*Organometallics* **2002,** *21,* 2407−2412

# Theoretical Study on the Regioselectivity of Nucleophilic Attack in Silyl-Substituted (Diphosphino)($\eta^3$-allyl)palladium Cations

Vicenç Branchadell,* Marcial Moreno-Mañas, and Roser Pleixats*

*Department of Chemistry, Universitat Autònoma de Barcelona, Cerdanyola, 08193-Barcelona, Spain*

*Received August 1, 2001*

A density functional study has been performed to explain the regioselectivity of nucleophilic attack in silyl-substituted (diphosphino)($\eta^3$-allyl)palladium cations. Optimized geometries of model cations **4b**,**d**,**e** (bearing at both ends of the allylic system Me and $SiH_3$, *t*-Bu and $SiMe_3$, and Ph and $SiMe_3$ groups, respectively) show that for unsymmetrical allyl ligands the shortest Pd−C(terminal) bond is the one corresponding to the carbon atom directly bonded to silicon, electronic factors being determinant. Energy barriers for the attack of an ammonia molecule at each one of the terminal allyl carbon atoms of **4b**,**d**,**e** have been calculated, electronic and steric effects being discussed. When the silicon group is the bulkiest one, both steric and electronic factors favor the attack at the carbon atom remote from silicon ($\gamma$-carbon). When the silicon substituent is the least sterically demanding, the attack at carbon bonded to silicon (α-carbon) is sterically more favorable, but electronic effects favor the attack at the $\gamma$-carbon.

## Introduction

The palladium(0)-catalyzed allylation of nucleophiles (the Tsuji−Trost reaction) is a synthetic method widely accepted due to its broad applicability and facile experimental procedure.[1] The simplyfied catalytic cycle (Figure 1) requires the formation of the ($\eta^3$-allyl)-palladium(II) complex **1**, an intermediate which can be attacked by nucleophiles at both termini of the allylic system. It is generally accepted that nucleophiles attack preferentially the less hindered allylic terminus, product **2** thus being predominantly formed, mainly if R = alkyl, aryl. However, the situation is more complicated. Thus, for a given nucleophile the regioselectivity depends on the electronic nature of the ligand L, acceptor ligands favoring attack at the more substituted terminus;[2] for a given allylpalladium system the regioselectivity can depend on the nucleophile, nonstabilized nucleophiles presenting some propensity for attack at the more substituted terminus.[3] Electronic effects are superimposed on steric effects mainly when R in Figure 1 is a polar group. Thus, electron-withdrawing groups (positive $\sigma_p$ values) direct the attack on complexes **1** at the more remote side ($\gamma$-attack: R′CO− and R′OCO-,[4] NC−,[4d,e,5] $PhSO_2$−,[6] $(R'O)_2P(O)$−,[7] PhS−[8]), whereas electron-donating groups favor the attack at the substituted

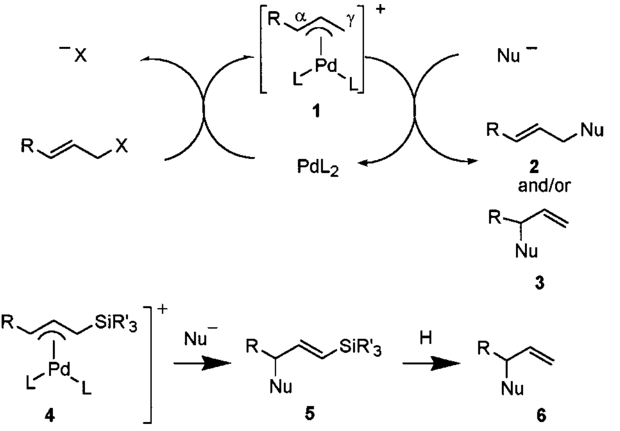


**Figure 1.** Catalytic cycle for the Tsuji−Trost reaction: $\gamma$-attack of a nucleophile at silyl-substituted ($\eta^3$-allyl)-palladium cations.

---

(1) For recent reviews see: (a) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (b) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, U.K., 1995. (c) Harrington, P. J. Transition Metal Allyl Complexes: Pd, W, Mo-assisted Nucleophilic Attack. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, Chapter 8.2. (d) Moreno-Mañas, M.; Pleixats, R. *Adv. Heterocycl. Chem*. **1996**, *96*, 73. (e) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, 2002.

(2) (a) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1975**, *97*, 2534. (b) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (c) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679. (d) Cuvigny, T.; Julia, M.; Rolando, C. *J. Organomet. Chem.* **1985**, *285*, 395. (e) Åkermark, B.; Vitagliano, A. *Organometallics* **1985**, *4*, 1275. (f) Åkermark, B.; Zetterberg, K.; Hansson, S.; Krakenberger, B.; Vitagliano, A. *J. Organomet. Chem*. **1987**, *335*, 133. (g) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (h) Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev*. **1996**, *155*, 35.

(3) Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun*. **1984**, 648.

(4) (a) Jackson, W. R.; Strauss, J. U. G. *Tetrahedron Lett.* **1975**, 2591. (b) Collins, D. J.; Jackson, W. R.; Timms, R. N. *Tetrahedron Lett.* **1976**, 495. (c) Jackson, W. R.; Strauss, J. U. *Aust. J. Chem*. **1977**, *30*, 553. (d) Tsuji, J.; Ueno, H.; Kobayashi, Y.; Okumoto, H. *Tetrahedron Lett.* **1981**, *22*, 2573. (e) Ognyanov, V. I.; Hesse, M. *Synthesis* **1985**, 645. (f) Ono, N.; Hamamoto, I.; Kaji, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1439. (g) Tanikaga, R.; Jun, T. X.; Kaji, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1185.

(5) Keinan, E.; Roth, Z. *J. Org. Chem*. **1983**, *48*, 1769.

(6) (a) Ogura, K.; Shibuya, N.; Iida, H. *Tetrahedron Lett.* **1981**, *22*, 1519. (b) Alonso, I.; Carretero, J. C.; Garrido, J. L.; Magro, V.; Pedregal, C. *J. Org. Chem*. **1997**, *62*, 5682.

10.1021/om0106940 CCC: $22.00
Publication on Web 05/09/2002

carbon atom (α-attack: R′O−,[9] anomeric oxygen atom in unsaturated carbohydrates[10]). The influence of other groups has been also described: in general, acetoxy (MeCOO−) induces α-attack,[11] although steric effects can reverse this propensity;[11a,b,d,12] the regioselectivity for R = fluorine depends on the nature of the nucleophile.[13] Evaluation of the effect of pure electronic factors has been studied in 1,3-diaryl systems featuring $p$-X-$C_6H_4$− groups at both allylic termini. These systems are thought to present the same steric hindrance for attack at any allylic terminus, and the regioselectivity is governed only by the difference in electronic effects arising by the presence of two different X groups with different $\sigma$ values. The result is that attack occurs with high preference at the terminus remote from the most electron-withdrawing group.[14]

The trimethylsilyl group clearly induces $\gamma$-attack or, in other words, attack at the remote terminus with respect to the silicon atom in cation **4** to give compounds **5**, independently of the nature of the group R. This was first observed by Trost and co-workers,[15] who suggested that the following factors should be considered to understand the experimental results: (i) steric hindrance in the attack by the nucleophile, (ii) charge distribution in the cationic complex **4**, and (iii) stability of the $\eta^2$-complex, the primary product of the reaction preceding the formation of **5**. Some years later Tsuji made similar observations and concluded that regioselectivities cannot be explained by simple comparison of steric bulkiness of the substituents.[16] Work by Trost and Tsuji was performed with carbon pronucleophiles of the malonate type: i.e., products with activated $CH_2$ groups. Other examples of the same regioselectivity with *malonate-type* nucleophiles[17] and 2-pyrimidinones[18] have been reported. Later Sato observed the same behavior using different nitrogen nucleophiles[19] as well as Grignard reagents.[20] Synthetic advantage has been taken from this regioselection by silyl groups. Thus, Romero has protonolized products of type **5** to afford compounds **6** in chemistry related to the preparation of HIV protease inhibitors.[21] Regioselectivity for hydride donors is different from the rest, both in the absence and in the presence of silicon.[17,22] The regioselectivity of attack to **4** is in principle unclear, since the $R_3Si$ group does not seem to be either electron-withdrawing or electron-donating according to Hammett $\sigma$ values ($\sigma_p$ in the range 0.00 to −0.07), and the same applies to the tributyltin group.[23] Concerning the relative steric hindrance caused by R and $Me_3Si$ in **4**, it is interesting to note that for R = Ph[19,21] and c-$C_6H_{11}$ [19,20] high selectivity favoring attack at the center remote from silicon has been reported. As a comparison, the *A* values from axial−equatorial equilibria in cyclohexanes are 2.15 (cyclohexyl), 2.9 (phenyl), and 2.5 (trimethylsilyl).[24] On the other hand, in the ($\eta^3$-1-methyl-1-(trimethylsilyl)allyl)chloro(triphenylphosphine)palladium(II) complex, the thermodynamically more stable isomer is found to be that with the $SiMe_3$ group in the anti position with respect to the central hydrogen atom,[25] thus indicating that steric hindrance between the Pd atom and the anti methyl group is larger than that between Pd and the anti trimethylsilyl group. Therefore, other reasons apart from steric hindrance should be invoked to explain regioselectivity induced by these group 14 elements, as already suggested by Trost[15] and by Tsuji.[16] We present here our results based on density functional calculations of several disubstituted allylpalladium cations. We have used ammonia as a model nucleophile,[14c,26] and we have studied the transition states corresponding to the attack at the allyl terminal carbon atoms.

## Computational Methods

All the calculations have been done using density functional (DFT) methods. The molecular geometries have been fully optimized using the hybrid Becke[27] functional for exchange and the correlation functional of Lee, Yang, and Parr[28] (B3LYP) implemented in the Gaussian-98 program.[29] In these calculations we have used the effective core potentials of Hay and Wadt[30] for Pd. For the remaining atoms, we have used the D95 basis set[31] supplemented with a set of d polarization functions for C, N, Si, and P. Harmonic vibrational frequencies have been calculated for all transition states to verify that they have one and only one imaginary frequency. The charge distribution has been analyzed from the natural orbital scheme

---

(7) (a) Zhu, J.; Lu, X. *Tetrahedron Lett.* **1987**, *28*, 1897. (b) Öhler, E.; Kanzler, S. *Synthesis* **1995**, 539. (c) Principato, B.; Maffei, M.; Siv, C.; Buono, G.; Peiffer, G. *Tetrahedron* **1996**, *52*, 2087.

(8) (a) Godleski, S. A.; Villhauer, E. B. *J. Org. Chem.* **1984**, *49*, 2246. (b) Godleski, S. A.; Villhauer, E, B. *J. Org. Chem.* **1986**, *51*, 486. (c) Yamamoto, Y.; Al-Masum, M.; Takeda, A. *J. Chem. Soc., Chem. Commun.* **1996**, 831.

(9) (a) Billups, W. E.; Erkes, R. S.; Reed, L. E. *Synth. Commun.* **1980**, *10*, 147. (b) Trost, B. M.; Merlic, C. A. *J. Org. Chem.* **1990**, *55*, 1127. (c) Chaptal, N.; Colovray-Gotteland, V.; Grandjean, C.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1991**, *32*, 1795. (d) Vicart, N.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1995**, *36*, 535. (e) Yamamoto, Y.; Al-Masum, M. *Synlett* **1995**, 969.

(10) (a) Brakta, M.; Lhoste, P.; Sinou, D. *J. Org. Chem.* **1989**, *54*, 1890. (b) Moineau, C.; Bolitt, V.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1103.

(11) (a) Lu, X.; Huang, Y. *J. Organomet. Chem.* **1984**, *268*, 185. (b) Trost, B. M.; Vercauteren, J. *Tetrahedron Lett.* **1985**, *26*, 131. (c) Genêt, J.-P.; Uziel, J.; Juge, S. *Tetrahedron Lett.* **1988**, *29*, 4559. (d) Trost, B. M.; Lee, C. B.; Weiss, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 7247.

(12) Sjögren, M. P. T.; Hansson, S.; Åkermark, B.; Vitagliano, A. *Organometallics* **1994**, *13*, 1963.

(13) Shi, G.; Huang, X.; Zhang, F.-J. *Tetrahedron Lett.* **1995**, *36*, 6305.

(14) (a) Prat, M.; Ribas, J.; Moreno-Mañas, M. *Tetrahedron* **1992**, *48*, 1695. (b) Moreno-Mañas, M.; Pajuelo, F.; Parella, T.; Pleixats, R. *Organometallics* **1997**, *16*, 205. (c) Branchadell, V.; Moreno-Mañas, M.; Pajuelo, F.; Pleixats, R. *Organometallics* **1999**, *18*, 4934.

(15) (a) Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 5942. (b) Trost, B. M.; Self, C. R. *J. Org. Chem.* **1984**, *49*, 468.

(16) (a) Tsuji, J.; Yuhara, M.; Minato, M.; Yamada, H.; Sato, F.; Kobayashi, Y. *Tetrahedron Lett.* **1988**, *29*, 343. (b) Tsuji, J. *Pure Appl. Chem.* **1989**, *61*, 1673.

(17) Lautens, M.; Delanghe, P. H. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2448.

(18) Falck-Pedersen, M. L.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1989**, *43*, 251.

(19) Inami, H.; Ito, T.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1993**, *34*, 5919.

(20) Urabe, H.; Inami, H.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1993**, 1595.

(21) Thaisrivongs, S.; Romero, D. L.; Tommasi, R. A.; Janakiraman, M. N.; Strohbach, J. W.; Turner, S. R.; Biles, C.; Morge, R. R.; Johnson, P. D.; Aristoff, P. A.; Tomich, P. K.; Lynn, J. C.; Horng, M.-M.; Chong, K.-T.; Hinshaw, R. R.; Jeffrey Howe, W.; Finzel, B. C.; Watenpaugh, K. D. *J. Med. Chem.* **1996**, *39*, 4630. (b) Romero, D.; Fritzen, E. L. *Tetrahedron Lett.* **1997**, *38*, 8659.

(22) (a) Ollivier, J.; Salaün, J. *Synlett* **1994**, 949−951. (b) Lautens, M.; Ben, R. N.; Delanghe, H. M. *Tetrahedron* **1996**, *52*, 7221.

(23) Falck-Pedersen, M. L.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1992**, *46*, 1215.

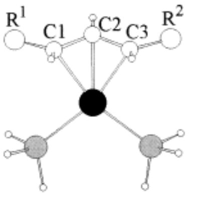
(24) Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; Wiley: New York, 1991.

(25) Ohta, T.; Hosokawa, T.; Murahashi, S.-I.; Miki, K.; Kasai, N. *Organometallics* **1985**, *4*, 2080.

(26) (a) Hagelin, H.; Akermark, B.; Norrby, P. O. *Chem. Eur. J.* **1999**, *5*, 902. (b) Delbecq, F.; Lepouge, C. *Organometallics* **2000**, *19*, 2716.

(27) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785



**4a** $R^1$=$SiH_3$; $R^2$=$SiH_3$
**4b** $R^1$=Me; $R^2$=$SiH_3$
**4c** $R^1$=TMS; $R^2$=TMS
**4d** $R^1$=*t*-Bu; $R^2$=TMS
**4e** $R^1$=Ph; $R^2$=TMS
**7a** $R^1$=Me; $R^2$=Me
**7b** $R^1$=*t*-Bu; $R^2$=*t*-Bu
**7c** $R^1$=Ph; $R^2$=Ph

**Figure 2.** Structure of disubstituted allylpalladium cations.

developed by Weinhold et al.[32] For isolated allyl radicals a spin-unrestricted formalism has been used.

Single point calculations on the B3LYP optimized geometries have been done to analyze the potential energy barriers using the extended transition state method of Ziegler and Rauk[33] implemented in the ADF program.[34] In these calculations we have used Becke's exchange functional[35] along with the Lee, Yang, and Parr[28] correlation functional (BLYP) and an uncontracted Slater type orbital (STO) basis set. The inner electrons have been treated by the frozen-core approximation.[36] For the valence space, the basis set used is triple-$\zeta$ for Pd and double-$\zeta$ for the remaining atoms. A set of d polarization functions has been added for C, N, Si, and P.

## Results and Discussion

The structures of the allylpalladium cations considered are schematically represented in Figure 2. The values of selected bond distances and the results from a natural atomic population analysis are shown in Tables 1 and 2.

**Table 1. Selected Geometry Parameters[a] and Charge Distribution[b] for Homodisubstituted Allylpalladium Cations[c]**

| | | | charge density | | | | |
|---|---|---|---|---|---|---|---|
| | Pd−C1 | Pd−C3 | C1 | C2 | C3 | Pd | $Pd(PH_3)_2$ |
| **4a** | 2.26 | 2.26 | −0.70 | −0.19 | −0.70 | 0.31 | 0.91 |
| **4c** | 2.28 | 2.28 | −0.72 | −0.20 | −0.72 | 0.30 | 0.84 |
| **7a** | 2.27 | 2.27 | −0.21 | −0.23 | −0.21 | 0.27 | 0.80 |
| **7b** | 2.30 | 2.30 | −0.21 | −0.24 | −0.21 | 0.28 | 0.78 |
| **7c** | 2.31 | 2.31 | −0.22 | −0.21 | −0.22 | 0.28 | 0.75 |

[a] Bond distances in Å. [b] In au. [c] See Figure 2.

**Table 2. Selected Geometry Parameters[a] and Charge Distribution[b] for Heterodisubstituted Allylpalladium Cations[c]**

| | | | charge density | | | | |
|---|---|---|---|---|---|---|---|
| | Pd−C1 | Pd−C3 | C1 | C2 | C3 | Pd | $Pd(PH_3)_2$ |
| **4b** | 2.29 | 2.25 | −0.21 | −0.20 | −0.71 | 0.29 | 0.86 |
| **4d** | 2.34 | 2.25 | −0.20 | −0.22 | −0.72 | 0.29 | 0.81 |
| **4e** | 2.32 | 2.27 | −0.21 | −0.21 | −0.73 | 0.28 | 0.80 |

[a] Bond distances in Å. [b] In au. [c] See Figure 2.

**Table 3. Energy[a] of the $\pi$ Orbitals[b] of Homodisubstituted Allyl Radicals**

| | $SiH_3$ | TMS | Me | *t*-Bu | Ph |
|---|---|---|---|---|---|
| $\pi$ | −8.63 | −7.80 | −7.88 | −7.78 | −8.95 |
| $n\pi$ | −5.77 | −5.20 | −4.58 | −4.50 | −4.60 |
| $\pi^*$ | 0.18 | 0.65 | 1.23 | 1.28 | 1.64 |

[a] In eV. [b] Only the energies of the α molecular orbitals are presented.

For the symmetric complexes (Table 1), the distances between Pd and the terminal carbon atoms of the allyl ligand (C1 and C3) range between 2.26 Å (**4a**) and 2.31 Å (**7c**). These values are determined both by the electronic nature of the substituents and by their steric requirements. The comparisons between $CH_3$ (**7a**) and $SiH_3$ (**4a**) and between *t*-Bu (**7b**) and TMS (**4c**) seem to show that alkyl groups are sterically more cumbersome than the silicon analogues.[25]

The charge on the $Pd(PH_3)_2$ fragment can be related to the relative electron donor−acceptor ability of the allyl substituents. The results presented in Table 1 show that the $Pd(PH_3)_2$ fragment is poorer in electrons when the allyl ligand has silicon substituents (**4a** and **4c**) than when the substituents are alkyl (**7a** and **7b**) or phenyl (**7c**). Therefore, silicon seems to act as an electron-withdrawing group with respect to alkyl or phenyl, in sharp contrast with the tabulated Hammett $\sigma$ values. The $\pi$-electron-withdrawing character of the α-Si group is consistent with the effect of substituents on the energies of the allyl $\pi$ orbitals. Table 3 presents the energies of these orbitals computed for several allyl radicals. We can observe that $SiH_3$ and TMS lower the energy of the allyl $n\pi$ and $\pi^*$ orbitals with respect to Me and *t*-Bu, respectively. In this way, the presence of a Si substituent favors the charge transfer to the allyl ligand when it is coordinated to a metal.

The $\pi$-electron-withdrawing effect of silyl and TMS can be explained through an electron delocalization from the $\pi$ and $n\pi$ orbitals of the allyl ligand to the $\sigma^*_{Si-H}$ or $\sigma^*_{Si-C}$ orbitals. These antibonding orbitals are polarized toward the Si atom due to the electronegativity difference between Si and H or C. It should be noted that the situation is different from that corresponding to the presence of a $\beta$-Si group, which acts as an electron donor.[37] The $\pi$-electron-withdrawing effect of a silicon group directly linked to a $\pi$-electron system has already been invoked in radical anions and carbanions.[38] More

---

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(30) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(31) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaeffer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, p 1.

(32) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(33) (a) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

(34) (a) Baerends, E. J.; Bérces, A.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Groeneveld, J. A.; Gritsenko, O. V.; Harris, F. E.; van den Hoek, P.; Jacobsen, H.; van Kessel, G.; Kootstra, F.; van Lenthe, E.; Osinga, V. P.; Philipsen, P. T. H.; Post, D.; Pye, C. C.; Ravenek, W.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Snijders, J. G.; Solà, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visser, O.; van Wezenbeek, E.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Ziegler, T. ADF 1999, Scientific Computing & Modelling NV, Amsterdam, The Netherlands, 1999 (http://www.scm.com). (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acta* **1998**, *99*, 391.

(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(36) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys. Lett.* **1973**, *2*, 41.

(37) (a) Macsári, I.; Szabó, K. J. *Organometallics* **1999**, *18*, 701. (b) Macsári, I.; Hupe, E.; Szabó, K. J. *Organometallics* **1999**, *18*, 9547. (c) Szabó, K. J. *Chem. Soc. Rev.* **2001**, *30*, 136.

recently, the role of the interaction between silyl $\sigma^*$ orbitals and the carbene lone pair of (phosphino)(silyl)-carbenes has been analyzed.[39]

Regarding the atomic charge on the allyl carbon atoms, it should be noted that silicon induces a large negative charge on the α-carbon atom. Regardless of the $\pi$-electron-withdrawing character of the α-Si group, the lower electronegativity of Si with respect to C and H leads to a strong polarization of the C−Si $\sigma$ bond and thus to a negative charge on the carbon atoms directly bonded to silicon.

Let us now consider the nonsymmetric complexes (Table 2). The values of the terminal Pd−C distances should be determined both by the electronic nature and by the steric requirements of the substituents. For the silicon-containing systems we can observe that the shortest Pd−C distance corresponds to the carbon atom bearing the silicon group. As we have already mentioned, α-Si acts as an electron-withdrawing group, so that the relative values of the Pd−C distances agree with our previously reported results showing that the shortest terminal Pd−C distance corresponds to the atom closest to the most electron-withdrawing group.[14c] In **4e**, this effect of TMS leads to a Pd−C3 bond 0.05 Å shorter than Pd−C1, regardless of the larger steric hindrance associated with the TMS group.

The presence of the silicon atom also induces a remarkable negative charge on the allyl carbon atom directly bonded to it, thus leading to a large charge asymmetry between both terminal allyl carbon atoms (C1 and C3). This charge difference would also favor that the shorter Pd−C distance is the one involving C3.

We have studied the nucleophilic attack of ammonia at the heterodisubstituted allylpalladium cations **4b**,**d**,**e**. In all cases, we have located the transition states and the reaction products corresponding to the attack of ammonia at the two allyl terminal carbon atoms (C1 and C3). The geometries of the transition states and reaction products are represented in Figures 3 and 4, respectively. The values of the corresponding energy barriers and reaction energies are shown in Table 4. For the transition states, the main component of the transition vector corresponds to the formation of the N−C bond. The corresponding imaginary frequencies range between 204i cm$^{-1}$ for **4d-tsC** and 276i cm$^{-1}$ for **4b-tsSi**.

For all transition states, we can observe that the value of the N−C distance is close to 2 Å. For **4b** and **4d** this distance is shorter when ammonia attacks the carbon atom directly bonded to the silicon substituent (C3). In contrast, for **4e** the N−C distance is shorter when the attack is produced on the phenyl-substituted allyl carbon atom (C1). The N−C distance at the transition states seems to be related to the steric requirements of the α-substituent. In this way, silyl and phenyl seem to be the least sterically demanding groups, whereas *t*-Bu involves the largest steric hindrance. The comparison between the steric requirements of TMS and *t*-Bu can be done from the values of the H(NH$_3$)−H(Me) distances at the **4d-tsC** and **4d-tsSi** transition states shown in Figure 3.

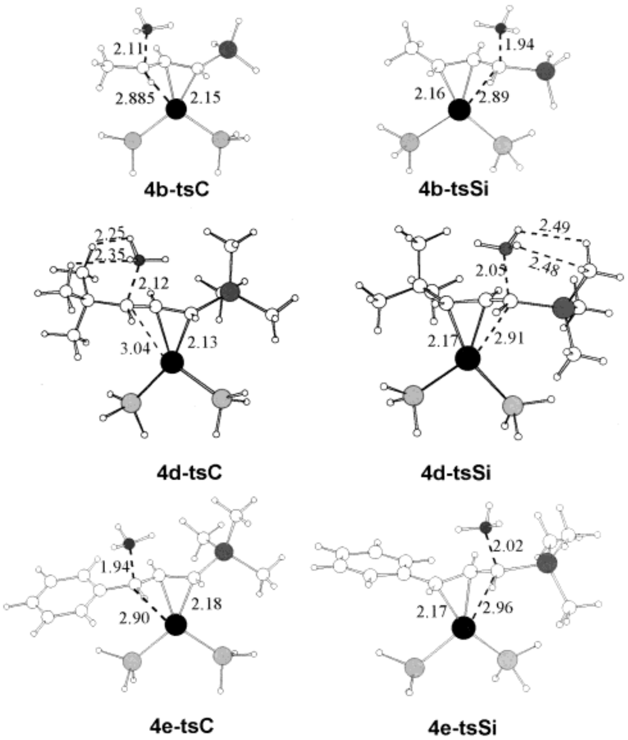


**Figure 3.** Geometries of the transition states corresponding to the nucleophilic attack of ammonia at heterodisubstituted allylpalladium cations. Selected distances are given in Å.

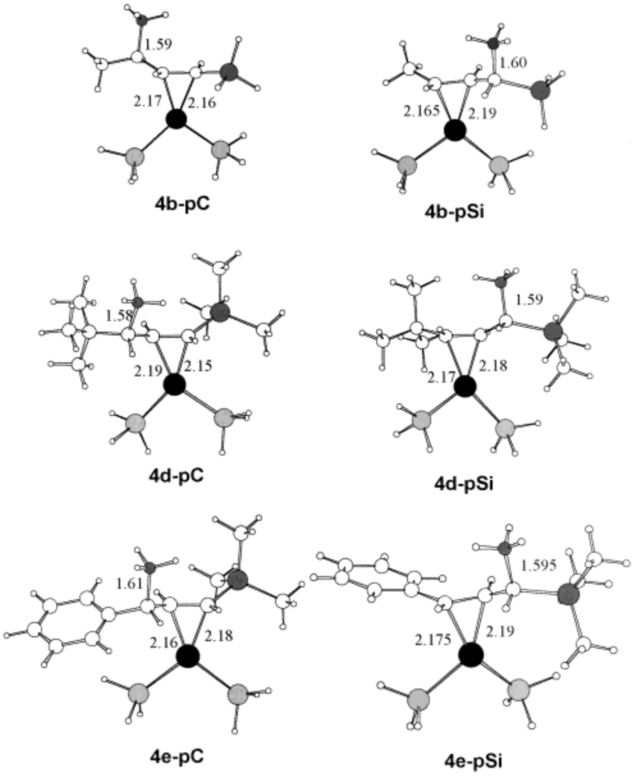


**Figure 4.** Geometries of the reaction products corresponding to the nucleophilic attack of ammonia at heterodisubstituted allylpalladium cations. Selected distances are given in Å.

Figure 3 and Table 4 show that there is a good correlation between the value of the N−C distance at the transition state and the charge transfer between the

---

(38) Bock, H.; Brähler, G.; Fritz, G.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 699.

(39) Kato, T.; Gornitzka, H.; Baceiredo, A.; Savin, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 998.

**Table 4. Energies[a] Relative to the Reactants and Charge Distribution[b] for the Transition States and Reaction Products Corresponding to the Nucleophilic Attack[c] of Ammonia at Heterodisubstituted Allylpalladium Cations**

| | | $\Delta E$ | $Q(NH_3)$ | $Q(Pd(PH_3)_2)$ |
|---|---|---|---|---|
| **4b** | tsC | 2.2 | 0.28 | 0.63 |
| | pC | −4.5 | 0.57 | 0.51 |
| | tsSi | 6.9 | 0.38 | 0.56 |
| | pSi | 3.3 | 0.56 | 0.47 |
| **4d** | tsC | 7.2 | 0.28 | 0.60 |
| | pC | 1.2 | 0.57 | 0.49 |
| | tsSi | 9.0 | 0.32 | 0.56 |
| | pSi | 4.7 | 0.56 | 0.44 |
| **4e** | tsC | 5.3 | 0.37 | 0.55 |
| | pC | −1.2 | 0.56 | 0.48 |
| | tsSi | 9.3 | 0.33 | 0.56 |
| | pSi | 1.4 | 0.56 | 0.47 |

[a] Computed at the B3LYP level of calculation; in kcal mol$^{-1}$. [b] In au. [c] See Figures 3 and 4.

nucleophile and the allylpalladium cation, as we can see from the values of the charge on the $NH_3$ fragment.

The computed potential energy barriers predict that the most favorable nucleophilic attack takes place at C1: i.e., the allyl carbon atom most remote from the silicon substituent, in excellent agreement with the experimentally observed regioselectivity. The reaction energies follow the same trend as the energy barriers, so that the most favorable transition state is the one leading to the most stable regioisomer.

To understand the origin of this regioselectivity, we have analyzed the different contributions to the potential energy barriers. The energy barrier can be decomposed into two terms:

$$\Delta E^{\ddagger} = \Delta E_{\text{prep}} + \Delta E_{\text{int}}$$

The first term, $\Delta E_{\text{prep}}$, is the preparation energy: i.e., the energy necessary to distort the ammonia and allylpalladium fragments from their equilibrium geometries to the geometries they have at the transition state. The second term, $\Delta E_{\text{int}}$, is the interaction energy between both fragments. This term can be further decomposed[32] in the contributions

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$

$\Delta E_{\text{elstat}}$ represents the electrostatic interaction between the prepared fragments, each fragment having the electron density that it would have in the absence of the other fragment. $\Delta E_{\text{Pauli}}$ is the Pauli repulsion term and arises from the orthonormalization of the occupied fragment orbitals to obtain an antisymmetrized product and accounts for the closed-shell repulsion between both fragments. Finally, $\Delta E_{\text{orb}}$ is the orbital interaction term that arises when the electron densities of the fragments are allowed to relax and takes into account the charge transfer between fragments and the polarization of both fragments.

For the energy partition we have used BLYP potential energy barriers, and the results obtained are presented in Table 5. By comparing Tables 4 and 5, we can see that the BLYP potential energy barriers are slightly lower than the B3LYP ones, but the predicted regioselectivity is the same in all cases. For **4b** we have also done the energy partition using model geometries, by placing an ammonia molecule 2 Å from the C1 and C3 allyl carbon atoms of **4b** and keeping the geometries of both fragments frozen. The N−C−C bond angle (105.6°) and the absolute value of the N−C−C−C dihedral angle (84.5°) have been taken as the average values of these angles in the tsC and tsSi transition states.

Table 5 shows that the preparation energy, which is mainly due to the allylpalladium fragment, is always positive. The interaction energy is stabilizing, but not enough to compensate for the preparation energy. Among the terms in which we have decomposed the interaction energy, there is a large repulsive contribution from the Pauli term, which is overcompensated by the stabilizing electrostatic and orbital terms. The electrostatic term is slightly more stabilizing than the orbital interaction term.

If we analyze the difference between the values corresponding to the two regioisomeric transition states, we can observe that for **4b**,**d** the preparation energy term is larger for tsSi than for tsC. This result is the consequence of a larger degree of geometry distortion of the allylpalladium fragment when ammonia attacks C3, which is the terminal allyl carbon atom with a shorter Pd−C distance. Moreover, the Pauli repulsion term is more destabilizing for tsSi than for tsC. This result can be related to the values of the N−C distance at the transition state (see Figure 3). When the attack is produced at C3, ammonia gets closer to the allylpalladium cation than when the attack is at C1 (see Figure 3). As both fragments get closer, stabilizing interactions ($\Delta E_{\text{elstat}}$ and $\Delta E_{\text{orb}}$) also increase, so that the difference in the interaction energy terms for both transition states is almost negligible. As a result, the main contribution to the regioselectivity is due to the difference in the preparation energy term. For **4b**, the results obtained from model geometries are qualitatively similar to the ones corresponding to the transition states: the Pauli repulsion term favors tsC, whereas the electrostatic and

**Table 5. Partition of the Potential Energy Barriers[a] Corresponding to the Nucleophilic Attack of Ammonia at Heterodisubstituted Allylpalladium Cations[b]**

| | **4b**[c] | | | **4d** | | | **4e** | | |
|---|---|---|---|---|---|---|---|---|---|
| | tsC | tsSi | $\Delta\Delta E^d$ | tsC | tsSi | $\Delta\Delta E^d$ | tsC | tsSi | $\Delta\Delta E^d$ |
| $\Delta E_{\text{prep}}$ | 13.1 | 18.7 | +5.6 | 14.8 | 16.2 | +1.4 | 15.2 | 16.3 | +1.1 |
| $\Delta E_{\text{Pauli}}$ | 75.1 (159.0) | 123.0 (166.4) | +47.9 (+7.4) | 79.8 | 93.2 | +13.4 | 125.7 | 100.2 | −25.5 |
| $\Delta E_{\text{elstat}}$ | −47.7 (−75.9) | −71.1 (−78.5) | −23.4 (−2.6) | −47.8 | −53.8 | −6.0 | −72.6 | −57.5 | +15.1 |
| $\Delta E_{\text{orb}}$ | −39.5 (−41.8) | −64.2 (−44.9) | −24.7 (−3.1) | −40.6 | −47.6 | −7.0 | −63.8 | −51.1 | +12.7 |
| $\boldsymbol{\Delta E_{\text{int}}}$ | −12.1 (41.3) | −12.3 (43.0) | −0.2 (+1.7) | −8.6 | −8.2 | +0.4 | −10.7 | −8.4 | +2.3 |
| $\boldsymbol{\Delta E^{\ddagger}}$ | 1.0 | 6.4 | +5.4 | 6.2 | 8.0 | +1.8 | 4.5 | 7.9 | +3.4 |

[a] See text for definitions. Values were computed using the BLYP functional and are given in kcal mol$^{-1}$. [b] See Figure 3. [c] Values in parentheses correspond to model geometries. [d] $\Delta E(\text{tsSi}) - \Delta E(\text{tsC})$.

orbital interaction terms favor tsSi. The values of the electrostatic interaction term are consistent with the electrostatic potential computed for the isolated **4b** cation at the points occupied by the nitrogen atom of ammonia in the model geometries (0.1841 au at 2.0 Å from C1 and 0.1585 au at 2.0 Å from C3).

For **4e** the results are different. Figure 3 shows that the transition state with the shortest N−C distance is tsC. As a consequence, the contribution of the Pauli repulsion is lower for tsSi than for tsC. The stabilizing interactions are also lower in absolute value for tsSi. In this case, the difference between the preparation energy terms is small and the largest contribution to the difference in potential energy barriers is due to the interaction energy term.

In summary, the terminal allyl Pd−C distances in the allylpalladium cations seem to be determined by electronic factors, in such a way that the shortest Pd−C distance is the one corresponding to the carbon atom directly bonded to silicon. The distance between the nucleophile and the allylpalladium cation at the transition state seems to be determined by steric factors. When the silicon substituent is the less sterically demanding group (as in **4b**,**d**), the transition state corresponding to the attack of the nucleophile at the α-carbon atom (C3) involves a greater geometry distortion of the allylpalladium moiety than for the other regioisomeric transition state. In these cases, the attack to C3 is sterically more favorable, but the electronic effects favor the attack at C1. On the other hand, when the silicon group is bulkier than the $\gamma$-substituent (as in **4e**), both steric and electronic factors tend to favor the attack at the same carbon atom.

**Acknowledgment.** Financial support from the DGESIC (Project PB98-0902) and CIRIT-Generalitat de Catalunya (Project SGR2000-0062) and computer time from the “Centre de Supercomputació de Catalunya” are gratefully acknowledged.

OM0106940