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Palladium/Norbornene Catalytic System: Chelation as a Tool To Control Regioselectivity of Pd(IV) Reductive Elimination

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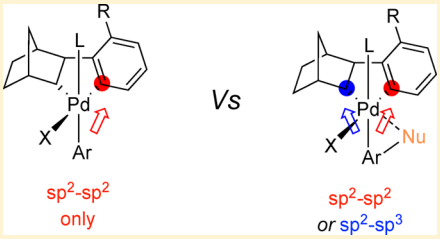
ABSTRACT: Palladium/norbornene joint catalysis gives rise to a unique system in which the three most common formal oxidation states of the metal are at work in the same cycle (0, II, and IV). This paper summarizes a selection of synthetic applications and the feasibility of Pd(IV) formation by oxidative addition of aryl halides. On this intermediate, the presence of a suitable chelating group could trigger unexpected aryl−norbornyl coupling, further broadening the scope of readily available polycyclic frameworks.



Catalytic methods represent important tools for the formation of C−C bonds under mild conditions.[1] In this field, palladium chemistry displays a dominant role as it offers the opportunity to form several bonds of different types in one-pot reactions, often with a remarkable functional group tolerance. Palladium sequences of renown synthetic interest usually involve the Pd(0)/Pd(II) redox couple, as, for instance, in the case of Heck, Negishi, and Suzuki couplings for which the Nobel prize in 2010 was awarded.[2] As a common feature, these coupling methods usually require inert conditions, reductive, and basic environments.

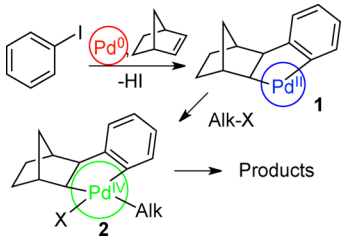
More recently, an increasing number of reactions featuring Pd(II)/Pd(IV) catalytic cycles have also been reported.[3] These protocols are usually performed under oxidizing conditions and are often tolerant to oxygen and acids. Except for a recent report from the group of Sanford merging palladium catalysis and ruthenium photoactive complexes,[4] in most cases two-electron processes are believed to be at work.

These two redox couples are thus apparently impossible to merge, as Pd(0) intermediates are sensitive to oxidant and acids while formation of Pd(IV) complexes is usually disfavored in reducing environments. Nevertheless a quite unique catalytic system was originally reported by Catellani in which the three most common formal oxidation states of palladium are at work.[5] An oxidant as mild as an alkyl halide is able to trigger formation of Pd(IV) intermediate **2** in this case, probably owing to the electron-rich character of the in situ formed alkylaromatic palladacycle **1** (Scheme 1).

Many synthetic applications of the palladium/norbornene joint catalytic system have been reported so far, mainly by the groups of Catellani and Lautens.[6]

Replacing C(sp^3)−X reagents with aryl halides represents a method to access a myriad of scaffolds containing the biaryl unit, a key, common motif in many molecules whose applications range from material sciences to medicinal chemistry.[7] Owing to a broad synthetic interest for further functionalization, a number of sequences exploiting the in situ formation of biphenyl−Pd(II) complex **3** have been reported (Scheme 2).

Scheme 1. Reaction Intermediates Highlighting the Different Formal Oxidation States of the Metal



All of the cascades involving biaryl formation share a key common synthetic requirement, the so-called *ortho effect*: an R substituent has to be present on the Ar−X in order to achieve efficient catalysis. Experimentally, this issue is likely the result of steric factors, since both electron-donating and -withdrawing groups could be tolerated.

From a mechanistic point of view, the reaction of an aryl halide with a Pd(II) complex is similarly challenging. While oxidative addition of alkyl halides to Pd(II) species delivers relatively stable Pd(IV) complexes,[8] the reaction of aryl halides represents a more ambiguous case. These substrates are less prone to oxidative addition, and at the same time the rate of the subsequent sp^2−sp^2 reductive elimination is considerably faster than that of aryl−alkyl coupling, preventing an easy access to kinetically stable complexes. To this end, it is remarkable that the first complete characterization of a Pd(IV) complex formed in this way has been reported by Vicente in 2011, exploiting the positive effect on oxidative addition of a chelating arm on the reacting iodobenzoic acid **4** coupled with the relative inertness toward subsequent reductive elimination of the resulting octahedral Pd(IV) complex **5** (Scheme 3).[9]

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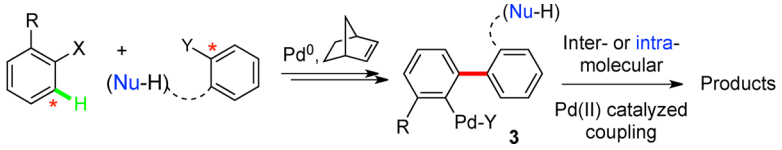
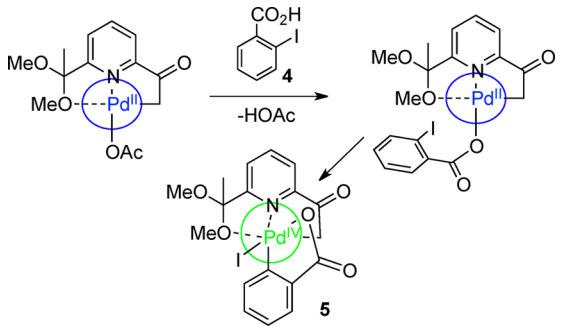
Scheme 2. Functionalized Biaryl Synthesis through Pd/Norbornene Catalysis



Scheme 3. Pd(IV) Complex by Oxidative Addition of an Aryl Halide Possessing a Chelating Group



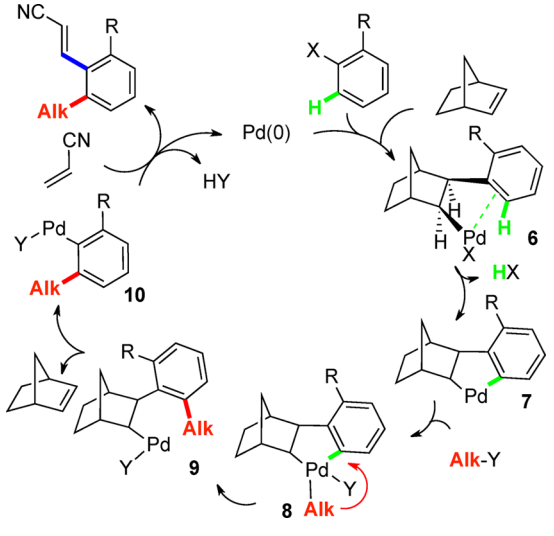
We recently found a close correlation between the *ortho effect* and the mechanism of the reaction of an Ar–X on complex **1** upon a detailed study by means of DFT modeling.[10]

In this paper, we will very briefly summarize a few synthetic applications of palladium/norbornene joint catalysis. The scope of applications of this catalytic system exceed the limits of this paper, and furthermore, excellent reviews on the subject have been reported.[6] The latter section will present recent findings underlying the impact of chelating groups on the aryl halide reacting on the Pd(II) metallacycle.

REACTIONS INVOLVING ALKYL HALIDES

A general catalytic sequence involving alkyl halides is presented in Scheme 4. The cascade is initiated by oxidative addition of an aryl halide to Pd(0). Norbornene, which acts as a cocatalyst,[11] could then reversibly insert into the metal–carbon bond to yield *cis,exo*-arylnorbornylpalladium complex **6**.[12] This rigid and strained cyclolefin is rather reluctant to undergo β-hydrogen elimination.[13] C–H bond activation could thus take place at the insertion intermediate **6**, delivering the alkyl aromatic metallacycle **7**.[14] At this point, an alkyl halide could oxidatively add on Pd(II) affording a Pd(IV) intermediate **8**.[8] Regioselective sp^2–sp^3 reductive elimination is observed at this stage. The presence of a R substituent is not required for the selectivity of the step[6] in contrast to the unselective reaction of aryl halides on metallacyles **7** not possessing an R substituent (vide infra). Then, steric hindrance triggered extrusion of norbornene from **9** could occur, leading to functionalized arylpalladium(II) species **10**. This complex can undergo a variety of termination steps to deliver the desired product and regenerate the metal catalyst. For the sake of simplicity, we illustrate the case of a Heck coupling for this general picture,[5] while more elaborated sequences will be presented later. To increase the readability of schemes, C–C bonds formed upon reductive elimination from Pd(IV) complexes are highlighted in red throughout the paper, while bonds formed in the termination step are highlighted in blue.

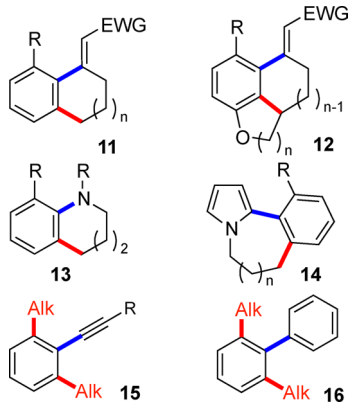
Scheme 4. Simplified Mechanism of an Alkylation/Heck Coupling



The reaction course has been established on the basis of studies in which intermediates **6**–**9** were characterized mostly thanks to stoichiometric reactions.[6] If the reacting aryl halide is unsubstituted (R = H), a second ortho-alkylation is possible in the same cycle. In this case, upon Pd(IV) reductive elimination yielding **9**, a second C–H activation occurs before deinsertion of norbornene, yielding a metallacycle as **7** (in which R has become the alkyl fragment of the first alkylation) which can react further with a second molecule of alkyl halide.

Polycyclic frameworks could be targeted through this methodology. Cyclizations could be achieved either via an intramolecular termination step or by employing an aryl halide possessing a tethered C(sp^3)–halogen function (Scheme 5). Besides examples of Heck coupling delivering **11** and **12**,[15] the sequence could feature a Buchwald–Hartwig amination (**13**)[16] or the direct arylation (**14**)[17] at the 2-position of an electron-rich pyrrole ring. Recently, an elegant access to tetrasubstituted helical alkenes has been reported on the basis of this strategy.[18]

Scheme 5. Selected Synthetic Applications of Sequences Involving Cyclizations and Dialkylations



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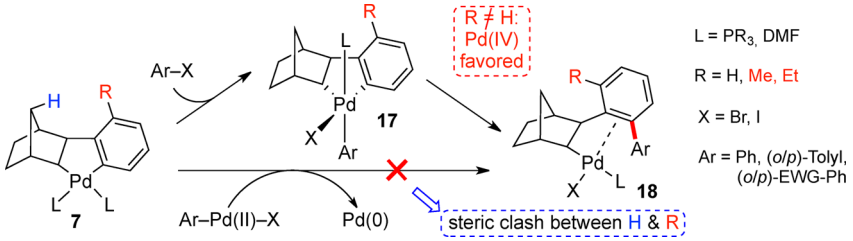
Scheme 6. Rationalization of the Ortho Effect: R Substituents Inhibit a Bimetallic Pathway Opening the Way to Pd(IV) Formation



Reaction of unsubstituted halobenzenes (R = H) delivers the corresponding 2,6-dialkylated products. As an example, an intermolecular Sonogashira[19] and Suzuki[20] coupling, yielding products **15** and **16**, respectively, could terminate the cascade.

RELEVANCE OF PD(IV) COMPLEXES IN REACTIONS OF ARYL HALIDES

As mentioned in the introduction, we begin to study these sequences from a computational point of view in order to understand the following empirical observation. In sharp contrast to reactions involving oxidative addition of an Alk-X on **7** (Scheme 4), the presence of a substituent (R ≠ H) on **7** is required to obtain the biaryl unit upon coupling with an Ar-X species (Scheme 6). This observation has been referred to as *the ortho effect*, and it applies to each different method employing Pd/norbornene joint catalysis reported so far.[6]

The mechanism of the reaction of an aryl halide on **7** was similarly debated. In a computational study on simplified structures, Echavarren and Cardenas proposed that a bimetallic pathway between two palladium(II) complexes was favored over an oxidative addition yielding a Pd(IV) species.[21] Since the origin of the ortho effect seemed due to steric reasons, we decided to model both pathways avoiding any simplification of intermediates. Main trends are presented in Scheme 6.[10]

For unsubtituted metallacycles **7** (R = H), an oxidative addition to Pd(IV) turned out to be less favored over a bimetallic pathway as proposed on model structures (by 4−12 kcal/mol in ΔG depending on reactants and ligands). However, the C−C reductive eliminations from a bimetallic intermediate proved to be unselective, with negligible differences between sp^2−sp^3 and sp^2−sp^2 barriers being obtained. In other words, the reacting Ar− moiety could be transferred to both the aliphatic and the aromatic site of **7**. These results correlate with the experimental lack of selectivity observed employing unsubstituted halides.

The presence of an R group as small as a methyl substituent is sufficient to invert the energetic convenience of the reaction, making formation of Pd(IV) intermediates **17** the most feasible reaction route (by 2−8 kcal/mol in ΔG). A steric strain emerges in the bimetallic pathway between R and a proton of norbornene (in blue, Scheme 6) causing this shift in the favored manifold.

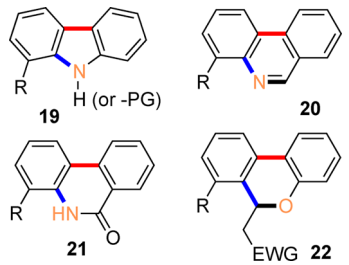
The Pd(IV) complex **17** is pentacoordinated since oxidative addition of aryl halides, being a concerted, SN_2-like process, could occur only upon ligand substitution on the starting metallacycle. Octahedric complexes by association of a second ligand molecule, although expectedly stabilized by enthalpy, are not competent for catalysis. Their lower flexibility originates higher reductive elimination barriers compared to their pentacoordinated counterparts to yield **18** (by 4−6 kcal/mol in ΔG). In all cases, from both octahedric and trigonal bipyramidal Pd(IV) intermediates, sp^2−sp^3 reductive elimination proved to be disfavored over biaryl formation ($\Delta\Delta G$ vary among +4 and +12 kcal/mol).[22]

SYNTHESIS OF FUSED AZA- AND OXA-POLYCYCLIC FRAMEWORKS

We then turned our attention to Ar-X substrates possessing an ortho chelating group, reasoning that for entropic reason it should be possible to have chelation at the Pd(IV) stage, yielding an octahedric complex instead, as observed in the case mentioned in the introduction (Scheme 3).[9]

In the literature, various methods for the synthesis of heteroatom-containing polycyclic frameworks have been reported through Pd/norbonene catalysis (Scheme 7). Several

Scheme 7. Heterocycles Employing Possibly Chelating Heteroatoms (Orange) Tethered on Aryl Bromide



five- and six-membered heterocycles could be efficiently obtained in one step employing aryl bromides possessing a suitably tethered heteroatom that can chelate palladium. Examples include the synthesis of carbazoles **19**,[23] phenanthridines[24] **20**, and phenanthridinones **21**[25] in which a *N*-arylation step terminates the sequence. Phenanthridines **20** could be obtained from bromobenzylamines in one pot by merging Pd/norbornene catalysis with an oxidative dehydrogenation using dioxygen.[24a] Dibenzopyrans **22**[26] are synthesized by sequential Heck coupling/oxa-Michael cyclyzation (the same strategy has been adopted using protected bromoanilines, providing dihydrophenanthridines instead).[27]

In all these cases, upon modeling geometries for the key Pd(IV) intermediates, the lowest energy species were found for octahedric complexes in which the intramolecular nucleophile chelates the metal. An intriguing exception is represented by protected bromoanilines, used in the synthesis of carbazoles. Acetyl- or tosyl-protected bromoanilines show lower energies for pentacoordinated Pd(IV) complexes, as both the nitrogen and the oxygen atoms are unable to bind palladium. Nevertheless, computed reductive elimination barriers in the latter case fit experimental evidence, providing a preference for

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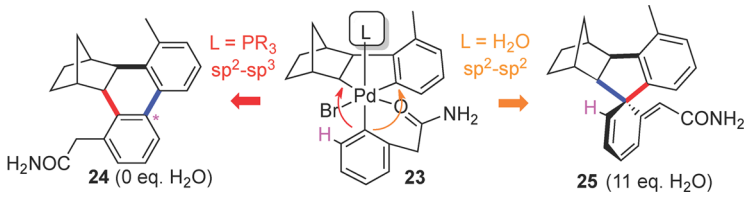
Scheme 8. Exception to the Ortho Effect; Water Is Able to Restore Usual Reactivity at the Pd(IV) Stage



sp^2–sp^2 coupling (as mentioned above for the general reactivity in the absence of chelating groups).

CHELATION OF PD(IV) COMPLEXES AS A TOOL TO CONTROL REGIOSELECTIVITY

We wondered if a switch in the usual reactivity could have been obtained by a suitable chelation of the metal in the key Pd(IV) intermediate that determines the outcome of these sequences.

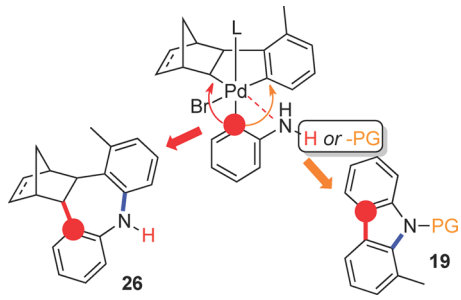
Indeed, replacing bromobenzylamines successfully used in the synthesis of phenanthridines with the corresponding acetamides, a phenanthrene derivative (**24**) breaking the commonly observed selectivity has been obtained (Scheme 8).[28] Even more surprisingly, the preference for sp^2–sp^3 reductive elimination could be inhibited by adding a few microliters of water, obtaining **25** instead.

We found a rationale to account for the observed selectivity on the basis of DFT modeling. We ruled out the possibility of the bimetallic pathway by comparing the energy of its highest energy transition states with the oxidative addition yielding a Pd(IV) intermediate. The latter is favored by more than 20 kcal/mol in ΔG. We next examined the reactivity of this complex, and we found that the unusual sp^2–sp^3 reductive elimination from the octahedral Pd(IV) complex **23** is caused by the chelating acetamido fragment. Chelation is released in the transition state of sp^2–sp^3 bond formation, while it remains in place in the aryl–aryl coupling step. The former species, owing to its lower coordination, is thus able to offset the usual reactivity ($\Delta\Delta G$ of −3.0 kcal/mol). As anticipated above, calculated barriers are lower for pentacoordinated species, owing to the higher flexibility of both organic fragments and metal d-orbitals. In comparison, calculated barriers employing benzylamines,[24a] for which chelation is not released during aryl–alkyl coupling, show a preference for sp^2–sp^2 coupling by 5.4 kcal/mol in ΔG. It is worthnoting that for late transition metals, in general, the order of reactivity of C–C bond-forming reductive elimination follows the sequence sp^2–sp^2 > sp^2–sp^3 > sp^3–sp^3.[29] A keen example of this trend is offered by the Negishi coupling.[2b] In this domain, development of efficient methods for sp^2–sp^3 and, moreover, sp^3–sp^3 bond formation via organozinc reagents has been a challenging goal for a long time.[30] A second C–H activation concludes the cascade in this case delivering phenanthrene derivative **24**. By using norbornadiene, the method allows the synthesis of functionalized aromatic polycyclic compounds thanks to a sequential retro-Diels–Alder reaction, which smoothly occurs under reaction conditions.

In the presence of water, the sp^2–sp^2 transition state is favored (by more than 10 kcal/mol in ΔG) thanks to partial ligand displacement, delivering a more reactive species that can compel aryl–alkyl coupling. The cascade in this case is ended by an unusual 5-*exo* migratory insertion into a double bond of the aryl amide ring, favored by the minimal steric hindrance of the H_2O molecule and β-hydrogen elimination from the benzylic CH_2 which delivers spiro compound **25**.

The chelation-assisted exception to the ortho effect could be efficiently applied to the one-pot assembly of synthetically challenging dibenzoazepines **26** (Scheme 9).[31]

Scheme 9. Selectivity toward Carbazoles or Dibenzoazepines Could Be Controlled through Chelation



Expectedly, the presence of a coordinating ortho substituent on the bromide partner favors the oxidative addition to Pd(IV) while disfavoring the viability of a bimetallic pathway owing to its steric demand ($\Delta\Delta G$ of the highest energy transition states for the latter pathway are lower by more than 10 kcal/mol).

In sharp contrast to the reactivity exerted by protected bromoanilines delivering carbazoles **19** (vide supra),[23] free anilines could trig sp^2–sp^3 coupling at the Pd(IV) stage. The chelation, giving rise to a strained four membered cycle, is evidenced by a nitrogen–palladium distance which is nearly 0.4 Å shorter than that found in modeled structures employing protected anilines. Once the aryl–alkyl coupling took place, a Buchwald–Hartwig C-amination could end the sequence, delivering the seven-membered ring. As in the previous case, the use of norbornadiene allows a concise access to dibenzoazepines. The reliability of our computational approach is further assessed by the comparison of the favored barrier for protected and unprotected anilines. In both cases, experimentally observed selectivity is the favored pathway by modeling (−2.8 and −1.8 kcal/mol $\Delta\Delta G$, respectively). As these two C–C bond-forming steps are not reversible, calculated values fit well with the complete selectivity found.

CONCLUSION

The palladium/norbornene catalytic system is a valuable tool in organometallic chemistry, allowing the straightforward synthesis of complex polycyclic scaffolds. Many applications of this reactivity have been reported in the last two decades showing its potential. We are aware that a limited selection only has been presented in this paper. This choice has been made to introduce the topic and to show how this chemistry could still be full of surprises disclosing unexpected reactivity. The role of chelating groups as a tool to control the selectivity of Pd(IV) reductive elimination is a keen example in this context. From a

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more general perspective, our recent contribution in this field suggests once more the importance of acquiring a deeper understanding on reaction mechanism in order to design and develop novel synthetic methods.

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Notes

The authors declare no competing financial interest.

Biographies

Giovanni Maestri completed his Ph.D. at the University of Parma with Prof. Marta Catellani. Since 2011, he was a postdoctoral researcher in the group of Prof. Max Malacria at the UPMC before moving to the ICSN.

Max Malacria obtained his Ph.D. from the University of Aix-Marseille III with Prof. Marcel Bertrand and was appointed Assistant in 1974 at the University of Lyon I with Prof. J. Goré. He was a postdoctoral fellow with Prof. K. P. C. Vollhardt at the University of California at Berkeley before moving back to the University of Lyon I in 1983. In 1988, he became a Full Professor at the UPMC. In 1991, he joined the Institut Universitaire de France. Since 2011, he has been the director of the ICSN in Gif sur Yvette.

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