Palladium Catalysis

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Dinuclear Palladium Complexes—Precursors or Catalysts?**

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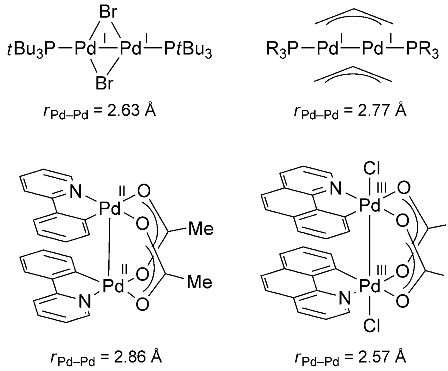
density functional theory · dinuclear catalysis · reaction mechanisms · palladium · redox chemistry

The basis of palladium coupling chemistry lies in a bond-forming step between electrophile and nucleophile, facilitated by complexation of one or both components to the transition metal. In classic "textbook" mechanisms, a single palladium atom acts as pivot for sequential addition, coupling, and elimination steps. The rich organometallic chemistry of palladium is not based entirely on monopalladium complexes; di- and oligonuclear species are common and frequently feature Pd–Pd bonds. In their classic review of this field, Murahashi and Kurosawa identify diverse families of dinuclear complexes, most with Pd–Pd bonds.[1]

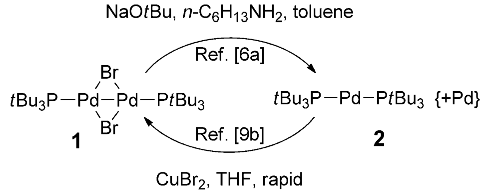
Dinuclear palladium complexes with various combinations of metal oxidation states (Pd^0, Pd^I, Pd^{II}, and Pd^{III}) have been isolated/characterized. Computational studies, especially those employing density functional theory (DFT), have given insight into structure and bonding. Consideration of the electron configuration in d^9–d^9 Pd^I–Pd^I and d^7–d^7 Pd^{III}–Pd^{III} dimers indicates that the metal–metal interaction constitutes a formal bond. However, electronic structure calculations also suggest that a closed-shell d^{10}–d^{10} attraction is present in Pd^0 dimers,[2a] and that d_{z^2} orbital overlap along the Pd^{II}–Pd^{II} axis results in appreciable metal–metal σ-bonding.[2b] Examples of dimers that were studied computationally are shown in Scheme 1. Key experimental structural parameters (Pd–Pd and Pd–ligand distances) are well reproduced in these studies using DFT calculations of the sort implemented by contemporary electronic structure programs.[2,3] The simplicity and accuracy of DFT is particularly appealing for the study of transition-metal chemistry, because its description of both dynamical and static electronic correlation, the latter of which arises from partially filled d subshells, and the near degeneracy of $(n+1)$s and nd subshells, is difficult to rival with more expensive computational methods.[4]



Scheme 1. Characterized dinuclear Pd complexes studied with DFT.

With the introduction of bulky and potentially monocoordinated phosphines in Pd catalysis, attention was directed to suitable precatalysts for their delivery. It was quickly found that the well-characterized Mingos–Vilar 30-electron dimer **1**,[5] based on $PtBu_3$, was one of the most effective and, in addition, a stable crystalline solid.[6] Early work did not formally distinguish between a mononuclear or a dinuclear catalyst, although it was noted that dimer **1** was weakly reactive toward aryl halides, and that the catalyst needed promotion by a strong base in amination reactions. Depending on the conditions, complexes **1** and $Pd(PtBu_3)_2$ **2** could be readily interconverted in control experiments (Scheme 2). A recent ESI-MS study of a Suzuki–Miyaura reaction showed a prominent peak of a $[L_2Pd_2X]^+$ dimer ($L = Cy(C_5H_{10}N)_2P$) under turnover conditions.[7]

Recent work by Schoenebeck and co-workers has clarified the matter and shows that dipalladium complex **1** provides a source of the highly reactive 12-electron $[Pd(PtBu_3)]$ complex. If not intercepted by a sufficiently reactive electrophile, this forms diphosphine complex **2** with some Pd loss.



Scheme 2. Examples of conditions for the interconversion of complexes **1** and **2**.

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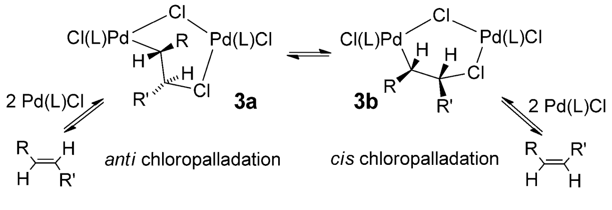
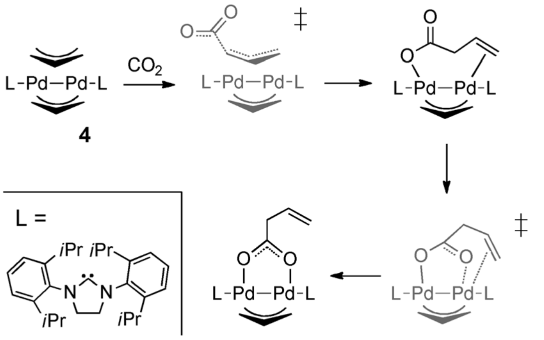
Recent DFT studies had indicated that product **2** is far less reactive toward aryl electrophiles.[8] In their earlier paper on this topic,[9a] it is stated that for complex **1**, "the likely scenario for precatalyst activation is via a reductive mechanism". Through direct NMR observations, it was shown that a combination of arylboronic acid, water, and KF caused the conversion of dimer **1** into **2**, whereas the reaction with individual components was ineffective. If the catalytic Suzuki–Miyaura reaction was carried out with 4-ClC_6H_4OTf (present from the outset) in THF, the Cl-displacement product was obtained in 76% yield under standard conditions; the corresponding yield was 5% if the electrophile was only added after full conversion of **1** into **2**. Potential pathways for the dissociation of dinuclear Pd^I complex **1** in the absence of additives have been considered computationally by Schoenebeck. Calculations (M06 L) suggest that disproportionation to mixed Pd^{II}/Pd^0 species is unfavorable (ΔG_{diss} is 38 kcal mol^{-1}), whereas homolysis to monomeric $[Pd^IBr(PtBu_3)]$ is more likely (ΔG_{diss} 26 kcal mol^{-1}). Subsequent oxidative insertion into the Ar—Cl bond proceeds with a barrier of 14 kcal mol^{-1}, The overall barrier, however, is higher than that computed for $[Pd(PtBu_3)]$, which further militates against a catalytic Pd^I monomer. The reverse reaction was shown in their more recent paper.[9b] Using either $CuBr_2$ or AgBr in THF as 1-electron oxidants, rapid conversion of **2** into **1** was observed together with the formation of stable cubic tetramers $[LMBr]_4$ (M = Cu or Ag). It follows that appropriate oxidants will accelerate catalytic turnover when **2** is used as catalyst, which was duly demonstrated in a model Suzuki–Miyaura reaction in THF with 4-AcC_6H_4Cl as electrophile. Notably, the iodide analogue of **2** is unreactive. For this reason, the combination of CuI and **1** in Suzuki–Miyaura coupling of ArCl (as opposed to CuBr and **1**) leads to the formation of this unreactive bridged dimer and depresses catalytic reactivity.

Does this mean that dimeric palladium species do not contribute directly in catalysis? Not so. Harvey, Lloyd-Jones, and co-workers recently demonstrated that a Cl-bridged dipalladacycle with vicinal C—Pd bonds is an essential intermediate in the *cis–trans* isomerization of disubstituted alkenes catalyzed by the monomeric complex $[PdCl_2(tBuCN)_2]$. This intermediate is derived initially by chloropalladation of the alkene, through the reversible step **3a**⇄**3b** (Scheme 3); both *syn* and *anti* addition and elimination is permitted.[10] According to calculations (B3LYP-D3), inner-sphere chloropalladation occurs with an activation barrier of 22.9 (*syn*) and 19.2 (*anti*) kcal mol^{-1}, while interconversion between the two adducts is relatively facile through C—C bond twisting, the transition state lying only 4–5 kcal mol^{-1} higher in energy.



Scheme 3. A dimeric complex formed by 1,2-chloropalladation permits *cis–trans* isomerization about the alkene C—C bond, following the Pd—Cl elimination step.

The catalytic carboxylation of allyl stannanes or allyl boranes occurs under very mild conditions, employing 30-electron bis(allyl)dipalladium catalysts.[11] The most active known catalysts for this transformation are those in which palladium is ligated by a carbene, as in **4**. Experimental studies indicate that an intact dimeric species is the likely catalyst and that only one of the two allyl groups is involved in turnover (Scheme 4). The bridging allylic carboxylate formed by CO_2 insertion into the Pd—allyl bond and rearrangement has been isolated and characterized. DFT calculations (M06-2X) indicate that nucleophilic attack by an η^1-allyl ligand on CO_2 is rate-limiting.



Scheme 4. The mechanism of catalytic carboxylation via complex **4**, derived by computation.

In summary, a combination of mechanistic and computational studies can enrich our understanding of palladium catalysis and help to extend its ever-increasing boundaries. Structural insight into Pd—Pd bonding in dimers and higher aggregation states from computational studies will aid synthetic efforts to develop improved Pd and other transition-metal catalysts.[12]

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