Theoretical Evidence for Low-Ligated Palladium(0): [Pd−L] as the Active Species in Oxidative Addition Reactions

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Received February 9, 2006

The oxidative addition of PhI to Pd^0 has been studied by DFT with a continuum representation of the solvent. It is shown that the preferred number of ligands on palladium is lower than would be expected from “conventional wisdom” and the 18-electron rule. The most favored oxidative addition is obtained when Pd is coordinated by only the aryl iodide and one additional ligand in a linear arrangement. The calculations indicate that p-orbitals on the central metal are *not* involved in bonding in any of the complexes described herein, in good agreement with classic ligand field theory and also with a recent bonding analysis by Weinhold and Landis, but in apparent violation of the 18-electron rule.

Introduction

Palladium(0) phosphine complexes are among the most versatile transition metal catalysts used for organic synthesis,[1] applications including an array of C−C and C−X cross-coupling reactions,[2,3] and isomerizations of alkenes.[4] One of the most commonly employed palladium phosphine catalysts is $Pd(PPh_3)_n$, which is either generated in situ from a palladium(II) salt or added directly as Pd^0 (some commonly employed sources are $Pd(PPh)_4$ or $Pd(dba)_2 + 2\ PPh_3$). Several studies have dealt with the mechanism of Pd^0-catalyzed reactions, the majority leading to the conclusion that the active species is a “highly unsaturated” 14-electron complex $Pd(PPh_3)_2$, with a low-energy nonreactive “less unsaturated” 16-electron complex $Pd(PPh_3)_3$ as the major species in solution.[5] The first step in the generally accepted catalytic cycle is oxidative addition of ArX (Figure 1), which has sometimes been suggested to be the rate-limiting step, particularly for X = Cl. The use of aryl chlorides is highly desirable for economic reasons, and thus a detailed understanding of the oxidative addition mechanism is important for further methodological improvements. For some Pd^0-catalyzed transformations, addition of anions such as chloride increases the reaction rate, which has been explained by formation of a tricoordinate anionic $[Pd(PPh_3)_2X]^-$ species, which is suggested to be more reactive than the neutral $Pd(PPh_3)_2$ complex.[6] However, under phosphine-free reaction conditions, monoligated palladium has been suggested to be the active species.[7] Recent theoretical results also challenge the generally accepted view on ligation state and stability. It is increasingly becoming recognized that transition metals do *not* employ p-orbitals for bonding and thus have only a valence shell of one s- and five d-orbitals, which can accommodate up to 12 electrons with “normal” bonding. Coordination numbers beyond this depend on the formation of linear three-center−four-electron bonds (ω-bonds), which employ only one metal orbital for bonding to two ligands.[8] Overall, this new view of bonding in metal complexes can rationalize all observations that earlier were perceived as being a result of the 18-electron rule. This new view also quite naturally includes phenomena like square planar d^8-complexes, which have always been viewed as exceptions.

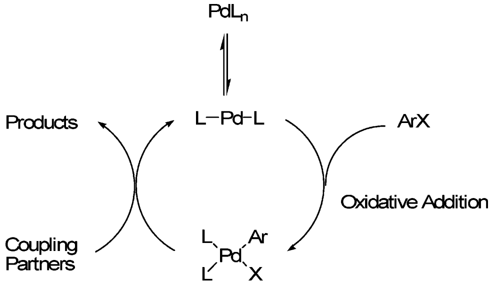

Figure 1. “Textbook” mechanism for palladium(0)-catalyzed cross-coupling reactions.

Herein are reported the results of a theoretical study on the stability of both neutral and anionic palladium complexes containing one, two, or three ligands, as well as the relative reactivity of these complexes toward oxidative addition of phenyl iodide. The effect of the coordination number on stability and reactivity is then discussed in more detail.

Results

Neutral Complexes of the Type PdL_n. For a number of palladium(0) complexes containing *n* ligands ($n = 1-3$) the

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(1) Negishi, E. I., Ed. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley-Interscience: New York, 2002.

(2) (a) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636. (b) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437. (c) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (d) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581, (e) Heck, R. F.; Nolley, J. P. *J. Org. Chem.* **1972**, *37*, 2320. (f) Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* **1984**, *25*, 3137.

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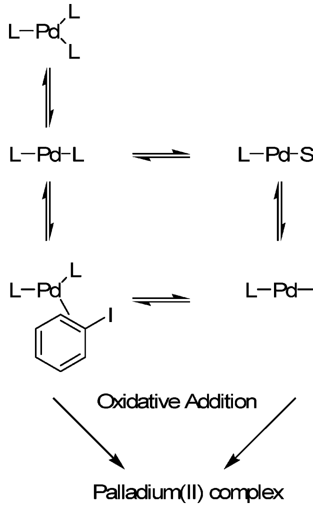
10.1021/om060126q CCC: $33.50

Scheme 1. Oxidative Addition Takes Place on Either a Di- or Tricoordinate Palladium(0) Complex[a]



[a] In the current work the stabilities and reactivities of these are investigated.

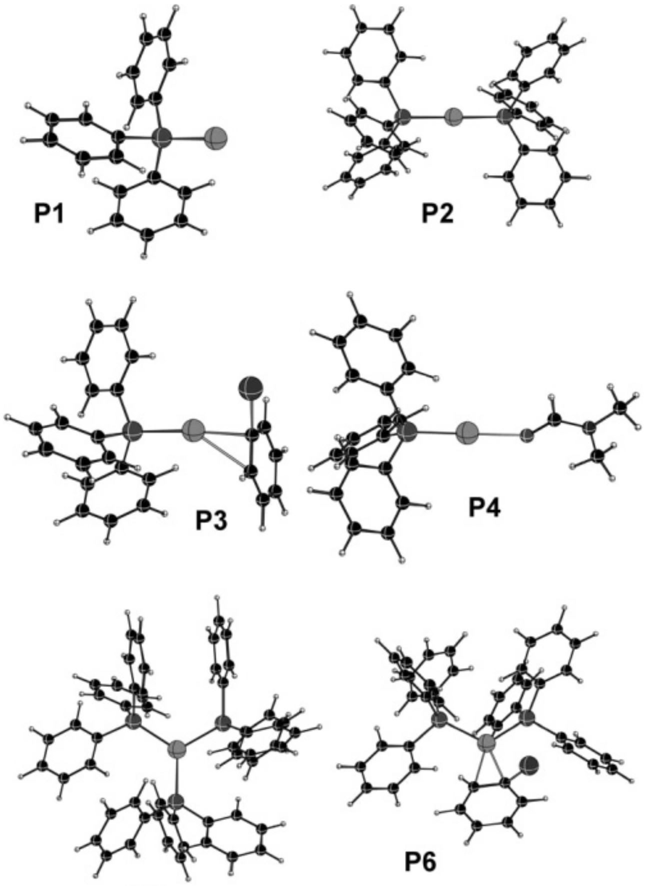


Figure 2. Structures of neutral palladium(0) complexes.

Table 1. Relative Potential Energies (kJ/mol) of a Series of Neutral Pd^0 Complexes

entry	complex	CN[a]	ΔG_{gas}	ΔE_{DMF}	"ΔG_{DMF}"[b]
P1	Pd(PPh$_3$)	1	82	102	53
P2	Pd(PPh$_3$)$_2$	2	0	0	0
P3	Pd(PPh$_3$)(PhI)	2	60	53	46
P4	Pd(PPh$_3$)DMF	2	63	40	43
P5	Pd(PPh$_3$)$_3$	3	44	26	84
P6	Pd(PPh$_3$)$_2$(PhI)	3	100	68	124

[a] Coordination number of Pd. [b] See Computational Details.

Table 2. Relative Potential Energies (kJ/mol) of [PdL$_n$Cl]$^-$

entry	complex	CN[a]	ΔE_{DMF}	"$\Delta G_{\mathrm{Estimate}}$"[b]
Cl1	[Pd(PPh$_3$)Cl]$^-$	2	0	0
Cl2	[Pd(PhI)Cl]$^-$	2	35	35
Cl3	[Pd(DMF)Cl]$^-$	2	50	50
Cl4	[Pd(PPh$_3$)$_2$Cl]$^-$	3	32	72
Cl5	[Pd(PPh$_3$)(PhI)Cl]$^-$	3	50	90

[a] Coordination number of Pd. [b] See Computational Details.

geometries have been optimized both in the gas phase and with a solvent model describing DMF, a commonly employed solvent in these types of reactions (Figure 2). Relative gas-phase free energies, potential energies in solution, and estimated free energies in solution are presented in Table 1.

The gas-phase calculations show a strong stabilization of 82 kJ/mol on going from PdPPh$_3$ to Pd(PPh$_3$)$_2$. Coordination of a third PPh$_3$, on the other hand, was found to lead to destabilization by as much as 44 kJ/mol. When applying a solvent model in the calculations, the results are similar when going from PdPPh$_3$ to Pd(PPh$_3$)$_2$, although less in favor of the dicoordinate species than for the gas-phase calculations. More interesting is that formation of tricoordinate Pd(PPh$_3$)$_3$ is found to be endergonic by 84 kJ/mol in solution. This value is of such magnitude that it can be expected that the concentration of Pd(PPh$_3$)$_3$ is basically infinitesimal. Replacing one phosphine in Pd(PPh$_3$)$_2$ with an explicit DMF solvent molecule was found to be endergonic by 43 kJ/mol. The difference between the monocoordinate complex P1 and the solvent complex P4 gives an indication of the limitations of the continuum solvation model. The continuum cannot give an accurate description of actual coordination of the solvent to the metal, but the effect of including an explicit coordinating solvent molecule is still relatively small, giving a contribution of only 10 kJ/mol.

The monocoordinate complex Pd(PPh$_3$) has an unexceptional structure, with a Pd–P bond of 2.24 Å. The dicoordinate complexes (Table 1, entries P2 and P3) are all linear, or nearly so. In Pd(PPh$_3$)$_2$, the Pd–P bonds are elongated by 0.1 to 2.34 Å, due to the trans-influence. In Pd(PPh$_3$)DMF the Pd–P bond is shorter, 2.23 Å, a value that clearly shows the weak trans-influence of a neutral oxygen atom. The two tricoordinate complexes adopt a trigonal structure, almost perfectly so for both Pd(PPh$_3$)$_3$ and Pd(PPh$_3$)$_2$(PhI), in which the P–Pd–P angle is 114°. In the Pd(PPh$_3$)$_3$ complex the Pd–P distances are calculated to be 2.41, 2.40, and 2.39 Å, respectively. In accordance with the view of Weinhold and Landis,[8] the three phosphines all donate into the *same* 5s-orbital on palladium (a four-center–six-electron bond), weakening the bond to each individual phosphine compared to the dicoordinated state. All the descriptions above are for the complexes optimized in DMF. The gas-phase optimization yielded essentially identical structures.

Anionic Complexes of the Type [PdL$_n$Cl]$^-$. Anionic complexes with *n* neutral ligands ($n = 1-2$) and one chloride have been characterized. All have been fully optimized with a solvent model using parameters for DMF (Table 2).

A similar trend is seen for the anionic complexes as for the neutral ones; that is, going from a dicoordinate species to a tricoordinate one does not lead to further stabilization, but rather to destabilization. The two dicoordinate complexes that do not contain any triphenylphosphine are found to be relatively stable, not sufficiently so to be present in detectable amounts, but most definitely of a low enough energy to allow them to be intermediates in a catalytic cycle.

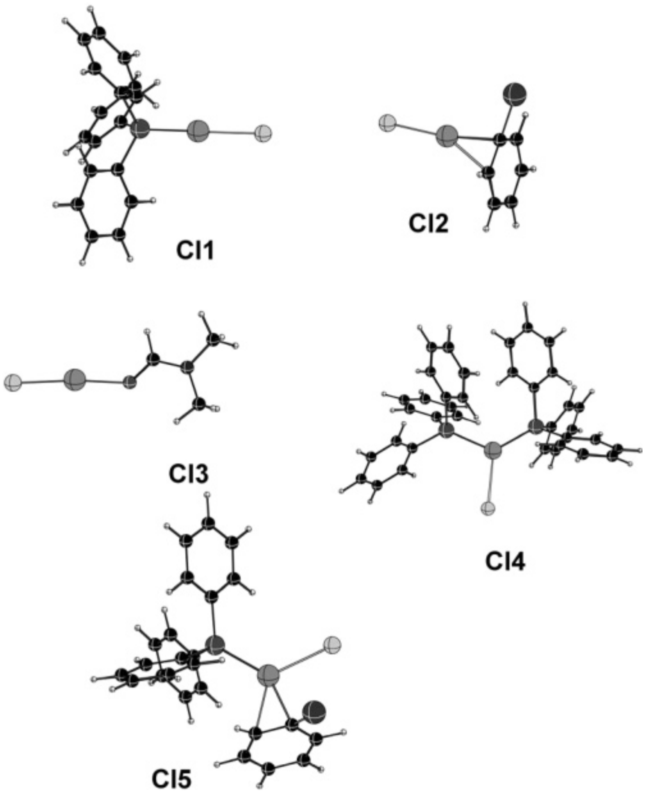


Figure 3. Anionic palladium(0) chloride complexes.

Table 3. Relative Potential Energies (kJ/mol) of [PdLOOCH]$^-$

entry	complex	CN[a]	ΔE_{DMF}	"$\Delta G_{\mathrm{Estimate}}$"[b]
F1	$[Pd(PPh_3)(OOCH)]^-$	2	0	0
F2	$[Pd(PhI)(OOCH)]^-$	2	25	25
F3	$[Pd(DMF)(OOCH)]^-$	2	33	33
F4	$[Pd(PPh_3)_2(OOCH)]^-$	3	10	50

[a] Coordination number of Pd. [b] See Computational Details.

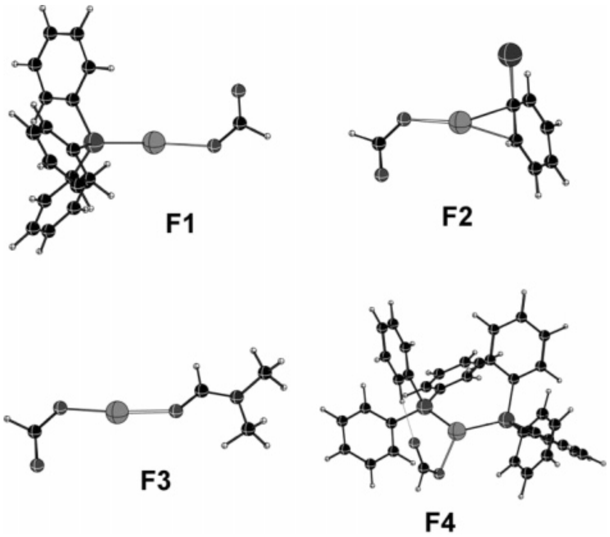


Figure 4. Anionic palladium(0) formate complexes.

For the anionic complexes the calculated geometries are also in line with what would be expected, with linear geometries for the dicoordinate species and trigonal planar for the tricoordinate ones. In the dicoordinate complex $[Pd(PPh_3)Cl]^-$ the Pd−P bond was found to be 2.23 Å, which is 0.11 Å shorter than the same distance in $Pd(PPh_3)_2$, and likely a consequence of the lower trans-influence of chloride compared to that of triphenylphosphine, while the Pd−Cl bond was calculated to be 2.47 Å. In the solvent complex $[Pd(DMF)Cl]^-$ the Pd−Cl bond was found to be slightly shorter, 2.39 Å, while in the substrate complex $[Pd(PhI)Cl]^-$ it was calculated to be 2.44 Å. The structure of $[Pd(PPh_3)_2Cl]^-$ is distorted such that the two P−Pd−Cl angles are not identical (109° and 124°). The Pd−P distances are 2.31 and 2.38 Å, where the longer bond is to the phosphine with the largest angle to chloride. In this complex the Pd−Cl bond distance is calculated to be as much as 2.73 Å, which is 0.26 Å longer than the Pd−Cl distance in the complex with one phosphine less. This indicates a relatively weak Pd−Cl interaction in $[Pd(PPh_3)_2Cl]^-$. All structures described are for optimizations in DMF and are shown in Figure 3.

Anionic Complexes of the Type $[PdL_n(OOCH)]^-$. Anionic complexes with a formate ligand have been fully optimized with a solvation model describing DMF. Carboxylates are components of many Pd-catalyzed reactions, and the formate can serve as a model for these. In none of the complexes can we see any evidence of steric interactions that would invalidate this model. The relative energies of the palladium formate complexes are displayed in Table 3.

Formation of the tricoordinate species with two triphenylphosphines is found to be endergonic by ca. 50 kJ/mol in DMF (Table 3, entry F1 vs F2). This number differs in magnitude from the same comparison for the chloride system (Table 2, entry Cl1 vs Cl4), which may in part be due to a stabilizing hydrogen-bonding interaction between the formate moiety and one of the phenyl hydrogens. For the formate complexes a solvent complex $[Pd(DMF)(OOCH)]^-$ was also characterized, and formation of this species was calculated to be endergonic by 33 kJ/mol from $[Pd(PPh_3)(OOCH)]^-$ and DMF.

Structurally the dicoordinate complexes are linear, with the formate coordinating to palladium in an η^1-fashion. The Pd−P distance in $[Pd(PPh_3)(OOCH)]^-$ is identical to the same distance in the chloride analogue, 2.23 Å, while the Pd−O distance is 2.22 Å. In the tricoordinate complex the Pd−P distances are 2.34 and 2.35 Å, while the Pd−O bond is 2.41 Å, which is considerably longer than in the analogue with only one phosphine, thus indicating a weaker Pd−O bond in the tricoordinate complex. All structures described are for optimizations in DMF (Figure 4).

Transition States for Oxidative Addition of Phenyl Iodide to Palladium(0). Two types of transition states have been characterized for the oxidative addition of phenyl iodide to the Pd^0 complexes described above. All have been fully optimized including a solvent model, which has proven to be crucial for these types of species in recent work by Senn and Ziegler, where it was demonstrated that the transition state found in gas-phase calculations did not exist when a solvent model was applied.[9] Similarly, the transition state found when a solvent model was incorporated in the calculations was of a type that could not exist in the gas phase. The first transition state found in the present investigation is one where phenyl iodide has been oxidatively added to $Pd(PPh_3)_2$ (Table 4, entry 1). The second type of transition state found is one where palladium is ligated to only one more ligand than the phenyl iodide (Table 4, entries 2−4).

It is clear that the oxidative addition is facilitated by a lower coordination number on the palladium. While the barrier for oxidative addition to $Pd(PPh_3)_2$ was found to be 13 kJ/mol, oxidative addition to the complexes containing just one more

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[9] Senn, H. M.; Ziegler, T. *Organometallics* **2004**, *23*, 2980.

Table 4. Transition State Energies (kJ/mol) Relative to the Respective Prereactive Complexes

entry	oxidative addition transition state complex	CN[a]	ΔE_{DMF}
TS1	$Pd(PPh_3)_2(PhI)$	3	13
TS2	$Pd(PPh_3)(PhI)$	2	2
TS3	$[PdCl(PhI)]^-$	2	1.2
TS4	$[Pd(OOCH)(PhI)]^-$	2	0.2

[a] Coordination number of the corresponding prereactive complex.

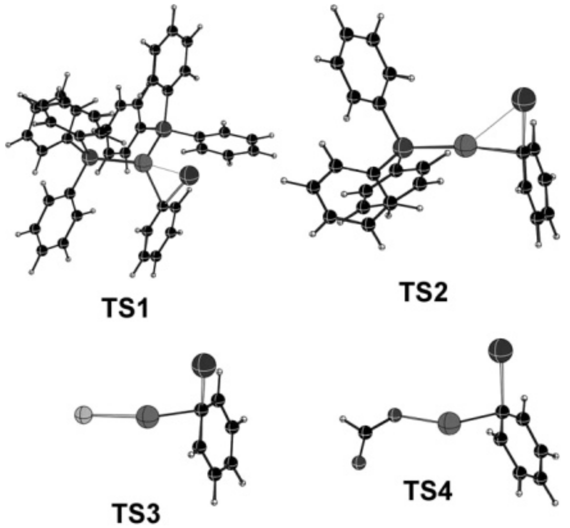

Figure 5. Transition state structures for oxidative addition to palladium(0).

ligand than the phenyl iodide takes place essentially without any barrier (Figure 5). These results are in line with previously published results for palladium(0) alkyne systems, for which it was found that a lower coordination number facilitates oxidative addition.[7] Reactions of complexes with coordination numbers higher than 3 have been studied before and always contain a ligand dissociation from palladium as a crucial prereactive step.[11]

Comparison of Anionic and Neutral Complexes. Since there is a larger degree of uncertainty when comparing neutral and anionic molecules (as opposed to comparison of species of the same charge) when a solvent model is applied, this will be touched upon only briefly here. The equilibrium between $Pd(PPh_3)_2$ and $[Pd(PPh_3)Cl]^-$ is found to be in favor of the former by 58 and 46 kJ/mol in DMF and THF, respectively. For the formate species the numbers are also in favor of $Pd(PPh_3)_2$ but by 41 and 27 kJ/mol for DMF and THF, respectively. At the level of theory used (B3LYP/LACVP*) these values are within the error limit for small anions. In fact, it seems that the continuum model employed here consistently overestimates the solvation energy for the small anions, for example by 63 kJ/mol for Cl^- in DMSO.[10]

Discussion

Di- or Tricoordinate Palladium(0)? From the results above it is obvious that the coordination number of palladium(0) in solution is likely to be lower than what has hitherto been suggested in the literature. In all cases, both in the gas-phase calculations and when applying a solvent model in the calculations, the result is that going from a dicoordinate to a tricoordinate Pd^0 species results in an increase in free energy. The consequence of this is that the often made assumption that tricoordinate complexes are more stabilized than dicoordinate ones is now cast in doubt. Several previous studies have dealt with the stability and reactivity of tricoordinate palladium species,[11] but few have taken into account the possibility of lower coordination,[12] which is probably a consequence of adherence to the time-honored “18-electron rule”. However, taking into account the observation that 5p-orbitals are not involved in binding of ligands to Pd, as seen in all our current calculations, the linear 14-electron complex should be regarded as a favored hypervalent state with one ω-bond,[8] analogous to the isoelectronic Ag^+ complexes.

When scrutinizing the early studies of Pd complexes in solution, it becomes apparent that the actual experimental results consist of observation (e.g., by NMR spectroscopy) of multiple species with unclear identity, but with a consistent concentration dependence, allowing a precise determination of the *relative* number of ligands on Pd. However, it is not clear to us how the *absolute* number of coordinating ligands has been determined. In some cases, the assumption has simply been that the highest order complex observed must be identical to either the crystallographically observed coordination or the 18-e complex with four ligands. The current results cast the original assumptions in doubt. The state in the crystal, where the influence of entropy is minor, is determined by the potential energies of the possible complexes and how they pack. On the other hand, in solution, the coordination state is strongly dependent on the entropic contribution, with each ligand loss corresponding to a free energy gain of around 40 kJ/mol at room temperature. Thus, our current results, with higher coordination states being favored by potential energy, but lower coordination states being favored by free energy in solution, are fully compatible with earlier experimental results, but not with the original interpretation of those results.

Looking at the kinetic studies for oxidative addition to palladium, the general observation is that the reaction order in phosphine is negative, usually -1. This has been interpreted as oxidative addition of a PdL_2 complex in equilibrium with a less reactive but more stable PdL_3 species. However, the experimental results basically show only that the rate-determining TS contains fewer phosphine ligands than the resting state of the catalyst and are therefore equally in line with the current results, which indicate that the resting state is PdL_2 and that oxidative addition occurs from complexes of the type $L-Pd-PhI$, where one ligand again has been lost before reaction.

We also note that only moderately active π-acceptors have been studied here. The calculated difference between di- and triligated Pd is not very large and can probably be reversed by use of strongly electron-accepting ligands such as dba, which would be expected to favor higher coordination states of Pd.[13] In the extreme cases, binding of electron-deficient alkenes to Pd^0 gives a bonding pattern more reminiscent of palladacyclopropane, which would be expected to behave as a Pd^{II} species and accept two ligands trans to the two coordinating alkene carbons.

As stated above, the preference for di- over triligated states mainly arises from an entropic contribution in solution. Thus, chelating ligands would be expected to override this preference. Looking at the geometry of our calculated tricoordinated Pd

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[10] Ahlquist, M.; Kozuch, S.; Shaik, S.; Tanner, D.; Norrby, P.-O. *Organometallics* **2006**, *25*, 45.

[11] (a) Kozuch, S.; Shaik, S.; Jutand, A.; Amatore, C. *Chem. Eur. J.* **2004**, *10*, 3072. (b) Goossen, L. J.; Koley, D.; Hermann, H.; Thiel, W. *Chem. Commun.* **2004**, *19*, 2141. (c) Goossen, L. J.; Koley, D.; Hermann, H.; Thiel, W. *Organometallics* **2005**, *24*, 2398. (d) Kozuch, S.; Amatore, C.; Jutand, A.; Shaik, S. *Organometallics* **2005**, *24*, 2319.

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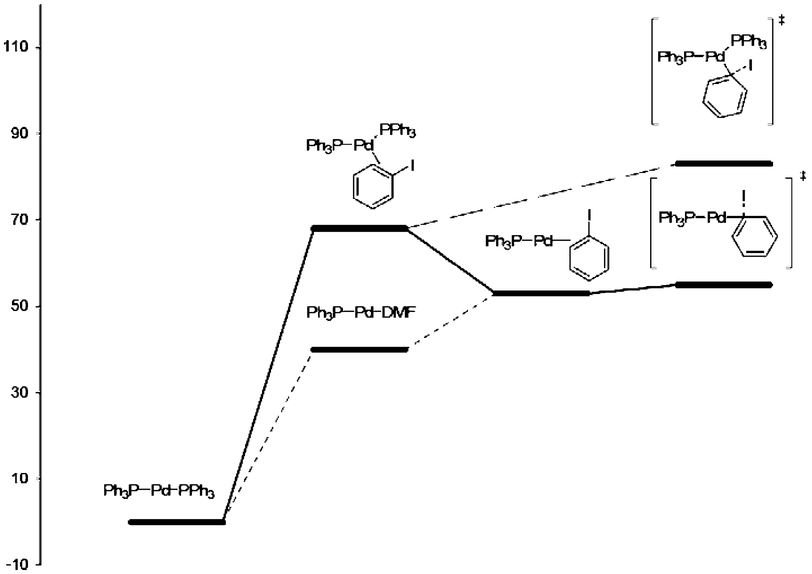

Figure 6. Potential energy diagram for the reaction between $Pd(PPh_3)_2$ and PhI. All energies are in kJ/mol.

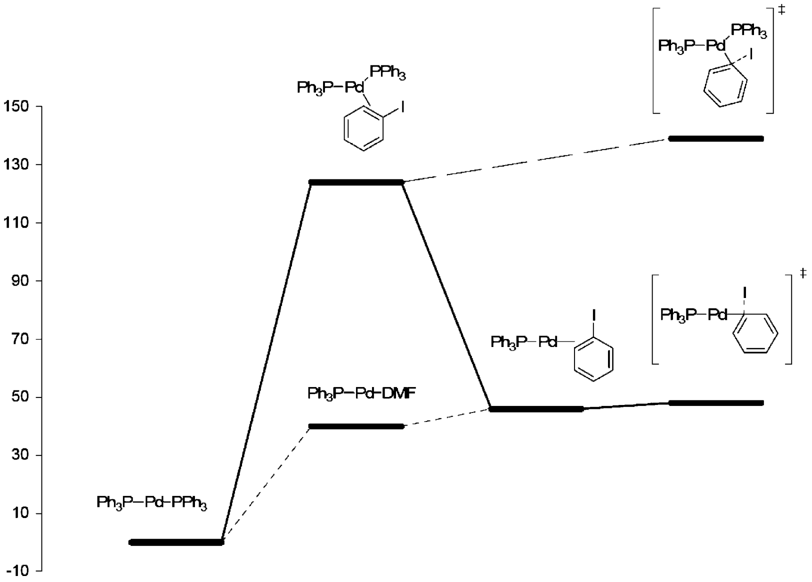

Figure 7. Free energy ("ΔG_{DMF}") diagram of the reaction between $Pd(PPh_3)_2$ and PhI. All energies are in kJ/mol.

complexes, we would expect that a bidentate phosphine with a small or moderate bite angle would accept another ligand trans to one of the phosphines.

Reactivity toward Phenyl Iodide. Oxidative addition is frequently the first step in any *catalytic* cycle involving palladium(0) phosphine species. Although several theoretical studies of oxidative addition have been performed, none have dealt with the possibility of a lower coordinated palladium species, including a solvent model in the calculations.[9,11,14] Our results for the ground states suggest that palladium in solution prefers a dicoordinate structure over a tricoordinate one. A previous study has shown that, in the gas phase, oxidative addition of phenyl bromide to palladium(0) with the model ligand PH_3 is more facile if palladium is coordinated to only one more ligand than phenyl iodide.[15] Since it has been shown that gas-phase calculations do not necessarily yield the same results as solution-phase calculations,[9] we decided to investigate the oxidative addition step including a solvent model. In our experience, utilizing PH_3 as a model for aryl and alkyl phosphines has often proved to give results that differ substantially from the ones for the full system.

For the neutral complexes, the starting point of the reaction is $Pd(PPh_3)_2$ (Figures 6 and 7). For the general case, formation of $Pd(PPh_3)_2(PhI)$ is the first possibility. From here there are basically two paths: either oxidative addition directly on this species or dissociation of one ligand to form the dicoordinate species $Pd(PPh_3)(PhI)$, which could also be formed by a dissociative path via the solvent complex $Pd(PPh_3)DMF$.[12] From the results above the path involving solvent is strongly favored. Oxidative addition involving $Pd(PPh_3)_2(PhI)$ takes place via TS1 with a barrier of 15 kJ/mol. The dicoordinate complex $Pd(PPh_3)(PhI)$, which is found to be more stable than $Pd(PPh_3)_2(PhI)$ by 78 kJ/mol, undergoes oxidative addition via TS2 with virtually no barrier (2 kJ/mol). The consequence of these results is that

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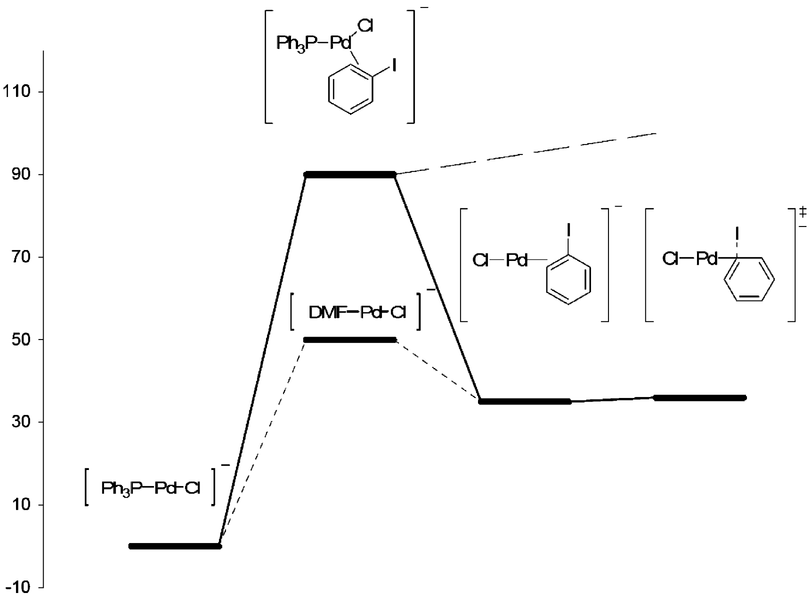

Figure 8. Free energy ("$\Delta G_{\mathrm{Estimate}}$") diagram for oxidative addition to anionic palladium(0) chloride complexes (values in kJ/mol).

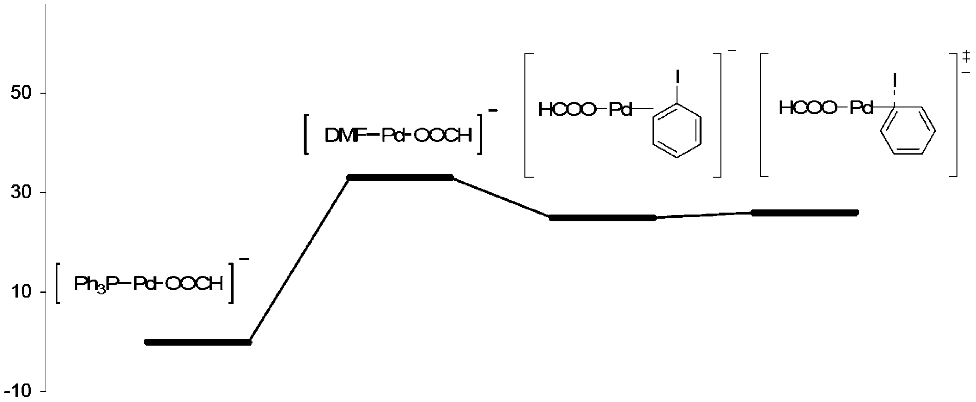

Figure 9. Free energy ("$\Delta G_{\mathrm{Estimate}}$") diagram for oxidative addition to anionic palladium(0) formate complexes (values in kJ/mol).

the species on which the oxidative addition takes place is most likely the one with only one phosphine, Pd(PPh$_3$)(PhI), which is formed either via ligand exchange on Pd(PPh$_3$)$_2$ or via the solvent complex Pd(PPh$_3$)DMF. These findings are in line with the theoretical results found recently for palladium acetylene systems, where lower coordination number was shown to increase the reactivity of palladium(0) toward oxidative addition of phenyl iodide.[7] This is also in line with the experimental observations by Beeby et al. that additional triphenylphosphine above 1 equiv relative to the palladium concentration retards the rate of oxidative addition of phenyl bromide.[16] Similar results have been observed by several groups for oxidative addition to palladium(0) complexes containing sterically demanding ligands.[17]

The results for oxidative addition to the anionic palladium(0) species are similar to the ones for neutral analogues (Figure 8). Formation of a tricoordinate complex from [Pd(PPh$_3$)Cl]$^-$ and phenyl iodide is found to be endergonic by 90 kJ/mol. Dissociation of the phosphine then leads to a more stable complex. This dicoordinate prereactive complex [Pd(PhI)Cl]$^-$ is 35 kJ/mol higher in energy than the corresponding phosphine complex [Pd(PPh$_3$)Cl]$^-$. Another possible path for the formation of [Pd(PhI)Cl]$^-$ is via the solvent complex [Pd(DMF)Cl]$^-$. Formation of [Pd(DMF)Cl]$^-$ from [Pd(PPh$_3$)Cl]$^-$ and DMF was found to be endergonic by 50 kJ/mol, compared to the path via the tricoordinate [Pd(PPh$_3$)(PhI)Cl]$^-$ complex. The solvent complex path is thus favored by 40 kJ/mol. Oxidative addition on the prereactive complex [Pd(PhI)Cl]$^-$ occurs with a very low barrier, 1.2 kJ/mol, via TS3 (Figure 5). Oxidative addition on [Pd(PPh$_3$)Cl(PhI)]$^-$ was not considered since it is already higher in energy than [Pd(PhI)Cl]$^-$, and the barrier for the neutral analogue was found to be 13 kJ/mol compared to the almost barrier-free oxidative addition on the low-coordinate complexes.

Similarly, the complexes with a formate ligand undergo oxidative addition with a low barrier via a palladium species coordinated to only the formate and the phenyl iodide (Figure 9). Ligand exchange that leads to formation of the solvent complex [Pd(DMF)OOCH]$^-$ is endergonic by 33 kJ/mol. The subsequent formation of the prereactive complex from [Pd(DMF)OOCH]$^-$ and phenyl iodide is exergonic by 7 kJ/mol.

Explanation of the "Anion Effect". For Pd^0-catalyzed processes under certain conditions, an increase in reaction rate has been observed when anions are added to the reaction mixture. This has previously been explained in terms of formation of a highly reactive tricoordinate [Pd(PPh$_3$)$_2$X]$^-$ species.[6] However, this explanation is in contradiction to the

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[16] Beeby, A.; Bettington, S.; Fairlamb, I. J. S.; Goeta, A. E.; Kapdi, A. R.; Niemelä, E. H.; Thompson, A. L. *New J. Chem.* **2004**, *28*, 600.

[17] (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (b) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685 (c) Barrios-Landeros, F.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 6944.

present results, since if an anionic species is present in solution it is much more likely to be the dicoordinate complex $[Pd(PPh_3)X]^-$. In our calculation of the chloride system the dicoordinate species is found to have a 72 kJ/mol lower free energy than the tricoodinate one. For the corresponding formate species the difference was calculated to 50 kJ/mol, also here in favor of the dicoordinate species.

When comparing the neutral and anionic complexes, a preference for the neutral ones is found. This, however, might be an effect of an overestimation of the solvation energy of the free anionic ligands. In a study of the solvation energy of small anions with a solvation model describing DMSO, it was found that it overestimates the free energy of solvation by 63 kJ/mol for the chloride anion. Thus, it might very well be so that the $[Pd(PPh_3)Cl]^-$ complex is more stable than $Pd(PPh_3)_2$, but since the solvation model overestimates the stability of the chloride, the result is the opposite in the calculations. It should be noted that this does not affect the equilibrium between the di- and tricoordinate species, since these compare molecules of the same charge.

From the results above it is clear that the "anion effect" is not likely to be due to formation of the previously suggested species $[Pd(PPh_3)_2X]^-$, since it is both a low-concentration species[8] and also less reactive toward oxidative addition than $[Pd(PPh_3)X]^-$. Thus, in the presence of anions there is a possibility for formation of anionic palladium complexes of the type $[Pd(PPh_3)X]^-$. For oxidative addition of phenyl iodide, a relatively poor ligand for palladium(0), two paths can be followed from this complex. The first possibility is formation of a solvent complex ($[Pd(Solv)X]^-$ and then ligand exchange to yield the prereactive complex $[Pd(PhI)X]^-$. The second involves an association of PhI to $[Pd(PPh_3)X]^-$ to yield the prereactive complex via the tricoordinate $[Pd(PPh_3)(PhI)X]^-$. In both the anionic and the neutral mechanisms described above, the barriers for the oxidative addition at the dicoordinate prereactive complexes were found to be very low. Therefore, there has to be another explanation for the "anion effect". One possibility is that the formation of the prereactive complexes is more favored for the anionic complexes than for the neutral analogues, which is exactly what is observed in the calculations described above. The energy required for formation of $Pd(PPh_3)(PhI)$ from $Pd(PPh_3)_2$ was 46 kJ/mol, while formation of $[Pd(PhI)X]^-$ from $[Pd(PPh_3)X]^-$ was endergonic by 35 and 25 kJ/mol for $X = Cl^-$ and HCOO, respectively. A rationale for this observed difference in ability to form the dicoordinate prereactive complex could be that in the neutral complex PPh_3 acts as an electron acceptor. Another electron-accepting ligand such as the electrophile PhI is then disfavored. For the anionic analogues the situation is very different. Since palladium in these cases is coordinated only to an electron-donating ligand (the anionic one), ligation of the electrophile PhI is more favored. The overall effect can be viewed as a push−pull effect between the ligands, where palladium is merely acting as a carrier of electron density from a nucleophilic species to an electrophilic one. An identical effect has been observed for palladium(0) alkyne complexes, where the push−pull effect was so pronounced in some complexes that the palladium(0) was better viewed as being an anionic palladacyclopropene palladium(II) complex (Figure 10).[7]

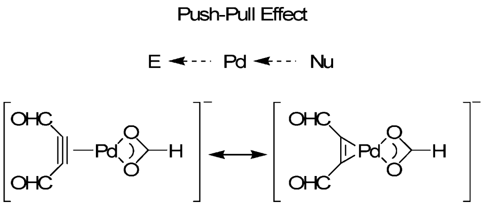

Figure 10. "Push−pull effect" in palladium complexes.

Conclusions

All our results indicate that it is necessary to re-evaluate the nature of the palladium(0) species present in solution and relevant to many of the most commonly used Pd^0-catalyzed organic reactions. In every case, an increase in potential energy was found when going from a dicoordinate to a tricoordinate palladium(0) species. As a consequence of these findings, the most reactive species in neutral solution is found to be $Pd(PPh_3)(Solv)$, with $Pd(PPh_3)_2$ substantially less reactive, in contrast with earlier proposals where $Pd(PPh_3)_3$ has been assumed to be the dominant species in solution. The often observed effect of "phosphine poisoning" at high phosphine concentrations then originates from the equilibrium between $Pd(PPh_3)_2$ and $Pd(PPh_3)(Solv)$ rather than the equilibrium between $Pd(PPh_3)_3$ and $Pd(PPh_3)_2$. Our results also strongly suggest that anionic Pd^0 complexes, which are presumed to be formed upon addition of chloride, are not of the previously suggested type $[Pd(PPh_3)_2X]^-$, but are much more likely to be species containing only one phosphine ligand, $[Pd(PPh_3)X]^-$. On the basis of this observation, a cogent explanation can be advanced for the "anion effect" sometimes observed in Pd^0-catalyzed organic reactions. Rationalized from the results above, the "anion effect" is found to be due to the fact that formation of a prereactive "push−pull" complex (Figure 10) is more favored for the anionic complexes than for the neutral analogues.

Computational Details

To include both steric interactions and the correct electronics we have included the complete ligand and substrate in all calculations, to avoid artifacts from calculations on small model systems. All calculations were performed with the Jaguar 4.2 program package[18] using the hybrid functional B3LYP.[19] The basis set used was LACVP*, which applies the 6-31G* basis set for all light elements and the Hay−Wadt ECP and basis set for palladium and iodine.[20] To simulate solvent, the Poisson−Boltzmann self-consistent reaction field (PB-SCRF) incorporated in Jaguar 4.2 was used.[21] PB-SCRF is a continuum solvation model, where the molecule is put into a reaction field consisting of surface charges on a solvent-accessible surface constructed using a hypothetical spherical solvent probe molecule with the indicated radius.[22] The wave function and the reaction field charges are solved iteratively until self-consistency is reached. The parameters for the two solvents simulated have been set to $\epsilon = 38$, probe radius = 2.47982 for DMF and $\epsilon = 7.43$, probe radius = 2.52372 for THF.

To get an estimate of the Gibbs free energy in solution, the vibrational component of the free energy, calculated by harmonic normal-mode analysis employing an analytic Hessian calculated in the gas phase, was added to the free energy calculated by optimization of the geometry in the solvation model. This procedure is valid only when the gas-phase and solvated geometries are very similar, and thus could only be applied to neutral complexes in

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(18) DFT calculations made with the Jaguar 4.2 program package from Schrödinger Inc., Portland, OR: http://www.schrodinger.com.

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(22) For a discussion of implicit solvation models, see: Cramer, C. *Essentials of Computational Chemistry: Theories and Models*; Wiley: New York, 2002.

this study. The most significant contribution to the vibrational component was from a change in molecularity, which added 42−58 kJ/mol. Earlier experimental[23] and theoretical[24] studies have yielded similar results. For the anionic complexes, only the molecularity contribution to the free energy was considered. Since no gas-phase calculations were performed for the anionic species, a conservative estimate of 40 kJ/mol to account for molecularity is made.

Acknowledgment. P.O.N. is grateful to Professor Clark Landis for illuminating discussions. We thank the Technical University of Denmark for support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM060126Q

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