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Electronic differentiations in palladium-catalyzed allylic substitutions

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Abstract

The "*trans* rule" in Pd-catalyzed allylic substitutions predicts *trans* to phosphorus additions of nucleophiles to Pd–allyl intermediates, e.g., with P,N-ligands. This computational study reveals that not only the intrinsic electronic differentiation between P- (i.e., PH_3) and N-ligands (i.e., *para*-X-substituted pyridines), but also the "late" or "early" nature of the transition structures is crucial for strong *cis* vs. *trans* discriminations and hence for selectivity. Although *para*-nitro pyridine exhibits less intrinsic electronic differentiation than *para*-dimethylamino pyridine, the higher reactivity of the Pd–allyl-intermediate and the earlier nature of the transition structure yield a higher sensitivity for electronic differentiation for $X{=}NO_2$ than $X{=}NMe_2$.

Keywords: Palladium; Catalysis; Allylic substitution; Transitions structures; Computations

1. Introduction

Palladium catalyzed allylic substitutions are frequently employed for stereoselective C–C- and C-heteroatom couplings [1]. Attempts to design highly selective catalysts [2] were especially successful with three different concepts, i.e., "side arm guidance" of nucleophiles by Hayashi's bifunctional ferrocene ligands [3], "chiral pockets" generated by Trost's C_2-symmetric diphosphanes based on 2-(diphenylphosphino)benzoic acid (dppba) [4] and by different donor atoms and steric asymmetry, e.g. in P,N-ligands such as phosphinooxazolines (PHOX, Scheme 1) [5].

Enantioselectivies with such P,N-ligands arise from synergetic combinations of steric differentiation, i.e., more stable *exo* vs. less stable *endo* Pd-η^3-allylic intermediates, as well as electronic differentiation, i.e., preferential attack of nucleophiles *trans* to phosphorus (Scheme 2) [6–8].

Memory effects can be explained by analogue *trans*-stabilizations of allylic nucleofuges in Pd–ene complexes [9]. The positions *trans* to phosphane are more favored for both, the departing nucleofuge (e.g., chloride, carbonate, etc.) and the attacking nucleophile (e.g., malonate, Scheme 3). If low temperatures suppress Pd–ene rearrangements [10], a α-memory effect can be observed [9a].

We have recently reported chelating fencholates [11], which were employed in enantioselective organozinc catalysts [12], in chiral *n*-butyllithium aggregates [13], in Cu-catalysts for enantioselective 1,4-additions [14], and as modular fenchyl diphenylphosphinites (FENOPs) in Pd-catalysts for allylic substitutions [15]. Higher enantioselectivities are found for phenyl- and anisyl fenchylphosphinites due to Pd-arene π-coordinations, than for the pyridine derivative with a Pd–N-contact. The "*trans* to P attack" is preferred kinetically in the transition structures (Scheme 4).

This phenomenon of "*trans* phosphane" preference is subject of our computational analysis on electronic differentiations in Pd-catalyzed allylic substitutions.

2. Results and discussion

Electronic differentiations by dissimilar ligand atoms contribute to the relative energies of competing transition structures in Pd-catalyzed allylic substitutions [16]. This kinetic effect is measured intrinsically for attacks of the

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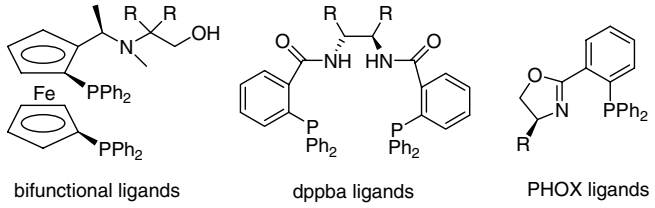
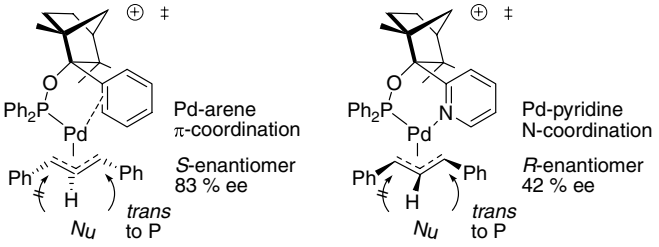
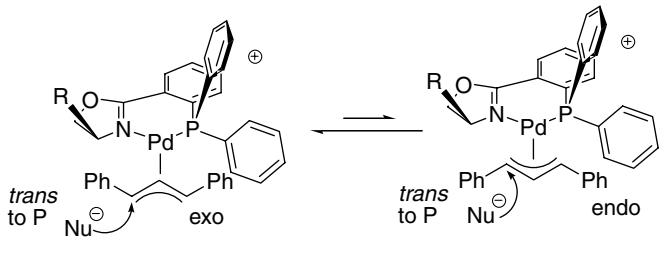


Scheme 1. Prominent ligands for enantioselective Pd-catalyzed allylic substitutions.



Scheme 4. Pd-π arene coordination gives higher enantioselectivities with an other sense in phenyl and anisyl fenchylphosphinites (FENOPs) than in the pyridine analogue.



Scheme 2. *Trans* to phosphorus attack of nucleophiles on Pd–PHOX allyl complexes (R: e.g., *i*Pr) by electronic differentiation. Steric effects favor *exo* over *endo* allyl arrangements.

neutral nucleophile ammonia in the gas phase [17]. Thermodynamically, electronic differentiations are evident from relative Pd–ene product complex stabilities [9a]. Pyridine ligands with electron donating or electron withdrawing *para*-substituents (–NMe_2, –H, –NO_2) are employed here to reveal such kinetic and thermodynamic differentiations in Pd(PH_3)allyl model species for *trans* or *cis* to phosphorus attack of NH_3 (Scheme 5, Tables 1 and 2) [18,19].

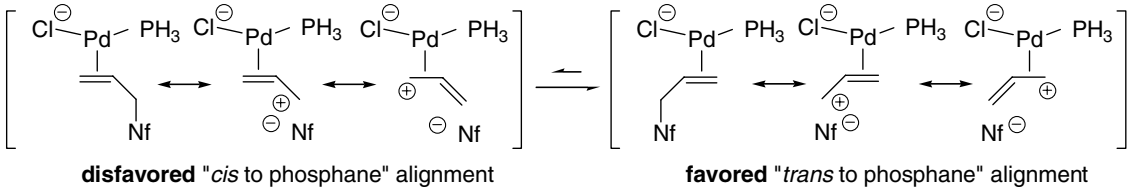
The computed activation energies (E_a) range from 10.79 to 4.13 kcal mol^{-1}, the electronic reaction energies (E_r) are endothermic from 10.25 to 3.32 kcal mol^{-1} (Scheme 6, Table 2). Lower activation energies (E_a) for NH_3 additions are apparent for more electron withdrawing ligands (X=NO_2), due to higher electrophilicities of the Pd–allyl educt complexes. Less endothermic electronic reaction energies (E_r) are apparent for more electron withdrawing ligands (i.e., X=NO_2), pointing to the dominating electron donating character of the ene-ligand in the product complexes (Scheme 6, Table 2).

Both, transition structures and Pd–ene product complexes exhibit higher stabilities for "*trans* to phosphorus" orientations of the NH_3 unit, in agreement with the "*trans* rule" in Pd-catalyzed allylic substitutions with P,N-ligands [7–9a]. In Pd–ene product complexes, the degree of electronic differentiation between these *cis* and *trans* alignments is stronger for the electron donating NMe_2 substituent (ΔE_r^{Prod} : 0.99 kcal mol^{-1}) than for the electron withdrawing NO_2 group (ΔE_r^{Prod} : 0.63 kcal mol^{-1}, Table 2), the pyridine ligands hence function dominantly as electron donors. This supports earlier findings on the strong back-bonding (σ^*-acceptor) character and *trans*-influence of phosphane ligands in Pd–ene complexes [9a].

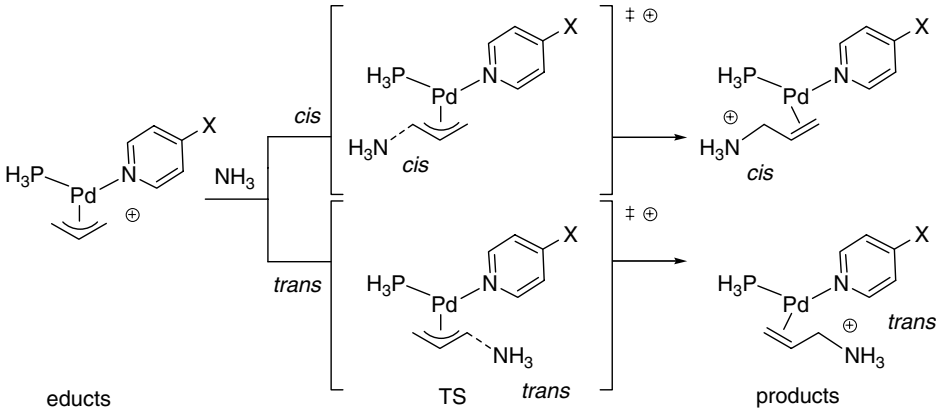
Surprising however is the *decreasing* electronic differentiation between *cis* and *trans* alignments in transition structures in the order $NO_2 > H > NMe_2$ (Table 2). The largest TS differentiation (and hence the highest selectivity) is apparent for the electron withdrawing NO_2 group (ΔE_a^{TS} : 1.89 kcal mol^{-1}, Table 2), which in contrast yields the poorest differentiation in Pd–ene product complexes (ΔE_r^{Prod} : 0.63 kcal mol^{-1}, Table 2).

The geometries of transition structures and Pd–ene product complexes (Table 3) provide answers for this inconsistent *increase* (TS) or *decrease* (products) of *cis*–*trans* differentiations. As found earlier in Pd–ene complexes, *trans*-phosphane situated allylic nucleofuges (i.e., $-NH_3^+$) are not only more stable than *cis*-isomers, but also show longer N–C_α distances and more delocalized allylic units with stronger C_α–C_β=C_γ bond length equalization [9a].

In Pd–ene product complexes, *trans* alignments show longer H_3N–C_α distances than *cis* orientations (Fig. 1, Table 3). These H_3N–C_α distances increase for Pd–ene products with more electron donating X substituents (longest for *trans* NMe_2: 1.611 Å, Table 3), tending to displace the $-NH_3^+$ nucleofuge. While a localized $H_3N^{(+)}$–$C_\alpha H_2$–$C_\beta H$=$C_\gamma H_2$ ligand exhibits longer C_α–C_β and shorter C_β=C_γ distances, the favored *trans* to phosphane



Scheme 3. The "*trans* to phosphane" alignment is electronically favored over the "*cis*" alignment in Pd–ene equilibrium complexes. This preference can also explain α-memory effects.



Scheme 5. For X=NMe_2, H and NO_2 electronic differentiations are computed for NH_3 additions to Pd–allyl educts and for formations of Pd–ene product complexes, *cis* and *trans* relative to PH_3.

Table 1
Total energies (a.u.) and imaginary frequencies (*i*, cm^{-1}) of Pd-species according to Scheme 5[a]

Pyridine X	Educts[b]	*cis*-TS	*trans*-TS	*cis*-Products	*trans*-Products
–NMe_2	−970.24080	−1026.73770 (*i* 268)	−1026.74049 (*i* 252)	−1026.73857	−1026.74015
–H	−836.32923	−892.83044 (*i* 261)	−892.83326 (*i* 243)	−892.83243	−892.83377
–NO_2	−1040.80638	−1097.31088 (*i* 254)	−1097.31389 (*i* 236)	−1097.31418	−1097.31519

[a] B3LYP/6-31G* (C,H,N,P,O), /SDD (Pd) optimized transition structures in most stable conformations. Energies include ZPE corrections scaled by 0.9806.
[b] Total energy of NH_3 (C_{3v}): −56.51410 H.

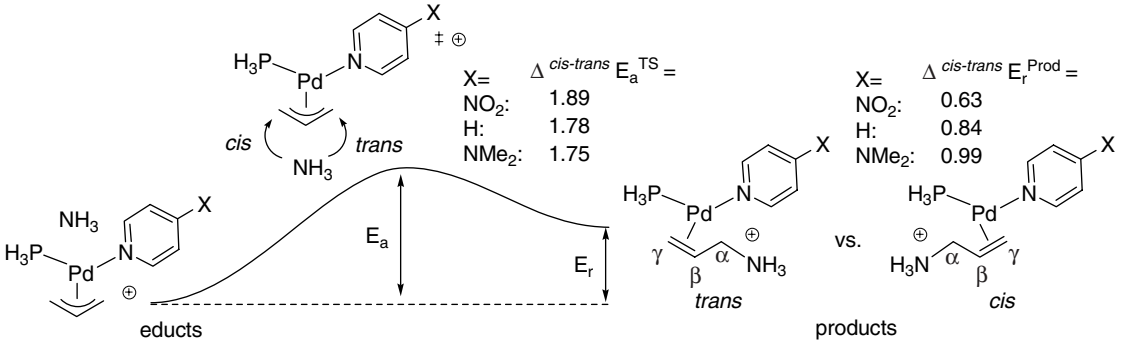
Table 2
Activation (E_a) and reaction (E_r) energies (kcal mol^{-1}) relative to Pd–allyl complexes and NH_3 according to Scheme 5[a]

Pyridine X	E_a (*cis*-TS)	ΔE_a^{TS}	E_a (*trans*-TS)	E_r (*cis*-prod.)	ΔE_r^{Prod}	E_r (*trans*-prod.)
–NMe_2	10.79	1.75	9.04	10.25	0.99	9.26
–H	8.09	1.78	6.31	6.83	0.84	5.99
–NO_2	6.02	1.89	4.13	3.95	0.63	3.32

[a] B3LYP/6-31G* (C,H,N,P,O), /SDD (Pd) optimized transition structures in most stable conformations. Energies include ZPE corrections scaled by 0.9806. See Table 1 for total energies.

alignments support more delocalized allylic structures. The C_α–C_β vs. C_β=C_γ bond length equalizations increase especially in *trans* Pd–ene complexes in the order NO_2 (1.482 vs. 1.433 = 0.049 Å) < H (1.479 vs. 1.435 = 0.044 Å) < NMe_2 (1.476 vs. 1.463 = 0.013 Å, Table 3). Hence, in Pd–ene product complexes, more delocalized allylic character with longer H_3N–C_α distances and stronger C_α–C_β vs. C_β=C_γ bond length equalizations parallels increasing energetic differentiations between favored *trans* and disfavored *cis* alignments (NO_2 < H < NMe_2). This supports earlier findings [9a].

The transition structures however exhibit *decreasing* H_3N–C_α distances in the order NO_2 > H > NMe_2, as more electrophilic and hence more reactive Pd–allyl species (X=NO_2) are earlier on the reaction coordinate with longer H_3N–C_α distances (Fig. 1, Table 3). Also in contrast to Pd–ene products, *trans*-TS exhibit shorter H_3N–C_α distances than *cis*-TS. Due to the largely delocalized allylic character



Scheme 6. With X=NMe_2, H and NO_2 electronic differentiations are computed for Pd–allyl model systems (relative *cis* vs. *trans* energies in kcal mol^{-1}, cf. Tables 1 and 2 for energies and Table 3 for geometries).

Table 3
Distances (Å) and angles (°) of transition structures (TS) and Pd–ene product complexes (cf. Scheme 5 and 6)[a]

Pyridine X	*cis*/*trans* Transition structures					*cis*/*trans* Pd–ene product complexes				
	$(H_3)N–C_\alpha$	$C_\alpha–C_\beta$	$(C_\alpha–C_\beta)–(C_\beta–C_\gamma)$	$C_\beta–C_\gamma$	P–Pd–C_β–C_γ	$(H_3)N–C_\alpha$	$C_\alpha–C_\beta$	$(C_\alpha–C_\beta)–(C_\beta–C_\gamma)$	$C_\beta–C_\gamma$	P–Pd–C_β–C_γ
$–NMe_2$	1.912	1.433	0.004	1.429	176.0	1.593	1.484	0.051	1.433	179.2
	1.879	1.431	−0.005	1.436	−11.3	1.611	1.476	0.013	1.463	−6.1
–H	1.957	1.429	0.003	1.426	176.5	1.587	1.486	0.055	1.431	179.3
	1.923	1.427	−0.007	1.434	−12.4	1.603	1.479	0.044	1.435	−4.7
$–NO_2$	1.996	1.426	0.003	1.423	175.7	1.582	1.489	0.060	1.429	179.9
	1.974	1.422	−0.012	1.434	−12.4	1.595	1.482	0.049	1.433	−5.0

[a] B3LYP/6-31G* (C,H,N,P,O), /SDD (Pd) optimized transition structures in most stable conformations.

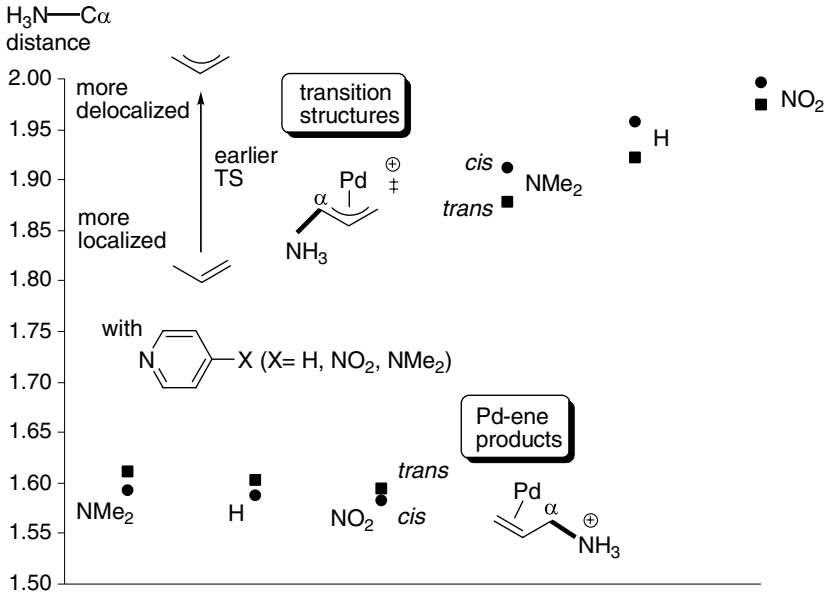


Fig. 1. $H_3N–C_\alpha$ distances of transition structures and Pd–ene products for *cis* and *trans* alignments in Å.

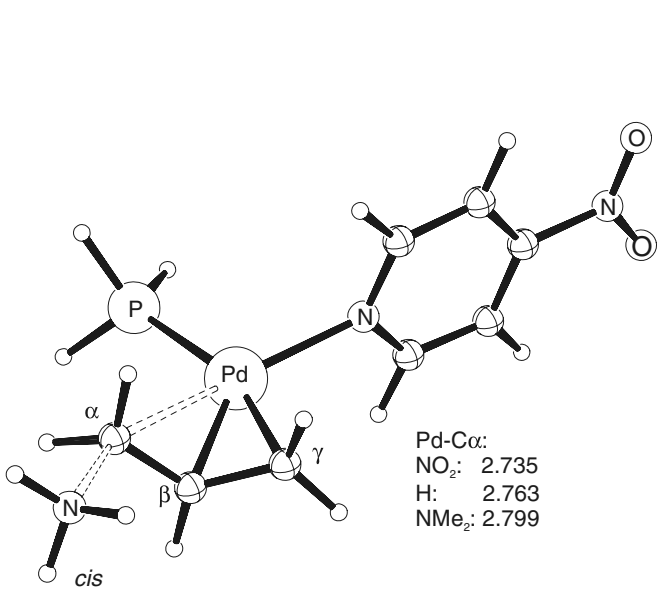


Fig. 2. Transition structure for the *cis* to phosphorus addition of NH_3 (B3LYP/6-31G* (C,H,N,P,O), /SDD (Pd)). Bond distances are given in Å. The electronic influence on C_α decreases with increasing Pd–C_α distance, i.e., it becomes smaller for later transition structures.

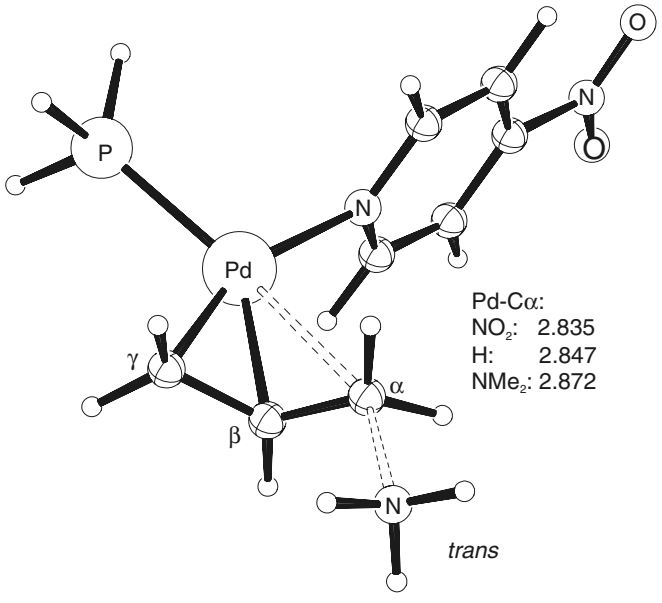
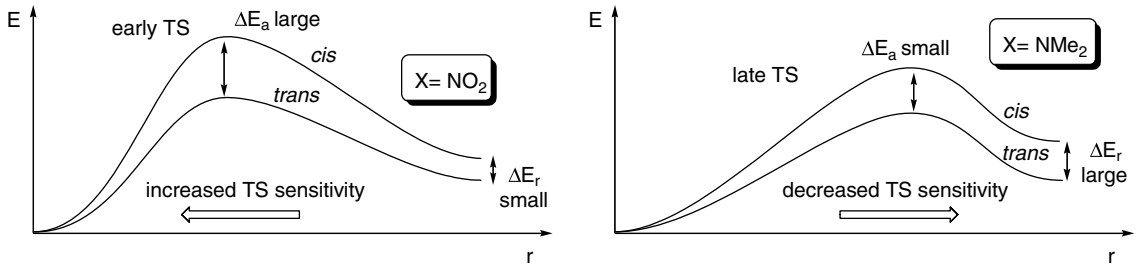


Fig. 3. Transition structure for the *trans* to phosphorus addition of NH_3 (B3LYP/6-31G* (C,H,N,P,O), /SDD (Pd)). Bond distances are given in Å. The electronic influence on C_α decreases with increasing Pd–C_α distance, i.e., it becomes smaller for later transition structures.



Scheme 7. The sensitivity for electronic differentiation is higher for earlier TS (X=NO_2) due to closer Pd–C_α contacts. This high sensitivity overcompensates the small intrinsic differentiation of NO_2 and yields for *para*-nitro substituted pyridines the highest *cis* vs. *trans* differentiation.

in the transition structures, the C_α–C_β vs. C_β=C_γ bond lengths are highly equalized and even are inverted for the *trans* transition structures (NO_2: 1.422 vs. 1.434 = −0.012 Å, Table 3).

The H_3N–C_α distances (synonymous with the reaction coordinate) nicely reflect geometrically the sensitivity for *cis* vs. *trans* differentiations (Fig. 1). For both, transition structures and Pd–ene products, the H_3N–C_α distances increase in the order $NO_2 < H < NMe_2$ (Fig. 1). Only in transition structures however, X=NO_2 vs. H vs. NMe_2 effect the H_3N–C_α distances stronger than a *cis* or a *trans* alignment (Fig. 1). The earlier *cis* and *trans* transition structures for X=NO_2 exhibit closer Pd–C_α contacts (2.735 and 2.835 Å, Figs. 2 and 3), and hence more intensive pyridine–Pd–allyl interactions, than for X=H (2.763 and 2.847 Å) and X=NMe_2 (2.799 and 2.872 Å). The closer and more intensive Pd–allyl contact in early transition structures explains why its higher sensitivities leads, despite the intrinsically smaller electronic differentiation (X=NO_2), to larger *trans* stabilizations (largest for X=NO_2: 1.89 kcal mol^{-1}) and hence to the highest predicted selectivity (Scheme 7).

3. Conclusions

Two competing effects are apparent from computational analyses of electronic *cis* vs. *trans* differentiations in Pd-catalyzed allylic substitutions. The intrinsic electronic differentiations in Pd-ene complexes are strongest for PH_3 and electron donating pyridine ligands (*para*-substituent X=NMe_2). The sensitivity for electronic differentiation in the transition structures however is much higher for earlier positions on the reaction coordinate, i.e. for more allylic structures with shorter Pd–C_α distances, apparent for electron withdrawing substituents, i.e. X=NO_2. Despite a smaller intrinsic electronic *cis* vs. *trans* differentiation, *para*-nitro pyridine (X=NO_2) gives rise to the highest *trans* stabilization (i.e. selectivity) due to its early transition structures. Hence, electronic differentiations are predicted to be largest for electron donating N-positions and electron withdrawing P-ligands. This electronic differentiation is best transformed to energetic *trans* vs. *cis* stabilization for earlier, allyl-like transition structures. Besides strong steric *exo* vs. *endo* differentiations, highest selectivities are hence predicted for combinations of stronger back-bonding P-ligands with only moderately electron donating N-ligands.

4. Computational details

All structures were fully optimized and characterized by frequency computations using GAUSSIAN 03 [20] with standard basis sets [21] and the B3LYP [22] hybrid-DFT method. Zero point energies and thermochemical analyses were scaled by 0.9806 [23].

Acknowledgements

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