Pergamon

Tetrahedron 56 (2000) 6493–6496

TETRAHEDRON

Electronic Differentiations in Palladium Alkene Complexes: *trans*-Phosphine Preference of Allylic Leaving Groups

Bernd Goldfuss* and Uli Kazmaier

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Dedicated to Prof. Günter Helmchen on the occasion of his 60th birthday

Received 27 June 2000; accepted 11 July 2000

Abstract—B3LYP-computations of $(Cl^-)(PH_3)$Pd–alkene complexes reveal a distinct preference for arrangements with *trans*-phosphine situated allylic chlorine atoms (e.g. for *E*-2-chloro-pent-3-ene 1.6 kcal/mol in the gas phase and 1.5 kcal/mol in THF solution). Geometrical analyses show that Pd–alkene complexes with *trans*-phosphine positioned allylic chlorine atoms exhibit more strongly evolved allylic character than the analog *cis*-phosphine complexes. These differentiations, caused by the Pd-ligands (i.e. Cl^-, PH_3), represent electronic origins for memory effects in Pd-catalyzed allylic substitutions.

Introduction

Memory effects in Pd-catalyzed allylic substitutions[1] are intriguing phenomena.[2] Symmetrically substituted allylic substrates (such as **1**) loose normally stereochemical information in Pd-catalyzed substitutions. After formation of Pd–alkene complexes (**2**) and ionization to *meso*-intermediates (**3**, $L_1{=}L_2$, e.g. PPh_3), nucleophilic attack to α- and γ-positions yields racemic substitution products (**4**, Scheme 1).

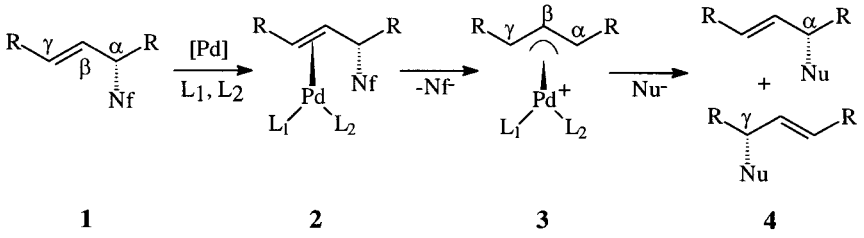
Conservation of chirality might occur, however, with different ligands at Pd ($L_1{\neq}L_2$) and configurational stability of the chiral Pd–allyl complex **3**.

Increased formations of α-allylic products have been observed in some cases.[3] This α-memory effect was explained by the formation of 'intimate ion pairs' between **3** and the leaving nucleofuge Nf^-, which guide the attacking nucleophile Nu^- to C_α, rather than to C_γ.[4] Alternatively, the allyl formation step (**2**→**3**) may determine the stereochemistry of **4** if rearrangements in **3** were suppressed:[5] Steric effects of the ligands (L_1, L_2) result in *torquo*-selectivity in the Pd–allyl complex formation (**2**→**3**).[6] Electronic differentiations between Pd-ligands ($L_1{\neq}L_2$, Scheme 1) likewise influence Pd–allyl complex formation (**2**→**3**),[7] but steric and electronic effects are hard to separate.[8]

To assess the pure electronic differentiations in alkene–palladium complexes, we here study structures and energies of 2-chloro-pent-3-ene Pd-complexes (**2**, R=Me, $L_1{=}PH_3$, $L_2{=}Cl^-$) computationally.[9] Chloride serves as a model nucleofuge (Nf, Scheme 1).

Results and Discussion

B3LYP optimized *E*-2-chloro-pent-3-ene Pd-complexes (Fig. 1) show the relative **5***trans*>**5***cis*>**6***trans*>**6***cis* order in stability (Table 1). Arrangements, which yield after the loss of Cl^- *syn–anti* allyl-complexes (**6***trans*, **6***cis*), are disfavored relative to *syn–syn* precursors (**5***trans*, **5***cis*).[10]



Scheme 1. Pd-catalyzed allylic substitution.

Keywords: allylic substitutions; memory effects; Pd-complexes; computer-assisted methods.
* Corresponding author. Tel.: +6221-54-8488; fax: +6221-54-4885; e-mail: bernd.goldfuss@urz.uni-heidelberg.de

0040–4020/00/$ - see front matter
PII: S0040-4020(00)00613-X

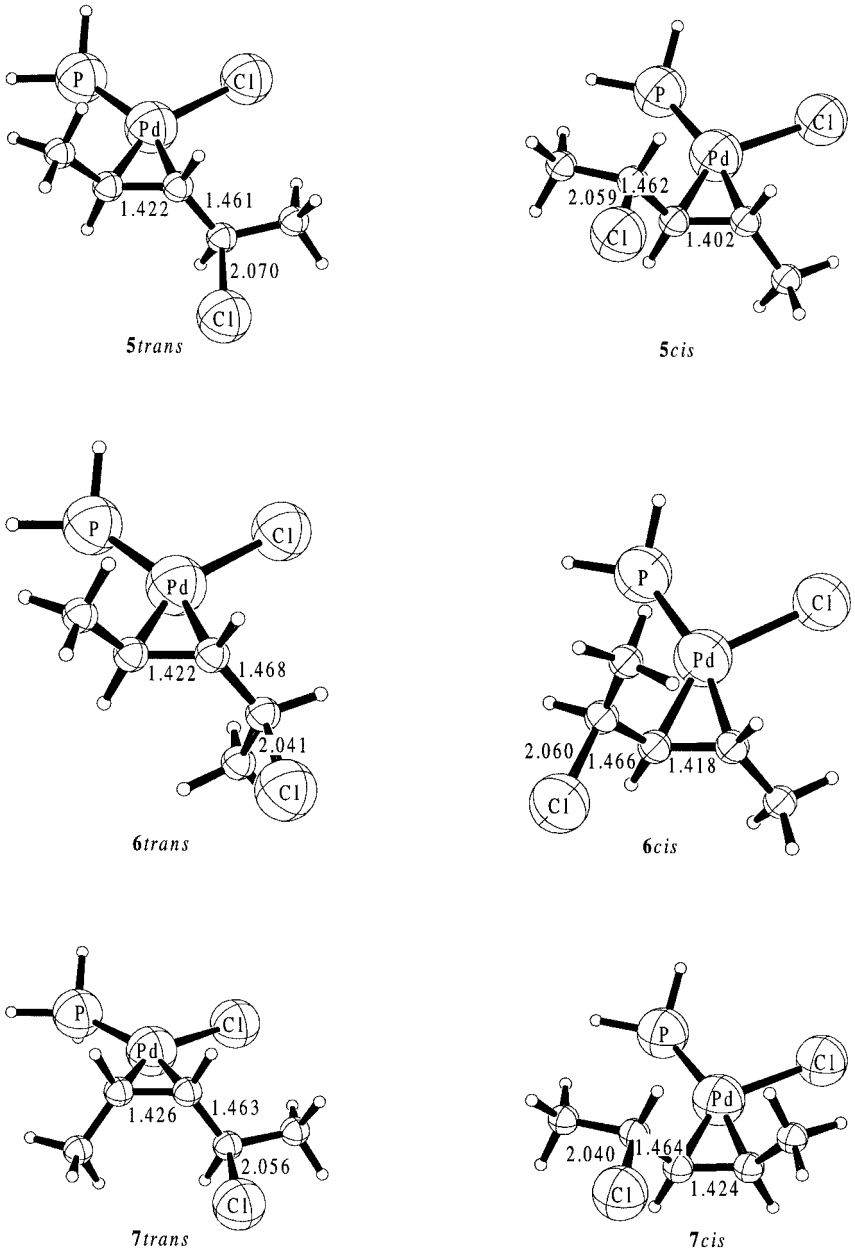


Figure 1. B3LYP/6-31+G*(C,H), LanL2DZdp-ECP (Pd, P, Cl) optimized structures.

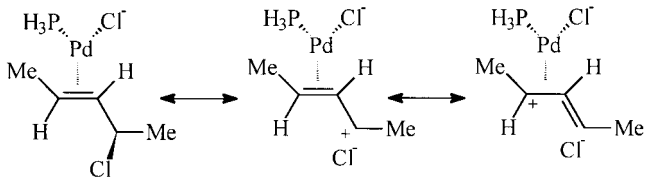
A preference of the allylic chlorine atom in a *trans*-PH_3 position is clearly apparent (**5***trans* vs. **5***cis*: 1.59 kcal/mol, Table 1). The same disposition for *trans*-PH_3 arrangements of allylic chlorine atoms also appears in the *Z*-2-chloro-pent-3-ene Pd-complexes **7***trans* and **7***cis* (1.63 kcal/mol, Fig. 1, Table 1).

The *trans*-phosphine preference of allylic nucleofuges (e.g. Cl^-) in Pd–alkene complexes can be rationalized by resonance structures shown in Scheme 2. The developing positive charge is better stabilized by the π-electron donating Cl^--ligand than by the σ^*-acceptor PH_3.[11]

The *trans*-phosphine preference of the leaving nucleofuge (Cl^-) in **5***trans* corresponds with the favored *trans*-phosphine attack of nucleophiles to Pd–allyl complexes.[8,12]

Table 1. Total energies (au), zero point energies (ZPE, kcal/mol) and relative energies (kcal/mol) of optimized *E*- and *Z*-2-chloro-pent-3-ene Pd-complexes (Fig. 1) (B3LYP/6-31+G* (C, H), LanL2DZdp with ECP (Pd, P, Cl). All structures were fully optimized and characterized as minima by frequency calculations)

5*trans*	**5***cis*	**6***trans*	**6***cis*	**7***trans*	**7***cis*
−361.08603	−361.08330	−361.08210	−361.08166	−361.08397	−361.08110
97.35	97.23	97.44	97.39	97.54	97.37
0.0	1.59	2.56	2.78	0.0	1.63



Scheme 2. Preference of the *trans*-phosphine position of the allylic chlorine atom.

Table 2. Total (au) and relative single point energies (the B3LYP/6-31+G* (C, H), LanL2DZdp with ECP (Pd, P, Cl) geometries and ZPE were employed (Table 1)) (kcal/mol) of *E*- and *Z*-2-chloro-pent-3-ene Pd-complexes (Fig. 1) with extended basis sets (B3LYP/6-311++G** (C, H), LanL2DZdp with ECP (Pd, P, Cl)) in the gas phase and in THF (PCM self-consistent-reaction-field)

	5*trans*	**5***cis*	**6***trans*	**6***cis*	**7***trans*	**7***cis*
Gas	−361.14363	−361.14089	−361.13966	−361.13926	−361.14162	−361.13872
	0.0	1.60	2.57	2.78	0.0	1.65
THF	−361.20061	−361.19805	−361.19823	−361.19710	−361.19853	−361.19591
	0.0	1.49	1.58	2.24	0.0	1.47

As a consequence of the *trans*-PH_3 arrangement, the allylic character is significantly more developed in the *trans*-structures of the *E*- and *Z*-olefin complexes (**5***trans* and **7***trans*) than in their *cis*-PH_3 analogs (**5***cis*, **7***cis*, Fig. 1). This effect is apparent geometrically from longer C_α–Cl (e.g. 2.07 Å in **5***trans* vs. 2.059 Å in **5***cis*) and C_β–C_γ distances (e.g. 1.422 Å in **5***trans* vs. 1.402 Å in **5***cis*) and shorter C_α–C_β bond distances (e.g. 1.461 Å in **5***trans* vs. 1.462 Å in **5***cis* Fig. 1) in structures with *trans*-PH_3 arranged chlorine atoms.

For an analysis of solvent effects, energies of Pd–alkene complexes were computed with extended basis sets and with Tomasi's Polarized Continuum Model (PCM) for the polar solvent THF (ϵ=7.6, Table 2). In the gas phase, no significant effect of increased C, H basis sets (i.e. 6-31+G*, Table 1 vs. 6-311++G**, Table 2) on the relative energies of the Pd–alkene complexes is apparent. The polar solvent THF stabilizes **5***cis*, **6***trans* and **6***cis* relative to **5***trans* as well as **7***cis* relative to **7***trans* (Table 2). However, the relative order of gas phase energies is retained in polar medium and the preference for arrangements with *trans*-phosphine situated allylic chlorine atoms is apparent also in THF (e.g. 1.49 kcal/mol for **5***trans* vs. **5***cis*, Table 2).

Conclusions

These studies show that the electronic differentiation of Pd-ligands (e.g. phosphines vs. chloride)[13] in alkene complexes can result in distinct preferences of *trans*-phosphine situated allylic nucleofuges (e.g. Cl^-), both in the gas phase and in polar solvents. Allylic nucleofuges stronger than Cl^- (e.g. carbonates) should increase these geometrical dispositions even more and might provide the basis for strong memory effects.

Computational Details

All structures were fully optimized with the B3LYP hybrid DFT method[14] in C_1 symmetry and were characterized as minima by frequency calculations.[15] For optimizations and frequency computations the 6-31+G* basis set was employed for the C and H atoms. The LanL2DZ-ECP basis sets[16] were augmented with diffuse s-, p- (Cl, P, Pd) and d- (Pd) functions (addition of outermost function multiplied by 0.25) and polarization d-functions for Cl (exp. 0.514), P (exp. 0.34) and a f-function for Pd (exp. 1.472).[17] Tomasi's Polarized Continuum Model (PCM-SCRF) was employed for solvent computations (THF, ϵ=7.6).[18]

Acknowledgements

We thank the Fonds der Chemischen Industrie (also for a Liebig grant to B. G.), the Deutsche Forschungsgemeinschaft, the Research Pool Foundation (University Heidelberg), the Degussa-Hüls AG and the BASF AG for support. B. G. is especially grateful to Prof. Dr P. Hofmann for generous support at Heidelberg.

References

1. Recent reviews on enantioselective allylic substitutions: (a) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203–214. (b) Trost, B. M.; Vranken, D. L. V. *Chem. Rev.* **1996**, *96*, 395–422.
2. (a) Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* **1981**, *22*, 1399–1402. These initial results were later disputed: (b) Trost, B. M.; Schmuff, N. R. *Tetrahedron Lett.* **1981**, *22*, 2999–3000. For a recent review see: (c) Poli, G.; Scolastico, C. *Chemtracts* **1999**, *12*, 837–845.
3. Normally, opposite ee's of **4** but of equal amount should result if different enantiomers of chiral ligands were employed. Matt P. v.; 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*, 265–284.
4. Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 235–236.
5. Suppression of rearrangements can be achieved at low temperatures: (a) Kazmaier, U.; Zumpe, F. L. *Angew. Chem.* **2000**, *112*, 805–807; *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 802–804. (b) Kazmaier, U.; Zumpe, F. L. *Angew. Chem.* **1999**, *111*, 1572–1574; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1468–1470.
6. (a) Pfaltz, A. *Synlett* **1999**, 835–842. (b) Pfaltz, A. *Acta Chem. Scand.* **1996**, *50*, 189–194.
7. (a) Butts, C. P.; Crosby J.; Lloyd-Jones, G. C.; Stephen, S. C.

Chem. Commun. **1999**, 1707–1708. (b) Lloyd-Jones, G. C.; Stephen, S. C. *Chem. Eur. J.* **1998**, *4*, 2539–2549. (c) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681–1687.

8. Enantiomer differentiation ionization: (a) Gais, H.-J.; Eichelmann, H.; Spalthoff, N.; Gerhards, F.; Frank, M.; Raabe, G. *Tetrahedron: Asymmetry* **1998**, *9*, 235–248. For enantioselective additions (the reverse step) analogous steric and electronic effects apply: (b) Steinhagen, H.; Reggelin, M.; Helmchen, G. *Angew. Chem.* **1997**, *109*, 2199–2202; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2108–2110.

9. For experiments and computations on β-silyl Pd–allyl complexes see: Macsari, I.; Szabo, K. J. *Organometallics* **1999**, *18*, 701–708.

10. Cf. Allylic 1,3-strain: (a) Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841–1860. (b) Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006–5017.

11. *trans* Effect and *trans* influence in metal complexes: Cotton, F. A.; Wilkinson, G. In: *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1998, p 1299.

12. (a) Blöchl, Togni, A. *Organometallics*, **1996**, *15*, 4125–4132. (b) Hayashi, T.; Kawatsura, Uozumi, Y. *Chem. Commun.* **1997**, 561–562.

13. Anionic Pd-catalysts: (a) Amatore, C.; Jutand, A. *Acc. Chem. Res.* **2000**, *33*, 314–321. Halide ligand effects in Pd-systems: (b) Wang, Z.; Zhang, Z.; Lu, X. *Organometallics*, **2000**, *19*, 775–780. (c) Lloyd-Jones, G. C.; Stephen, S. C. *Chem. Commun.* **1998**, 2321–2322.

14. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

15. 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98, Revision A.5; Gaussian: Pittsburgh, PA, 1998.

16. (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.

17. (a) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111–114. (b) Huzinaga, S., Ed. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: Amsterdam, 1984.

18. (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117–129. (b) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327–335.