

A DFT Study of the Effect of the Ligands in the Reductive Elimination from Palladium Bis(allyl) Complexes

Martín Pérez-Rodríguez,¹ Atualpa A. C. Braga,² Angel R. de Lera,¹ Feliu Maseras,²
Rosana Alvarez,^{*1} and Pablo Espinet^{*3}

¹ Departamento de Química Orgánica, Facultad de Química, Universidade de Vigo, Lagoas-Marcosende s/n, 36310 Vigo, Spain

² Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona, Spain

³ IUCINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

The effect of some selected ligands (L = empty, PMe₃, ethylene, maleic anhydride) in the reductive elimination of the palladium complexes *cis*-[Pd(η¹-allyl)(η¹-allyl)(PMe₃)L] and Pd(η¹-allyl)(η³-allyl)L to form hexa-1,5-diene was computationally studied using DFT methods. Among the various possible coupling processes (C1_{sp³}-C1⁰_{sp³}, C3_{sp²}-C3⁰_{sp²}, and C1_{sp³}-C3⁰_{sp²}), C3-C3⁰ bond formation is the most favored in all cases, as reported before for *cis*-[Pd(η¹-allyl)(η¹-allyl)(PH₃)₂]. Interestingly, the activation energy for this coupling changes with the L ligand: empty (4.6 kcal/mol) < MA (5.8 kcal/mol) < CH₂CH₂ (12.5 kcal/mol) < PMe₃ (17.3 kcal/mol). Therefore, tricoordinated Pd(η¹-allyl)(η¹-allyl)L complexes undergo reductive elimination at higher rates than the tetracoordinated counterparts. The order L = empty < L = MA is inverse to that found for carbon ligands (alkyl, aryl, alkenyl) that couple via direct C1-C1⁰ reductive elimination; the order L = empty < L = MA is also followed by the allyl groups when the disfavored C1-C1⁰ bond formation is considered. Structural analysis reveals that the C3-C3⁰ reductive elimination of *cis*-[Pd(η¹-allyl)₂(PMe₃)] is particularly favored by the small distortion of the original T-shaped geometry in the transition state, which preserves the hyperconjugative d_σ(C1-Pd)π*(C2dC3)-type interaction between the metal and the allyl substituents. The activation energies for the elimination of allyl groups are intermediate between those of alkenes/arenes and alkyls when palladium complexes with similar composition *cis*-[Pd(R)(R)(PMe₃)L] are compared. Although the effect is more moderate than in other carbon substituents, π-acceptor ligands (MA) and to a lesser extent olefins (exogenous or the same substrates/products) are efficient additives in this coupling, an electronic effect that is conveyed to the distant C3 and C3⁰ atoms by the entire interacting system. Consistent with this proposal, the transition state for the C3_{sp²}-C3⁰_{sp²} reductive elimination in *cis*-[Pd(η¹-allyl)(η¹-allyl)(PMe₃)L] shares both structural and electronic features with a pericyclic (homo)Cope rearrangement.

Introduction

Allylpalladium complexes play a prominent role in organometallic chemistry, due to their implication in a variety of processes,¹ ranging from the classical nucleophilic addition and cross-coupling to the oxidation of alkenes and conjugated dienes and recently to electrophilic attacks preceding subsequent transformations. Thus, the Pd-catalyzed coupling of allylstannanes or -silanes with allyl electrophiles (halides, carboxylates)²

affords 1,5-dienes by reductive elimination from bis(allyl)-palladium complexes,³ including the formation of carbocycles when appropriate precursors are used.⁴

Interestingly, bis(η³-allyl)palladium complexes are reluctant to undergo reductive elimination, and the presence of additional ligands is crucial for the success of the reaction.^{2c} Phosphines facilitate the reductive elimination,^{2c,5} most likely by conversion of [Pd(η³-allyl)₂] to the corresponding [Pd(η¹-allyl)(η³-allyl)-(PR₃)] complex, a species characterized by NMR.^{2a,c,6} Olefins, present either as reagents or as additives, also favor the reductive elimination of allyl groups. In this respect Kurosawa and co-workers showed that the allylic chloride substrates promoted

[†] Part of the Dietmar Seyferth Festschrift. With this paper we want to honor Dietmar Seyferth, a true gentleman, for his generous dedication to chemistry and, as editor, to the chemical community.

*To whom correspondence should be addressed. E-mail: espinet@qi.uva.es (P.E.); rar@uvigo.es (R.A.).

(1) (a) Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 1997. (b) De Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2004.

(2) (a) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* 1996, 118, 6641. (b) Szabo, K. *Chem. Eur. J.* 2000, 6, 4413. (c) Nakamura, H.; Aoyagi, K.; Shim, J. G.; Yamamoto, Y. *J. Am. Chem. Soc.* 2001, 123, 372. (d) Nakamura, H.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* 2001, 40, 17.

(3) Mendez, M.; Cuerva, J. M.; Gomez-Bengoa, E.; Cardenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* 2002, 8, 3620.

(4) Mendez, M.; Echavarren, A. M. *Eur. J. Org. Chem.* 2002, 15.

(5) (a) Krause, J.; Bonrath, W.; Poerschke, K. R. *Organometallics* 1992, 11, 1158. (b) Krause, J.; Goddard, R.; Mynott, R.; Porschke, K. R. *Organometallics* 2001, 20, 1992.

(6) (a) Benn, R.; Jolly, P. W.; Mynott, R.; Raspel, B.; Schenker, G.; Schick, K.-P.; Schroth, G. *Organometallics* 1985, 4, 1945. (b) Kuhn, O.; Mayr, H. *Angew. Chem., Int. Ed.* 1999, 38, 343. (c) Pichierri, F.; Yamamoto, T. Y. *J. Org. Chem.* 2007, 72, 861.

autocatalysis in Pd-mediated cross-coupling reactions and further extended the observation to exogenous olefins.⁷ Goliaszewski and Schwartz noted that 1,5-dienes were produced from allylic tin reagents and (π -allyl)palladium complexes only when maleic anhydride, a π -acidic ligand, was added.⁸ One of us (P.E.) examined the reason for the success of a Pd-catalyzed coupling of allylstannanes with allyl electrophiles, in contrast to the fact that the stepwise stoichiometric reaction did not work, and determined that coupling takes place only in the presence of excess electron-deficient olefins (the allyl halide substrate in the catalytic process or exogenous *p*-benzoquinone added to the bis(allyl) intermediate formed in the stoichiometric reaction).⁹

A comprehensive DFT study by Echavarren et al.³ looking into the role of phosphines on the formation of hexa-1,5-diene, starting with $[\text{Pd}(\eta^3\text{-allyl})_2]$, $[\text{Pd}(\eta^3\text{-allyl})(\eta^1\text{-allyl})(\text{PH}_3)_2]$, or $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PH}_3)_2]$, revealed that the lowest bar-

rier for the reductive elimination corresponded, unexpectedly, to C3-C3⁰ bond formation from $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PH}_3)_2]$ (in preference to the classical C1-C1⁰ mode exhibited by other carbon ligands), concluding that the role of phosphine was to form this complex with two σ -allyl groups. On the basis of this work and on our recent study showing that the reductive elimination barrier in alkyl-, vinyl-, or arylpalladium(II) complexes is dramatically affected by the nature of the ancillary ligands,¹⁰ we now consider the possible effect of different L ligands in the reductive elimination of bis(allyl)palladium complexes to produce hexa-1,5-diene, and try to understand why C3-C3⁰ bond formation from $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PH}_3)_2]$ is preferred to the classical C1-C1⁰.

Computational Methods

All computations have been performed using the Gaussian 03 software package.¹¹ To include electron correlation at an affordable computational cost, density functional theory (DFT)¹² was used by means of the Becke three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).¹³ The 6-31G* basis set for C, H, and P, in conjunction with the Stuttgart/Dresden relativistic effective core potential for Pd, were chosen to compute the geometries, energies, and normal frequencies. Stationary points were characterized by means of harmonic

analysis, and transition states were confirmed by the relationship between nuclei motion and the unique imaginary vibration frequency. All thermodynamic results were calculated at 298.15 K. PCM¹⁴ and COSMO-RS¹⁵ models, as implemented in Gaussian 03, were used to estimate the effect of the solvent (CH₃CN, DMF) at each optimized geometry. For some selected cases, topological analysis using Bader's theory of atoms in molecules was also applied.¹⁶ NICS values¹⁷ were computed using the gauge-independent atomic orbitals (GIAO) method¹⁸ as implemented in Gaussian 03.

Results

Reaction Modes and Conformational Diversity. In order to examine the effect of L on the coupling barrier, we have selected $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PMe}_3)\text{L}]$ complexes with L = empty (1), PMe₃ (2), and the two representative olefins ethylene (3) and the electron-deficient maleic anhydride (4) as likely coupling intermediates formed in the presence of ligands or coupling additives. Complex 2, $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PMe}_3)_2]$, is the reference case, as it corresponds to the complex studied by Echavarren with PH₃, found to be the intermediate in the preferred coupling pathway. Complexes 3 and 4 are chosen to test the effect of substituting a phosphine for a double bond (which may eventually represent an allyl reagent coordinated in an η^2 mode) or for a strong π -acceptor, respectively. Finally, 1 represents the hypothetical transient formation of the tricoordinated intermediate $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^1\text{-allyl})(\text{PMe}_3)]$ from the stable $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^3\text{-allyl})(\text{PMe}_3)]$.¹⁹ The coupling barriers from these plausible intermediates, starting from their conformations of minimum energy, Min- η^1, η^1 , were calculated by considering the transition states for the possible coupling pathways (C3-C3⁰, C1-C1⁰, C1-C3⁰, C1⁰-C3), shown in Scheme 1. As noted in Scheme 1, for TS-A and TS-B, two possible relative arrangements exist for the two allyl groups: synperiplanar and gauche. For TS-C and TS-D, the source of conformational complexity arises from the coordination mode (η^1 or η^3) of the allyl group trans to the phosphine.

For the sake of completeness, we also considered the structures presented in Scheme 2. In this case, the coupling starts from the minimum energy conformation (Min- η^1, η^3) of $cis\text{-}[\text{Pd}(\eta^1\text{-allyl})(\eta^3\text{-allyl})\text{L}]$ intermediates, evolves through TS-E, and results in the Pd(0) complex 11 with the coupling product coordinated to Pd(0). This additional path was calculated for L=empty (7), PMe₃ (8), ethylene (9), maleic anhydride (10).²⁰

A total of 32 processes were computationally studied and characterized (note the equivalence of the two C1-C3⁰ bond formation processes for L = PMe₃). For all the cases, the structures and energies of the starting minima (Min), the

(7) Kurosawa, H.; Emoto, M.; Ohnishi, H.; Miki, K.; Kasai, N.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* 1987, 109, 6333.

(8) (a) Goliaszewski, A.; Schwartz, J. *J. Am. Chem. Soc.* 1984, 106, 5028. (b) Goliaszewski, A.; Schwartz, J. *Organometallics* 1985, 4, 417.

(9) Albeniz, A. C.; Espinet, P.; Martí'n-Ruiz, B. *Chem. Eur. J.* 2001, 7, 2481.

(10) Perez-Rodriguez, M.; Braga, A. A. C.; Garcia-Melchor, M.; Perez-Temprano, M. H.; Casares, J. A.; Ujaque, G.; de Lera, A. R.; Alvarez, R.; Maseras, F.; Espinet, P. *J. Am. Chem. Soc.* 2009, 131, 3650.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc., Wallingford, CT, 2004.

(12) Kohn, W.; Sham, L. J. *Phys. Rev.* 1965, 140, A1133.

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

(14) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* 1981, 55, 117.

(b) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* 1997, 107, 3210.

(15) Eckert, F.; Klamt, A. *AIChE J.* 2002, 48, 369.

(16) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.

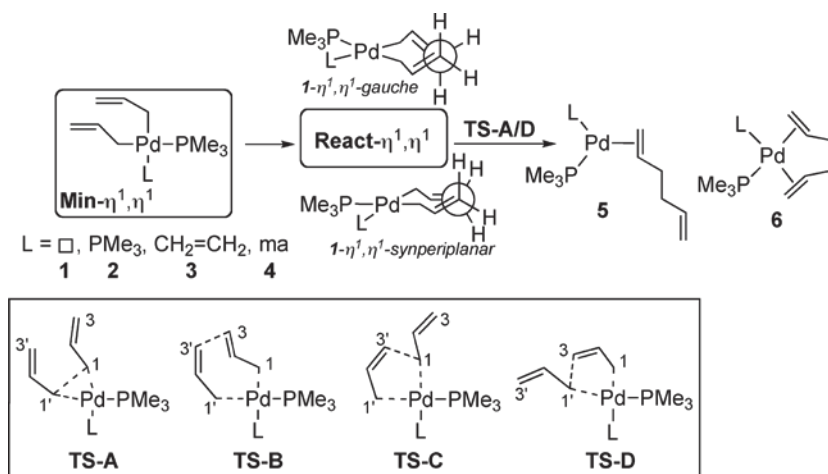
(17) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* 1996, 118, 6317.

(18) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* 1990, 112, 8251.

(19) Obviously the tricoordinated complex 1 is unstable compared to the alternative $[\text{Pd}(\eta^1\text{-allyl})(\eta^3\text{-allyl})(\text{PPh}_3)]$, but it might be formed as a transient intermediate by a change of hapticity of the $\eta^3\text{-allyl}$ group.

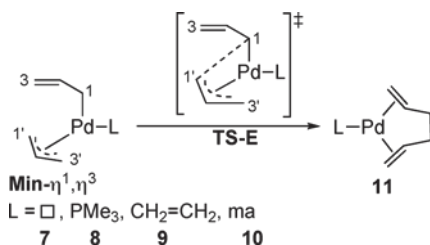
(20) The tricoordinated $[\text{Pd}(\eta^1\text{-allyl})(\eta^3\text{-allyl})]$ (7) would be an unstable intermediate (it is 13.6 kcal/mol less stable than the bis($\eta^3\text{-allyl}$) complex at the same level of theory) formed from $[\text{Pd}(\eta^3\text{-allyl})_2]$ by a change of hapticity, costing 21.3 kcal/mol. Since the calculated free energy coupling for reductive elimination from $[\text{Pd}(\eta^3\text{-allyl})_2]$ is 36.6 kcal/mol at the B3LYP/6-31G(d) level,³ it is unreasonable to think of $[\text{Pd}(\eta^1\text{-allyl})(\eta^3\text{-allyl})]$ as an accessible coupling intermediate.

Scheme 1. Reductive Elimination of *cis*-[Pd(η^1 -allyl)(η^1 -allyl)(PMe₃)L] to Pd(0) Complexes with Coordinated 1,5-Hexadiene, 5 and 6^a



^a Synperiplanar and gauche coupling conformations for the Pd η^1 - η^1 -coordinated allyl groups, as defined by the Newman projection of the forming bonds, were considered. Note that for L = empty 1,5-hexadiene 5 should be coordinated as a chelate in the Pd(0) complex.

Scheme 2. Reductive Elimination of Allyl Ligands from [Pd(η^3 -allyl)(η^1 -allyl)L]^a



^a For details, see the Supporting Information.

ready-to-couple conformation (React), the transition states (TS), and the products (5/6, 11) were first computed under vacuum. Furthermore, in order to determine solvent effects,

the structures were recalculated in CH₃CN and DMF. The effect of the solvent was shown to be small and predictable,²¹ in line with our previous results for other reductive elimination processes,¹⁰ and therefore will not be discussed further.

Energies of Activation. The thermodynamic data and relevant geometric parameters of each structure calculated for all the reductive elimination mechanisms through TS-A to TS-E are given in the Supporting Information. For the sake of brevity only the most relevant results will be discussed in the text, but a table collecting all the calculated energies is plotted here, to provide a general view (Figure 1). The computed activation free energies reported in Figure 1 (and in the Supporting Information) span from 4.6 to 29.0 kcal/mol. The conformational diversity of allyl coordination is not limited to transition states.

Szabo, established, in a computationally based rotation potential study, that the most stable conformer in [Pd(η^1 -allyl)(η^3 -allyl)(PH₃)] is found at a Pd-C1-C2-C3 dihedral angle of 105°, whereas the most destabilized conformation (5.9 kcal/mol less stable) occurs at 180°.^{2b} Here we have found that some of the conformations (React- η^1 , η^1) adopted by the allyl groups in

order to be ready to interact for reductive elimination in the complexes of Scheme 1 are energetically penalized with respect to the most stable conformer of each family (Min- η^1 , η^1). The values of the cost of these conformational changes correspond to the lower segment of the bars in Figure 1. The upper segment of the bars corresponds to the energy required to reach the TS from the reacting conformer (React- η^1 , η^1). The overall energy of activation (figures above the bars) for each coupling mode is the sum of the two segments.

An examination of all the values in Figure 1 shows that the lowest activation energy for each ligand 1–4 is in all cases that corresponding to the C3–C3⁰ coupling (TS-B), in coincidence with early studies by Echavarren et al. on bis(phosphine) (PH₃) palladium complexes.³ Hence, changing ligands produces an important effect on the activation free energy but does not extend to altering the coupling mechanism. On average, the pathway with the second smallest energy of the series corresponds to reductive elimination from the [Pd(η^1 -allyl)(η^3 -allyl)L] complex via TS-E (except for L = empty: 7.TS-E, 39.2 kcal/mol; 8.TS-E, 27.9 kcal/mol; 9.TS-E, 19.5 kcal/mol; 10.TS-E, 14.3 kcal/mol; see the Supporting Information), whereas the classic C1–C1⁰ coupling via TS-A is only the third.

When we put together all our computations on the entire series of reductive elimination of carbon substituents with PMe₃ as the ligand,¹⁰ the whole picture justifies the experimental reports that the C–C reductive elimination is slower for allyl than for vinyl and aryl fragments in palladium complexes.²² The reductive elimination of R–R starting from the same complex composition, for example *cis*-[Pd(R)₂(PMe₃)₂], increases in the following order: vinyl (11.5 kcal/mol) < phenyl (12.8 kcal/mol) < allyl C3–C3⁰ (16.4 kcal/mol) < methyl (28.6 kcal/mol) = allyl C1–C1⁰ (28.6 kcal/mol). Note that the allyl groups undergo reductive elimination at higher rates than for alkyl groups, albeit through mechanisms of very different nature (C3–C3⁰ coupling vs C1–C1⁰ coupling).

We had already studied the effect of the ancillary L ligands in other R–R couplings (R=Me, vinyl, Ph). Here we decided to examine the possible differences of the influence of the ligands for the case of allyl complexes, by comparing its effect in the C3–C3⁰ coupling (via TS-B) and in the C1–C1⁰ coupling (via TS-A), as the latter represents the less favorable

(21) Note that in practice any of these solvents is able to coordinate as a ligand, promoting η^3 - η^1 changes of the allyl hapticity. In fact, this is the reason for the observed fluxionality of (η^3 -allyl)palladium complexes in these solvents. See, for instance: (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975. (b) Pregosin, P. S.; Saltzman, R. *Coord. Chem. Rev.* 1996, 155, 35.

(22) Brown, J. M.; Cooley, N. A. *Chem. Rev.* 1988, 88, 1031.

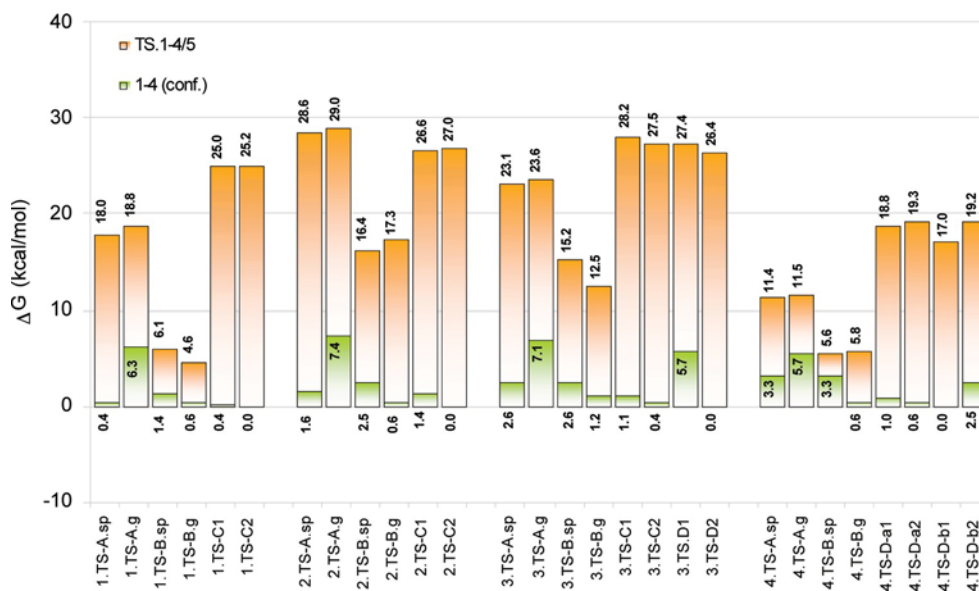


Figure 1. Energy values (in kcal/mol) computed for the transition structures TS (sum of the two segments) and nearest conformational minima (React- η^1, η^1 , lower segment) relative to the lowest energy conformer of the starting complexes 1–4 (Min- η^1, η^1). The values of the upper segment of the bars represent the energy difference between each transition state and the nearest React- η^1, η^1 conformational minimum.

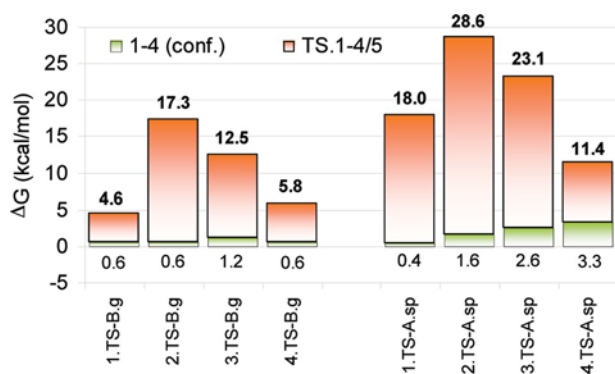


Figure 2. ΔG values (kcal/mol) computed for the lowest transition state structures TS-A and TS-B (sum of the two segments) and nearest conformational minima (React- η^1, η^1 , lower segment) relative to the lowest energy conformer (Min- η^1, η^1) of the starting complexes 1–4. The values at the upper segments of the bars represent the energy difference between each transition state and the nearest React- η^1, η^1 conformational minimum.

case where the allyls would couple as a kind of special alkyl compound. This comparison might eventually help to better understand the factors contributing to reduce the activation energy for the C3-C3⁰ coupling.

The energy values computed for the chosen processes are plotted separately in Figure 2. The two allyls can approach the coupling conformations (React- η^1, η^1) in synperiplanar (TS-A.sp or TS-B.sp) or gauche (TS-A.g or TS-B.g) conformations (Scheme 1), for which the stability differs, at most, by 3.3 kcal/mol. The lowest TS conformations have been chosen: namely, the synperiplanar conformations for TS-A and the gauche conformations for TS-B. Figure 2 shows clearly that the C3-C3⁰ bond formation in allyl complexes (from the TS-B.g gauche conformation) is preferred to the more classical C1-C1⁰ for reductive elimination. The stereoelectronic features of these reductive eliminations will be discussed in a later section.

A clear dependence of the calculated coupling activation free energy on the nature of the ancillary ligand L is found in each series. For the C1-C1⁰ coupling (TS-A.sp) the order is $\text{PMe}_3 > \text{ethylene} > \text{empty} > \text{ma}$, which is exactly the same previously reported for alkyls, vinyls, or aryls. For the TS-B.g (C3-C3⁰ coupling) energy, the trend is slightly different: $\text{PMe}_3 > \text{ethylene} > \text{ma} > \text{empty}$. The barrier is lowest for the tricoordinated complex in the latter case. The order of activation free energy associated with the rearrangement from Min- η^1, η^1 to the coupling-ready React- η^1, η^1 conformation and take only the upper part of the bar, associated with the coupling.

When the values found for the different ligands are compared, it can be noted that the barriers for the C3-C3⁰ coupling are roughly 50% of those for the C1-C1⁰ coupling (e.g. 17.3 vs. 28.6 kcal/mol for L= PMe_3), except for the case L = empty, where the C3-C3⁰ coupling drops to about 25% (4.6 kcal/mol vs 18.0 kcal/mol) of the corresponding value for C1-C1⁰ coupling. In other words, in comparison to the alkyl-like system, the allyl system finds, in all cases 1-4, an extra stabilization for the C3-C3⁰ transition state during the evolution from React-1- η^1, η^1 to TS-B.g. Moreover, in the tricoordinated case this extra stabilization is much more marked.

Regardless of the preferred bond formation event (via TS-A or TS-B), the elimination of hexa-1,5-diene from the tricoordinated $\text{Pd}(\eta^1\text{-allyl})_2(\text{PMe}_3)$ (4.6 kcal/mol, Figure 1) and from the tetra-coordinated *cis*- $[\text{Pd}(\eta^1\text{-allyl})_2(\text{PMe}_3)_2]$ (16.4 kcal/mol, Figure 1) complexes show values considerably smaller than that of $\text{Pd}(\eta^3\text{-allyl})_2$ (36.6 kcal/mol). Therefore, the experimental reports claiming an accelerating effect of phosphine on the reductive elimination of allyl groups are computationally confirmed.^{5,2c} The same applies to the effect of certain additives on the reaction, and the energy values of Figure 1 show the deep effect that the electronic properties of olefins present in reactants, ancillary ligands, or products have on the rate and substrate scope of the reductive elimination of palladium complexes.²³ The preferred reductive

Table 1. Geometric Parameters (Angles in deg and Distances in Å) for the Allyl Groups in the Selected Transition Structures TS-A.sp and TS-B.g for the Reductive Elimination in *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] Complexes (Figure 1)^a

	C1(L)-C2(L)-Pd-P	C1-Pd-C1 ⁰	C1-Pd	C1 ⁰ -Pd	C1-C1 ⁰	C3-C3 ⁰
1.TS-A.sp		56.55	2.190	2.281	2.120	3.791
1.TS-B.g		99.68	2.177	2.122	2.286	2.414
2.TS-A.sp		58.07	2.288	2.291	2.222	3.514
2.TS-B.g		94.39	2.266	2.265	3.324	2.128
3.TS-A.sp	1.30	57.72	2.298	2.232	2.235	3.580
3.TS-B.g	-63.30	97.68	2.221	2.209	3.335	2.260
4.TS-A.sp	173.86	57.45	2.283	2.305	2.205	5.735
4.TS-B.g	172.25	93.07	2.199	2.178	3.177	2.756

^a The forming bond distance is highlighted in boldface type.

elimination for allyls occurs via TS-B, and the electronic effects of the remaining ligands at Pd are felt at the allyl bond-forming atoms (C3 and C3⁰) despite their long distances to the metal. Thus, this effect that had been experimentally demonstrated and theoretically justified for the formation of ethane, butadiene, or biphenyl through C1-C1⁰ coupling^{10,24} is also operating for C3-C3⁰ coupling of allyls.

Optimized Structures. We have attempted to find a structural rationale for the effect of the palladium ligands in the reductive elimination of allyl groups via C1-C1⁰ and C3-C3⁰ bond formation. Table SI-1 (Supporting Information) collects the values of selected geometrical parameters for the computed minima and transition structures for the C1-C1⁰ and C3-C3⁰ reductive elimination that start from the *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] complexes. To aid in the discussion, the most significant bond angles and distances corresponding to the bond formation via TS-A.sp and TS-B.g, as the lowest energy alternatives of each coupling mode, are given in Table 1. Figure 3 depicts the minima and transition structures for the coupling of *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] complexes along these coupling modes, to highlight the differences between transition structures as a function of the ligand.

The C1-C1⁰ reductive elimination through A transition states follows the geometrical trends previously reported for methyl, vinyl, and phenyl groups.¹⁰ The tetracoordinated *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] reactant complexes 2-4 exhibit a square-planar geometry with minor deviations from planarity and evolve toward distorted tetrahedral-like geometries upon advancing to transition structures 2-4.TS-A.sp. The ethylene ligand shifts its orientation with respect to the coordination plane throughout the alkyl/alkyl, alkenyl/alkenyl, and aryl/aryl reductive elimination reaction paths, from perpendicular in the reactant complexes to parallel in the final Pd(PMe₃)(CH₂CH₂) complex. In the case of the allyl/allyl coupling, the rotation of the π -bonded ethylene ligand is almost complete before reaching the transition state in the TS-A structures (a similar effect is observed in cases TS-C and TS-D; see the Supporting Information), as shown by the values of the corresponding dihedral angles. C1-C1⁰ reductive elimination via the Y-shaped 1.TS-A.sp requires the approach of allyl(1) toward allyl(2) by ca. 30° on the coordination plane. An agostic interaction between the H atom of a methylene group and Pd was observed (H-Pd distance of 2.03 Å)²⁵ that fills the empty coordination site and donates electron density into the metal.

The transition states for the B pathways in complexes 2-4 follow trends similar to those described for A pathways. The

main difference is in the rotation of the π -bonded ethylene ligand. It is less advanced (ca. 30°) for the C3-C3⁰ TS-B mode, which is the least planar of the four transition states considered. Thus, for the alternative coupling modes the rotation of the ethylene complexes takes place *before* (C1-C1⁰, 3.TS-A.sp) or *after* (C3-C3⁰, 3.TS-B.g) the reductive elimination is complete.

The lowest energy path corresponds to the reductive elimination of the planar tricoordinated complex *cis*-[Pd(η^1 -allyl)₂(PMe₃)] via TS-B.g. This is a T-shaped planar structure that exhibits minor geometrical differences with the minimum.

The reductive elimination of the tricoordinated *cis*-[Pd(η^1 -allyl)₂(PMe₃)] complex is more special, since it shows not only the lowest transition state energy for TS-B.g of the series but also the largest relative destabilization for the alternative reductive elimination via TS-A.sp (from 4.6 to 18.0 kcal/mol; cf. 50% increase for the remaining ligands). A rationale can be obtained from the analysis of the structural differences between the two coupling modes. For the C1-C1⁰ reductive elimination the complex undergoes distortion from the T-shaped minimum to the Y-shaped transition structure TS-A by the in-plane movement of allyl(1) toward allyl(2) by ca. 30°, to reach the optimal C1-Pd-C1⁰ angle of ca. 67° in the transition state. In contrast, the geometry of the transition state is very close to the minimum with regard to the C1-Pd and Pd-C1⁰ bond angles and only requires a minor displacement for the C3-C3⁰ reductive elimination to occur (Table 2). Moreover, this movement only requires a minor change in the Pd-C1⁰ distance from the minimum to the transition structure (0.04 Å in C3-C3⁰ vs 0.1 Å in C1-C1⁰). Other parameters (forming C3-C3⁰ bond distance of 2.41 Å increase of 21% in C2dC3 bond distance) indicate the early but nonsymmetrical transition state TS-B.g. This directly produces an effect on the Pd-C1-C2-C3 dihedral angles.

The lower barrier associated to the C3-C3⁰ coupling can be related to changes in the planarity of the Pd-C1-C2-C3 units. In general, the C3-C3⁰ bond formation does not greatly alter the Pd-C1-C2-C3 dihedral angle relative to the minima (with changes of 18% in 1, 29% in 2, 2% for 3, and 29% in 4 for allyl(1) and of 3% in 1, 11% in 2, 3% for 3, and 0% in 4 for allyl(2)). These transition structures are stabilized at Pd-C1-C2-C3 angles close to 100° (1, 90°; 2, 77°; 3, 98°; 4, 119° for allyl(1) and 1, 109°; 2, 99°; 3, 108°; 4, 116° for allyl(2)). In contrast, for the C1-C1⁰ coupling mode, the Pd-C1-C2-C3 dihedral angles show a greater variation, with values spanning between 76 and 156° in the transition structures (1, 156°; 2, 150°; 3, 147°; 4, 76° for allyl(1) and 1, 135°; 2, 111°; 3, 138°; 4, 135° for allyl(2)). Thus, the geometries of the Pd-(allyl) fragments when *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] complexes advance toward the transition states show in general a progressive reduction of the side-by-side hyperconjugative $\sigma(C1-Pd)\pi^*(C2dC3)$ -type

(24) Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *Eur. J. Inorg. Chem.* 2007, 5390.

(25) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* 2007, 104, 6908.

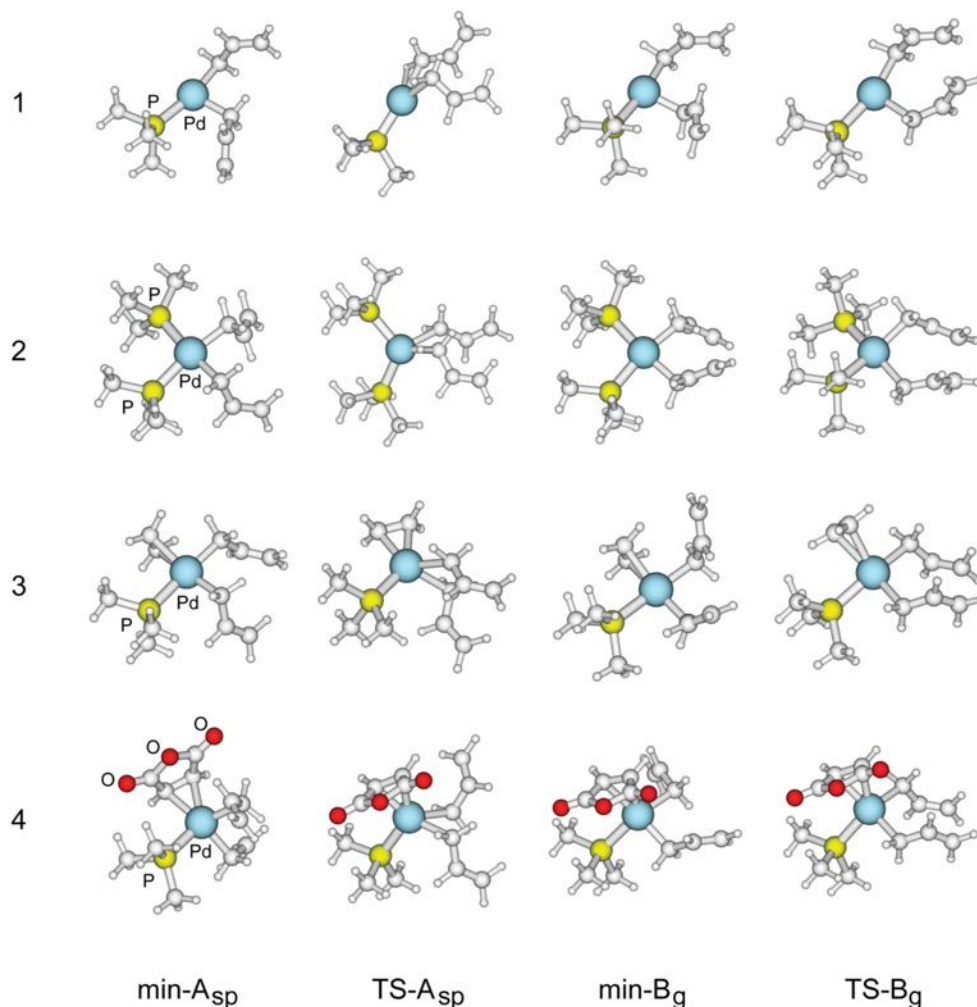
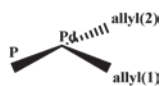


Figure 3. Minima and transition structures TS-A.sp and TS-B.g for the reductive elimination starting from the complexes cis -[Pd(η^1 -allyl) $_2$ (PMe $_3$)(L)]. For structures containing MA dark red balls represent O atoms, as indicated in min-A.sp for 4.

Table 2. P-Pd-C1 and P-Pd-C1 0 Bond Angles (in deg) in the Selected Transition Structures TS-A.sp and TS-B.g for the Reductive Elimination of Tricoordinated cis -[Pd(η^1 -allyl) $_2$ (PMe $_3$)] Complexes

		angle from P		difference
		min	TS	
1.TS-A.sp	allyl (1)	107.2	137.5	30.3
	allyl (2)	-167.3	-165.9	1.4
1.TS-A.g	allyl (1)	108.8	136.9	28.1
	allyl (2)	-166.6	-166.0	0.6
1.TS-B.sp	allyl (1)	107.2	102.6	-4.6
	allyl (2)	-167.3	-164.6	2.7
1.TS-B.g	allyl (1)	100.5	95.9	-4.7
	allyl (2)	-171.3	-164.5	6.8



interaction,^{2b} which is much greater in C1-C1 0 than in the alternative C3-C3 0 .

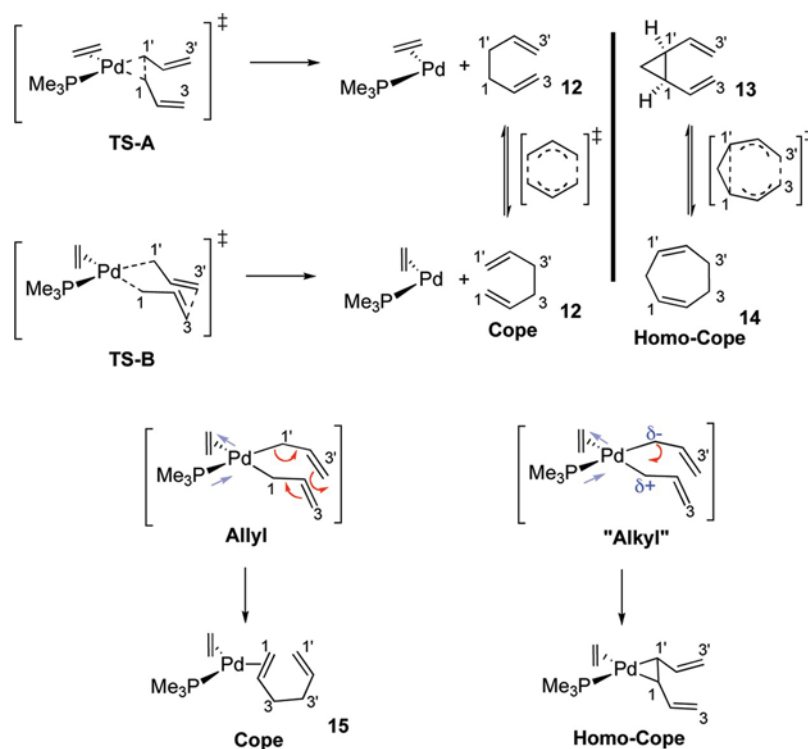
The case of 1.TS-B.g is again exceptional in this respect. The allyl(2) substituent in the C3-C3 0 bond formation does not relinquish the already favored $d_{\sigma}(C1-Pd) \rightarrow \pi^*(C2dC3)$ interaction of the minima (Pd-C1-C2-C3 113 $^\circ$) but undergoes further stabilization (to 109 $^\circ$) with minor changes in bond distances (Pd-C1 0 , C1 0 -C2 0 , C2 0 dC3 0). Conversely, the geometric requirements for C1-C1 0 bond formation are associated with greater destabilization of the Pd-C1-C2-C3 dihedral angle for the tricoordinated complex, which for allyl(2) increases

from 115 to 135 $^\circ$. Therefore, TS-B for the reductive elimination of tricoordinated Pd(η^1 -allyl) $_2$ (PMe $_3$) is particularly favored, whereas the alternative TS-A does not enjoy the same stabilization interactions. In addition, the smaller changes of the Pd-C1-C2-C3 dihedrals from the minima in C1-C1 0 bond formation take place in the case of MA. This explains the inversion in the order of activation energies for MA and empty complexes when C1-C1 0 and C3-C3 0 reductive eliminations are compared.

Reductive Elimination of Allyl Groups as a Pericyclic Reaction. Although prior examination of the electronic features of the C3-C3 0 allyl/allyl coupling using natural bond orbital (NBO) analysis revealed the partial formation of a π bond between C1 and C2, and their interaction with one of the metal lone pairs along the process,³ we have attempted to deepen our understanding of this bond formation. In this regard, we noticed structural similarities between the C3-C3 0 reductive elimination of palladium complexes and the [3,3]-homo-Cope sigmatropic rearrangement.²⁶ As shown in Scheme 3, forming hexa-1,5-diene (12) by C1-C1 0 and C3-C3 0 reductive elimination of cis -[Pd(allyl) $_2$ (PMe $_3$)L] complexes leads to the

(26) (a) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* 1989, 89, 165. (b) Piers, E. Rearrangement of Divinylcyclopropanes. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, Chapter 8.2, pp 971-998.

Scheme 3. Transition States (TS-A and TS-B) for Allyl-Allyl Reductive Elimination of the *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] Complexes^a



^a The analogy of the hexa-1,5-diene product (12) with that of the [3,3]-sigmatropic Cope rearrangement is shown. At right, aschematic view of the homo-Cope rearrangement from *cis*-divinylcyclopropane (13) to cyclohepta-1,4-diene (14) is depicted with the allyl units in the synperiplanar conformation.

structures of a degenerate [3,3]-sigmatropic Cope rearrangement. Furthermore, the transition structure of the C3-C3⁰ variant TS-B resembles that of a homo-Cope rearrangement of *cis*-divinylcyclopropane (13) to cyclohepta-1,4-diene (14).²⁷ In order to support this similarity and determine whether the C3-C3⁰ reductive elimination benefits from the particular features of the pericyclic processes, we set out to analyze the bonding properties, the aromaticity of the transition structures, and the electronic distribution, through MO analysis of the two reactions.

The topological analysis of the electron density of the transition structures TS-B using AIM¹⁶ confirmed its cyclic nature. Bond critical points and reaction paths for the transition structures of *cis*-[Pd(allyl)₂(PMe₃)(CH₂CH₂)] and the homo-Cope rearrangement are shown in Figure 4. A bond critical point was found connecting each pair of atoms on the cyclic structure. Moreover, only one single ring critical point of (3, δ 1) signature was found for the ring center, and no bond path was located between the C atoms bound to Pd. The values of electron density in the critical points are remarkably similar for both structures, with the exception of the bonds to Pd (with more diffuse d type orbitals), which are weaker and therefore the distances longer than those of the homo-Cope rearrangement.

Moreover, the HOMO-1 (74) orbital (Figure 5), a combination of the Pd p_z orbital and the π^* orbital of the allyl groups, shows an extended interaction area between Pd and the coordinated C atoms, as well as a σ type interaction between the terminal allyl carbons. The orbital structure and the electron pairing suggest that a redistribution of the σ C1-C1⁰ interaction (among others) toward the C3-C3⁰ region in 3.TS-B has taken

place similarly to what is considered to occur in a [3,3]-sigmatropic rearrangement. The ability of the metal to favor a σ -type bonding interaction of the allyl C1 atoms even at distances as large as 3 Å is what makes this process different from the classical pericyclic rearrangement. Furthermore, the charge responsible for the interaction is easier to convey than that of acovalent C-C bond, and therefore the activation energy of the metal-mediated bond formation is smaller with certain ligands (olefins) than those of analogous pericyclic reactions. We have computed activation energies of 16.8 kcal/mol for the boat-like²⁸ TS of a homo-Cope rearrangement of *cis*-divinylcyclopropane (cf. experimental value of $\Delta H^\ddagger = 18.8$ kcal/mol)²⁹ and of 33.6 kcal/mol for the Cope rearrangement of hexa-1,3-diene (cf. 34.2 kcal/mol for chairlike TS and 42.0 kcal/mol for a boatlike TS at the B3LYP/6-31G* level).³⁰ Even without the beneficial effect of the release of cyclopropane ring strain, the activation energies for the C3-C3⁰ reductive elimination from the *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] (L = ethylene, MA) complexes are smaller than that of the homo-Cope rearrangement.

The aromaticity of the transition structures was also analyzed as a further indication of the pericyclic nature of molecular rearrangements. A useful magnitude to estimate the aromaticity is the nucleus-independent chemical shift (NICS),^{17,31} since large negative NICS values corresponding to diatropic ring

(28) Ozkan, I.; Zora, M. *J. Org. Chem.* 2002, 68, 9635.

(29) Schneider, M. P.; Rau, A. *J. Am. Chem. Soc.* 1979, 101, 442.

(30) (a) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* 1997, 101, 8378. (b) Starorevov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* 2000, 122, 7377.

(31) (a) Schleyer, P. v. R.; Kiran, B.; Simiion, D. V.; Sorenson, T. S. *J. Am. Chem. Soc.* 2000, 122, 510. (b) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-S.; Kiran, B.; Jiao, B.; Puchta, R.; Hommes, N. J. R. *V. E. Org. Lett.* 2001, 3, 2465. (c) Gomes, J. A. N. F.; Mallion, R., B. *Chem. Rev.* 2001, 101, 1349. (d) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* 2005, 105, 3842.

(27) Hill, R. K. Cope, Oxy-Cope and Anionic Oxy-Cope Rearrangements. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: New York, 1990; Vol. 5, Chapter 7.1, pp 786-826.

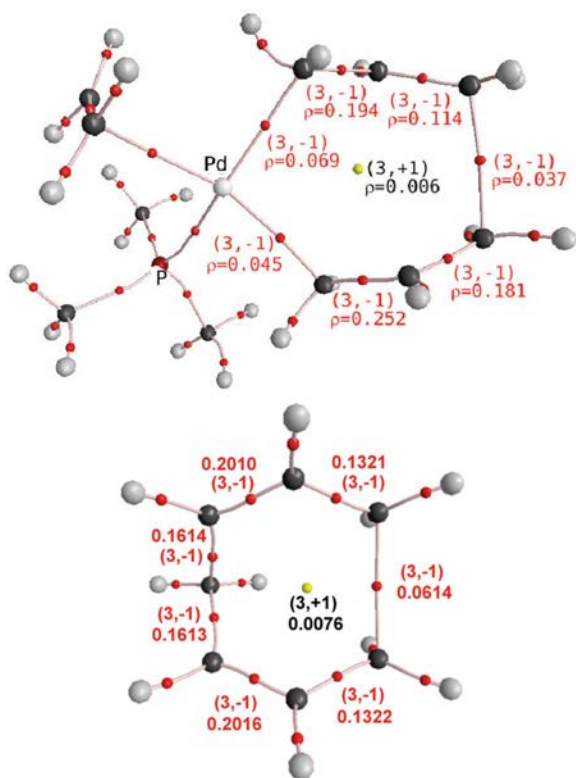


Figure 4. Critical points and reaction paths for 3.TS-B corresponding to the reductive elimination of the tetracoordinated complex *cis*-[Pd(η^1 -allyl)₂(PMe₃)(CH₂CH₂)] (top) and for the transition structure of the homo-Cope rearrangement (bottom). Bond critical points of (3,-1) signature between each pair of atoms of the ring, together with the values of the electron density, are marked in red.

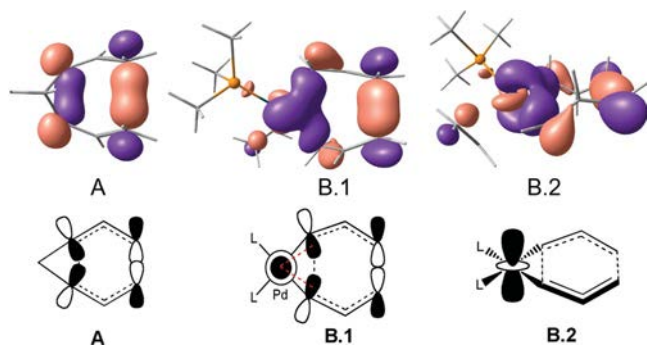


Figure 5. (Top) B.1/B.2: orbital representation corresponding to the transition structure of the reductive elimination of the square-planar complex *cis*-[Pd(η^1 -allyl)₂(PMe₃)(CH₂CH₂)] via C3-C3⁰ bond formation. Two regions of σ -type bonding interaction between the Pd-bonded C1-C1⁰ atoms and also between the C3-C3⁰ bond-forming atoms are clearly seen in HOMO-1 (B.1, front view; B.2, side view); A is a representation of the same orbitals for the homo-Cope rearrangement. (Bottom) Pictorial representation using p and d orbitals.

currents are associated to aromaticity (i.e., -9.7 for benzene at the ring center),¹⁷ whereas positive values are associated with paratropic ring currents and antiaromaticity.

With the exception of the ligand MA (which shows some loss of symmetry due to the coupling of ring currents of the interacting system and the ancillary ligand), the NICS(-3,3) values for the series of transition structures 1-4.TS-B are remarkably similar to those of the homo-Cope rearrangement (see the Sup-

porting Information). Thus, the estimation of the NICS(a,b) values for the transition structures suggests aromatic character of the reductive elimination by C3-C3⁰ bond formation.^{17,31}

Conclusions

The Pd-mediated allyl-allyl coupling reactions of *cis*-[Pd(allyl)₂(PMe₃)L] complexes, with L = empty, PMe₃, CH₂CH₂, MA, were theoretically studied. A comprehensive treatment of the reaction led us to consider a total of 32 reaction modes that, for each of the ligands, differ in the η^1 and η^3 hapticities and in the conformations adopted by the allyl ligands to favor the C1-C1⁰, C1-C3⁰, and C3-C3⁰ coupling modes.

As a general trend, all transition structures calculated from the tetracoordinated complexes lie halfway between the square-planar and the tetrahedral coordination geometries at palladium with different degrees of distortion. In contrast, tricoordinated complexes undergo reductive elimination through an almost planar transition structure with a distorted T or Y shape.

C3-C3⁰ coupling reactions were found to be the most favored in *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] complexes, in coincidence with the previous study of Echavarren et al.³ The values of the activation energies for the corresponding C1-C1⁰ modes with the same composition of the metal complex are at least 2-fold greater than those computed for the C3-C3⁰ counterparts.

For the most favorable C3-C3⁰ bond formation, the activation energies vary with the nature of the ligand and increase in the order empty < MA < CH₂CH₂ < PMe₃. Thus, tricoordinated complexes eliminate hexa-1,5-diene at higher rates, followed by the tetracoordinated complexes with π -acceptor ligands. The order of coupling energy the two most favorable C3-C3⁰ allyl coupling cases (empty < MA) is reversed with respect to the trend found earlier for the (necessarily C1-C1⁰) coupling of alkyl, aryl and alkenyl fragments, but would recover the usual trend (empty > MA) in the less favored C1-C1⁰ allyl coupling mechanism. Structural analysis sheds some light on this inversion, since the C3-C3⁰ reductive elimination of *cis*-[Pd(η^1 -allyl)₂(PMe₃)] is particularly favored by stereoelectronic effects associated with the small distortion required by the original T-shaped geometry to adopt the transition state geometry while maintaining the stabilizing side-by-side hyperconjugative d σ -(C1-Pd) π *-(C2dC3) type interaction.

Interestingly, the electronic effects of the substituent on Pd are transmitted to the distant C3 and C3⁰ bonding atoms. Closer examination of the C3-C3⁰ coupling revealed analogies with the homo-Cope sigmatropic rearrangement, including the occurrence of a cyclic transition state with aromatic features.³² The remarkable structural, energetic, and magnetic similarities with the homo-Cope rearrangement suggest that the C3-C3⁰ reductive elimination of *cis*-[Pd(η^1 -allyl)₂(PMe₃)L] complexes might be better described as a metallopericyclic reaction that benefits from the particular stereoelectronic features of the pericyclic orbital arrangement.

This C3-C3⁰ reductive elimination mechanism³ might as well occur in other bond formation reactions where allyl-metal complexes are involved. The Pd-catalyzed coupling of benzyl chloride and allyltributylstannane leading to an unexpected allylative dearomatization product³³ has been proposed to involve a reductive elimination from the C3 η^1 -allyl atom

(32) (a) von E. Doering, W.; Wang, Y. *J. Am. Chem. Soc.* 1999, 121, 10112. (b) Siebert, M. R.; Tantillo, D. J. *J. Am. Chem. Soc.* 2007, 129, 8686.

(33) Bao, M.; Nakamura, H.; Yamamoto, Y. *J. Am. Chem. Soc.* 2001, 123, 759.

and the para position of the η^3 -benzyl ligand.³⁴ Likewise, a transition state reminiscent of a C3-C3⁰ reductive elimination has been computed as the most favorable for the palladium-catalyzed conjugate addition of allyl(pinacol)boronates to styryl-activated enones.³⁵ Furthermore, computations on the enantioselective Tsuji decarbonylative allylation reaction of enol allyl esters suggest that the intermediate allyl palladium enolate rearranges most likely through the same type of cyclic seven-membered transition state, which in this case would resemble the Claisen sigmatropic rearrangement.³⁶

(34) Ariafard, A.; Lin, Z. *J. Am. Chem. Soc.* 2006, 128, 13010.

(35) Sieber, J. D.; Liu, S.; Morken, J. P. *J. Am. Chem. Soc.* 2007, 129, 2214.

(36) Keith, J. A.; Behenna, D. C.; Mohr, J. T.; Ma, S.; Marinescu, S. C.; Oxgaard, J.; Stoltz, B. M.; Goddard, W. A., III *J. Am. Chem. Soc.* 2007, 129, 11876.

Acknowledgment. We are grateful to the Spanish Ministerio de Ciencia e Innovación (INTECAT Consolider Ingenio 2010 (CSD2006-0003; CTQ2008-06647-C02-01; CTQ2007-67411/BQU; CTQ2009-14186/C02-01; “Juan de la Cierva” contract to A.A.C.B.), the Xunta de Galicia (Parga Pondal Contract to M.P.-R.), the Junta de Castilla y León (GR. 169/2008), and the ICIQ foundation for financial support. We also thank the CESGA for generous allocation of computational resources.

Supporting Information Available: Figures, text, and tables giving details of the computational methods and Cartesian coordinates for all the structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.