderbilt ultrasoft pseudopotentials. *Phys. Rev. B*, **47**, 1993, 10142–10153
12. Vanderbilt, D.: Soft self-consistent pseudopotentials in generalized eigenvalue formalism. *Phys. Rev. B*, **41**, 1990, 7892–7895
13. Perdew, J.P., Zunger, A.: Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, **23**, 1981, 5048–5079
14. Perdew, J.P., Chevary, J.A., Vosko, S.H., Jackson, K.A., Pederson, M.R., Singh, D.J., Fiolhais, C.: Atoms, molecules, solids and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B*, **46**, 1992, 6671–6687
15. Hamann, D.R., Schlüter, M., Chiang, C.: Norm-Conserving Pseudopotentials. *Phys. Rev. Lett.*, **43**, 1979, 1494–1497
16. Ryckaert, J.P., Ciccotti, G., Berendsen, H.J.: Numerical Integration of the Cartesian Equation of Motion of a System with Constraints: Molecular Dynamics of N-Alkanes. *J. Comp. Phys.*, **23**, 1977, 327–341
17. Straatsma, T.P., Berendsen, H.J.C., Postma, J.P.M.: Free energy of hydrophobic hydration: A molecular dynamics of noble gas in water. *J. Chem. Phys.*, **85**, 1986, 6720–6727
18. Nosé, S.: A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.*, **52**, 1984, 255–268
19. Hoover, W.G.: Canonical dynamics: phase-space distributions. *Phys. Rev. A*, **31**, 1985, 1695–1697