Palladium(0) alkyne complexes as active species: a DFT investigation†

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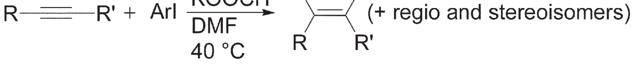
Alkynes have been found to be excellent ligands for Pd(0); the stability of a range of alkyne–Pd(0) complexes, and their reactivity in oxidative addition, have been investigated by DFT methods.

Palladium is one of the most frequently employed transition metals in catalytic organic transformations, in particular for formation of new C–C and C–X bonds.[1] For many catalytic cycles, the resting state is Pd(0), necessitating the use of ligands able to stabilize Pd(0) in solution. By far the most frequently employed ligands are phosphines. These have many excellent properties, but also drawbacks like sensitivity to air and water, and separation problems. Some palladium catalyzed reactions have been proven to proceed as well without as with added phosphines.[2,3] Two closely related examples of reactions that run well without phosphines are the hydroarylation[4] and hydrovinylation[5] reactions, which were first conducted in presence of triphenyl phosphine, but later performed under ligand free conditions (Scheme 1).

It was observed that under these conditions the hydrovinylation reaction did not yield the desired product when the alkyne was added subsequent to the other reagents,[2,3] but proceeded well if as little as five percent of alkyne was present at the initial stage and the rest was added successively. This indicates that alkynes are crucial for stabilization of the presumed active Pd(0) catalyst. Investigations of Pd(0) alkyne complexes as active species are rare,[4] and in no case have the stability and reactivity of the palladium(0) alkyne complexes been studied. Herein we report a systematic DFT investigation of the stability of Pd(0) complexes with several model ligands, both alkynes and other types of frequently employed ligand classes. We also investigate the ability of model complexes to partake in oxidative addition to a model substrate, phenyl iodide.[6]

Palladium(0) has an electron-rich d^{10} electronic configuration, with only one s-orbital available for accepting electrons from the ligand. Recent work has indicated that transition metals do not employ p-orbitals for bonding, but higher coordinations (termed "hypervalent") can be achieved through formation of 3-center-4-electron bonds (ω-bonds).[7] Backbonding forms an essential part of coordination to Pd(0), wherefore good ligands should be π-acceptors. Like electron-deficient alkenes,[8] alkynes have the possibility to interact with filled d-orbitals *via* one of the π*-orbitals (Fig. 1).



Scheme 1 Typical reaction conditions for the hydroarylation reaction.

Palladium(0) diacetylene has previously been studied by both experimental and theoretical methodologies.[9] The ideal structure was found to be one where the acetylenes are coordinating in a perpendicular fashion, allowing for backdonation from two orthogonal d-orbitals.

In the current study, the structure found for $Pd(HC{\equiv}CH)_2$ is basically identical to the one described by Wang and Andrews (Fig. 1).[9] The effect of replacing one or both of these acetylenes with other ligands is summarized in Table 1. We have included both electron-rich and electron-poor alkynes, formamide as a model for the solvent (DMF), ammonia as a model for simple amines, and both a model phosphine and the real ligand PPh_3.

It is clear that simple alkynes are strongly stabilizing ligands for Pd(0). Replacing one alkyne with any other ligand leads to a strong energy increase (Table 1, entries 6–9), well beyond the expected

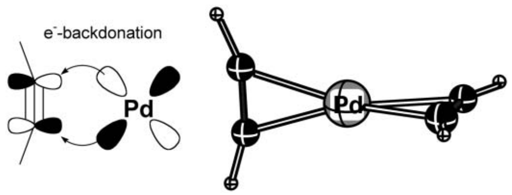


Fig. 1 Backbonding in Pd-acetylenes, and $Pd(H{-}C{\equiv}C{-}H)_2$ optimal geometry.

Table 1 Relative potential energies of $Pd^0L^1L^2$ complexes

Entry	L^1	L^2	Relative energy(kJ/mol)
1	H–C≡C–H	H–C≡C–H	0
2	Ph–C≡C–Ph	Ph–C≡C–Ph	26
3	Me–C≡C–Me	Me–C≡C–Me	40
4	OHC–C≡C–H	OHC–C≡C–H	10
5	OHC–C≡C–CHO	OHC–C≡C–CHO	1
6	H–C≡C–H	$HCONH_2$	52
7	H–C≡C–H	NH_3	55
8	H–C≡C–H	PH_3	26
9	H–C≡C–H	PPh_3	13
10	Me–C≡C–Me	PH_3	58
11	Ph–C≡C–Ph	PH_3	33
12	OHC–C≡C–H	PH_3	7
13	OHC–C≡C–CHO	PH_3	−3
14	OHC–C≡C–H	PPh_3	0

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† Dedicated to Professor David Tanner on the occasion of his 50th birthday.

confidence range of the methods employed here (*ca.* 10 kJ/mol). In the mixed phosphine/alkyne system (Table 1, entry 8), when the alkyne is substituted with formyls as a model of electron withdrawing groups, the net effect is a strong stabilization, by as much as 29 kJ/mol for butynedial (Table 1, entry 8 *vs.* 13). As expected, electron donating substituents instead destabilize the complex, by 32 kJ/mol for 2-butyne (Table 1, entry 8 *vs.* 10). This is fully in line with the postulate that the most important contribution to the bond strength comes from the backbonding, Fig. 1; electron withdrawing substituents lower the LUMO of the alkyne, thus increasing the energy gain from backbonding.

The structures of these palladium phosphine alkyne complexes have some interesting features. Whereas the ones with more electron-rich alkynes adopt a nearly linear structure, the ones containing the electron-poor alkynes are bent (Fig. 2). This bending effect is most profound for the most electron-poor alkyne butynedial. The backdonation in this complex is so strong that it is more correctly described as a pallada(II)cyclopropene, which should adopt a square planar structure with one open coordination site. Coordination of one more ligand would lead to a complex highly reminiscent of that observed by Elsevier and coworkers for an electron-deficient alkene complex.[8]

Anionic complexes similar to the ones described by Amatore and Jutand have also been studied.[10] To simulate the hydroarylation conditions, we have concentrated on the formate anion, but we have also included one example with an iodide.‡ The results are summarized in Table 2. The trends are similar to those for the neutral complexes. Alkynes substituted with electron withdrawing groups yield more stable complexes (Table 2, entries 4 & 5) and also give pallada(II)cyclopropene structures. This is especially clear in the presence of the potentially bidentate formate ligand: with an electron-rich alkyne, a linear complex is formed, whereas with the electron-poor alkyne, the structure optimizes to a square-planar pallada(II)cyclopropene with a bidentate formate ligand. (Fig. 3).

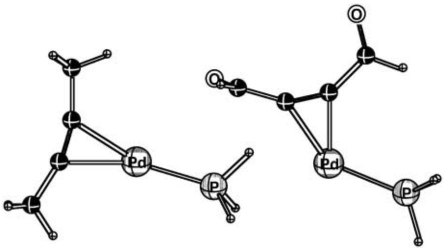


Fig. 2 Left: Pd(Me–C≡C–Me)PH$_3$, Right: Pd(OHC–C≡C–CHO)PH$_3$.

Table 2 Relative potential energies of anionic Pd^{0}LX$^-$ complexes

Entry	L	X$^-$	Relative energy(kJ/mol)
1	H–C≡C–H	$^-$OOCH	0
2	Me–C≡C–Me	$^-$OOCH	23
3	Ph–C≡C–Ph	$^-$OOCH	20
4	OHC–C≡C–H	$^-$OOCH	−40
5	OHC–C≡C–CHO	$^-$OOCH	−53
6	H–C≡C–H	I$^-$	49
7	(H–C≡C–H)$_2$	$^-$OOCH	−17
8	(OHC–C≡C–H)$_2$	$^-$OOCH	−54

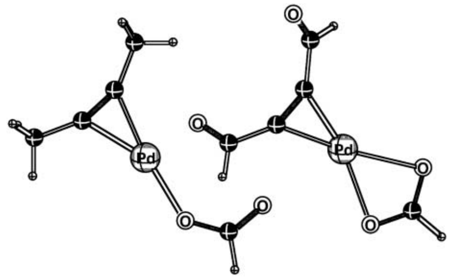


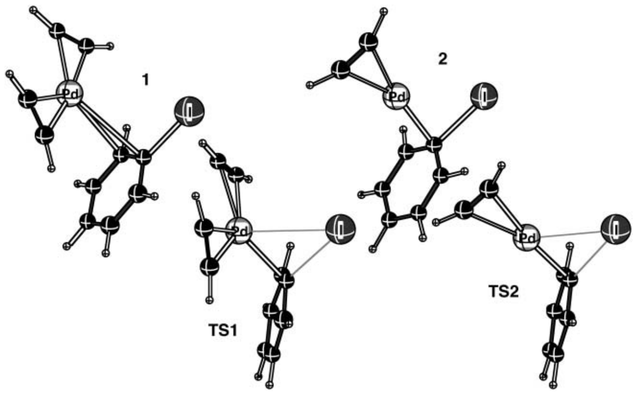
Fig. 3 Left: Pd(Me–C≡C–Me)OOCH$^-$, Right: Pd(OHC–C≡C–CHO)OOCH$^-$.

In the recently introduced nomenclature of Weinhold and Landis,[7] dicoordinate Pd(0) complex can formally be regarded as hypervalent, since both ligands donate into the same orbital on Pd. A third ligand can only be stabilized by backbonding. Two examples of tricoordinated complexes are included in Table 2, entries 7 & 8, which are stabilized by 14–17 kJ/mol relative to the dicoordinated analogs, entries 1 & 4. We note that association is disfavored entropically, by *ca.* 30 kJ/mol at ambient temperature, making dicoordination the favored binding mode, in good agreement with the binding model of Weinhold and Landis.[7]

In many Pd-catalyzed reactions, Pd(0) enters the catalytic cycle through an oxidative addition to yield a Pd(II) complex. Some DFT studies of this reaction step in the presence of phosphine ligands have recently appeared.[11–14] Building on the earlier studies and new results, we have studied four plausible pathways for oxidative addition of model alkyne complexes to phenyl iodide.

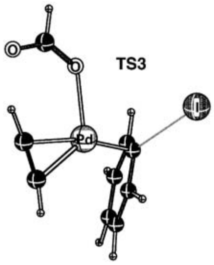
Goossen *et al.* have shown that oxidative addition to PhI proceeds *via* initial coordination of I to Pd, followed by rearrangement to a pre-reactive complex where one phenyl C–C bond coordinates to Pd, which then transfers the aryl group from I to Pd.[11] The same path has been located here starting from Pd diacetylene.[6] Formation of the I-coordinated intermediate is calculated to be endothermic by 39 kJ/mol, and rearrangement to the pre-reactive complex **1** costs another 2 kJ/mol.

The actual oxidative addition then takes place *via* a dissociation of the iodide, TS1. This transition state is similar to the ones described by Senn and Ziegler for addition to palladium diphosphines,[12] although it is an earlier transition state with a C–I distance of 2.47 Å. The iodide is only weakly interacting with palladium in the transition state, Pd–I = 3.16 Å. The barrier for oxidative addition from **1** is 54 kJ/mol, which yields an overall barrier of 95 kJ/mol from the separated reactants.

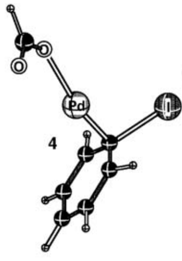


The possibility that complex **1** may dissociate one ligand before the actual oxidative addition has also been considered. Formation of the alternative prereactive complex **2** *via* dissociation of one of the acetylenes is endothermic by 16 kJ/mol relative to **1**. However, the oxidative addition can then take place *via* a concerted transition state (TS2) with a barrier of merely 5 kJ/mol. All together this yields a barrier of 65 kJ/mol from $Pd(HC{\equiv}CH)_2$ and PhI, substantially lower than TS1. In addition, due to the change in molecularity, TS2 is expected to be entropically favored relative to TS1, by approximately 30 kJ/mol at ambient temperature, leading to a very strong preference for TS2. Cundari and coworkers obtained a similar computational result employing phosphine ligands in the gas phase.[14]

We have also considered that anionic ligands may participate in the reaction, as originally suggested by Amatore and Jutand, and later supported by DFT calculations.[10,13] For the reaction of anionic $HCOO^{-}Pd(HC{\equiv}CH)$ with PhI, we were unable to locate a pre-reactive complex, but we could determine a bimolecular TS similar to that for the other paths, TS3, with a calculated barrier of only 69 kJ/mol.



TS3



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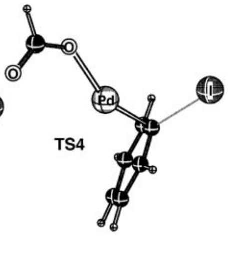

TS4

As for the neutral path, one acetylene may dissociate upon coordination of PhI. This exchange yields the anionic species **4** which contains no strongly stabilizing ligand, meaning that acetylene only has acted as a "carrier" of palladium(0). Starting from $HCOO^{-}Pd(HC{\equiv}CH)$ and PhI, the ligand-to-substrate exchange is endothermic by 58 kJ/mol: the palladium species formed is highly reactive and the oxidative addition *via* TS4 takes place with an insignificant barrier of 0.2 kJ/mol.

The calculated potential energy profiles are summarized in Fig. 4. On the free energy surface, both TS1 and TS3 will be destabilized relative to TS2 and TS4 due to the difference in molecularity. Our interpretation is that in the oxidative addition, Pd is only coordinated by the substrate and one additional ligand.

A direct comparison of anionic and neutral paths is strongly dependent on the solvation model, which has not been validated for this type of calculation.† Thus, from the computational results, we cannot conclude whether the neutral or anionic path is preferred. However, for the phosphine system, a strong effect of anions on the rate of oxidative addition has been demonstrated experimentally,[10] and we therefore believe it likely that either TS4 or TS2 can be active, depending on the relative concentration of formate and acetylene in the hydroarylation reaction.

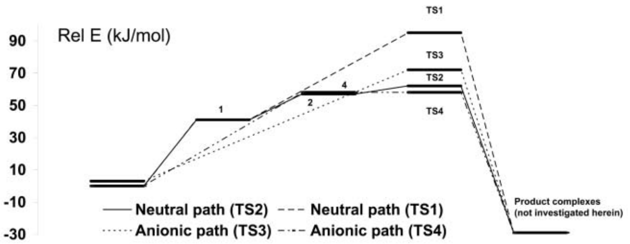

Fig. 4 Calculated reaction paths for oxidative addition to PhI.

To conclude, alkynes have a substantial stabilizing effect on Pd(0). We predict that alkynes in some cases can be better ligands than phosphines, which are currently the most frequently employed ligands in reactions catalyzed by Pd(0). Since the use of phosphines brings some practical problems, reactions where alkynes are substrates can in some cases better be performed in the absence of phosphines. Specifically, the success of the "ligand-free" hydroarylation and hydrovinylation of alkynes is rationalized by the current study.[2–5] However, the use of alkynes as ligands in other reactions is limited by the high reactivity of alkynes toward Pd(II) complexes.

Notes and references

‡ We note that direct comparison between neutral and anionic complexes suffers from the low reliability of our solvation model for the difference between localized and metal-centered anions; see ref. 13.

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