Pincer Complexes

Redox-Induced Collapse and Regeneration of a Pincer-Type Complex Framework: A Nonplanar Coordination Mode of Palladium(II)**

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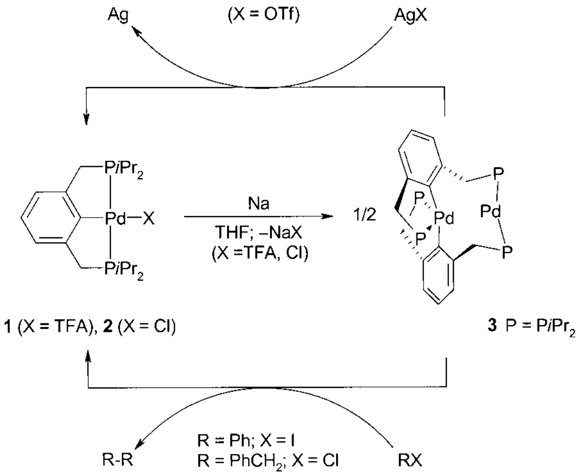
Pincer-type complexes constitute a large family of compounds that have attracted much recent interest.[1] Such complexes play important roles in organometallic reactions and mechanisms, catalysis, and the design of new materials. High stability of pincer-type complexes is often invoked as a key feature, which permits their use as catalysts at elevated temperatures. PCP-type d^8 metal complexes (PCP = phosphorous–carbon–phosphorous pincer ligand) have been utilized in various catalytic applications, such as efficient iridium(I)-catalyzed alkane dehydrogenation reactions and C–C bond-forming reactions in which PCP-Pd^{II} complexes were utilized,[1g,2] such as the synthetically important Heck coupling of aryl halides with alkenes.[3] We present herein an unprecedented process resulting in the facile collapse of a thermally very stable d^8 (Pd^{II}) pincer system under reducing conditions. This process leads to the formation of a novel binuclear Pd^0/Pd^{II} complex incorporating a 14e linear Pd^0 moiety and a completely nonplanar, "butterfly" type Pd^{II} 16e moiety. The complex is diamagnetic. Large deviations from planarity are totally unexpected for low-spin d^8ML_4 systems. Remarkably, the original PCP-Pd^{II} mononuclear framework can be regenerated upon direct oxidation of the binuclear complex, or upon its reaction with organic halides.

We anticipated that reduction of a square-planar, PCP-type d^8ML_4 complex to a d^{10} complex might lead to unprecedented transformations, since a $d^{10}ML_4$ complex is expected to be tetrahedral, thus rendering a meridional PCP arrangement unfavorable. This situation is of relevance to various catalytic reactions, such as Heck reactions catalyzed by PCP-Pd^{II} complexes. The traditional mechanism accepted for Heck reactions involves a Pd^0/Pd^{II} cycle, which would require reduction of the Pd^{II} center. Mechanisms based on Pd^{II}/Pd^{IV} have been postulated as well.[3a,4–6] Reduction of PCP-Pd^{II} complexes has been postulated also in the catalytic electrochemical reduction of CO_2, although the nature of the reduced species is unknown.[7]

When the palladium(II) complex **1** (Scheme 1) was reduced with sodium in THF at room temperature overnight, a color change from colorless to bright yellow took place. Monitoring the reaction by ^{31}P NMR spectroscopy, two new signals with the same intensity were observed at $\delta = 55.89$ and 36.96 ppm while the signal corresponding to the PCP-Pd-TFA complex (TFA = trifluoroacetate) decreased. The ratio between these two new signals did not change during reaction progress, or on modification of the reaction conditions, which suggests formation of a binuclear complex. The ^1H NMR as well as ^{13}C NMR spectra of the reaction product are complex but nevertheless support formation of a dinuclear product involving two pincer ligands coordinated in an unsymmetrical manner. The signals in the ^1H and $^1H\{^{31}P\}$ NMR spectra of the methylene groups at $\delta = 3.55$ and 2.82 ppm appear as doublets ($J_{HH} = 11.6$ Hz) consistent with *cis* coordinated phosphine ligands, while those at $\delta = 3.51$ and 3.00 ppm appear in ^1H NMR spectrum as a doublet ($J_{HH} = 15.9$) and a doublet of virtual triplets ($J_{HH,PH} = 15.9$, 4.9 Hz), respectively, and as doublets ($J_{HH} = 15.9$ Hz) in $^1H\{^{31}P\}$ NMR, consistent with *trans* coordinated phosphine groups.[8] The corresponding $^{13}C\{^1H\}$ NMR spectrum shows a broad singlet at $\delta = 42.37$ ppm, which correlates with the methylene protons signals at $\delta = 3.55$ ppm and 2.82 ppm, as well as a triplet resonance at $\delta = 38.36$ ppm (vt, $J_{PC} = 23$ Hz) which correlates with the methylene protons signals at $\delta = 3.51$ ppm and 3.00 ppm and hence is consistent with the assignments.



Scheme 1. Reduction of complexes **1** and **2** to form the binuclear complex **3** and its oxidation with silver cation or organic halides to regenerate pincer complexes (in which X can be Cl, I, or OTf depending on the reagent used); OTf = trifluoro methanesulfonate ($[CF_3SO_3]^-$).

The pentane-soluble pure reaction product was isolated as a yellow powder. Crystals of this complex were obtained by slow evaporation of its concentrated pentane solution at room

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Supporting information for this article (procedures for the preparation and characterization of complexes **2**, **3** and [PdX{2,6-$C_6H_3(CH_2PiPr_2)_2$}] (X = OTf, I), procedure for X-ray crystallographic determination of **3**) is available on the WWW under http://www.angewandte.org or from the author.

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temperature. An X-ray diffraction study (Figure 1) revealed that a novel binuclear palladium complex **3** was formed, incorporating a very rare, nonplanar diamagnetic Pd^{II} moiety and a 14 e Pd^0 center.[9] Thus, in an unprecedented process, the pincer system opened up and the aryl anchor was transferred from one palladium center to the other (Scheme 1). Complex **3** was formed in similar yield by the reduction of the complex PCP-Pd-Cl (**2**) under identical conditions.[10]

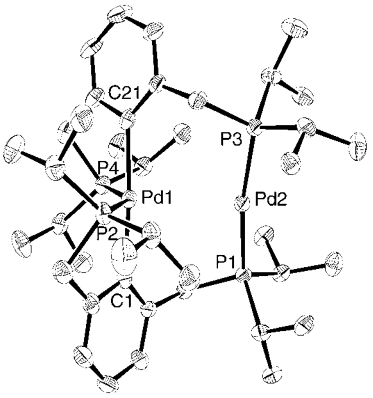

Figure 1. ORTEP diagram of a molecule of **3** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Pd1-C21 2.126(4), Pd1-C1 2.130(4), Pd1-P4 2.2878(13), Pd1-P2 2.2947(12), Pd1⋯Pd2 3.0389(11), Pd2-P3 2.2447(12), Pd2-P1 2.2492(12); C21-Pd1-C1 175.66(14), P4-Pd1-P2 144.82(4), P3-Pd2-P1 170.48(4).[15]

The solid-state structure of **3** shows a four-coordinate Pd^{II} center with a distorted butterfly environment (C21-Pd1-C1 175.66(14)°; P4-Pd1-P2 144.82(4)°) and a palladium(0) center complexed in a linear manner by two phosphine arms (P3-Pd2-P1 170.48(4)°) from different PCP ligands. The extremely rare butterfly environment of the palladium(II) center is probably mostly a consequence of steric effects and the rigidity of the PCP units resulting from the almost-linearly coordinated phosphine arms on the palladium(0) center.

A butterfly-type geometry is reported for the four-coordinate d^8 Ru^0 and Re^{-I} complexes $[Ru(CO)_2(PR_3)_2]$, $[Ru(CO)(NO)(PR_3)_2]^+$ and $[Re(NO)_2(PR_3)_2]^+$. However, in these cases the large deviation from planarity is due mainly to the strong back bonding to the carbonyl and nitrosyl ligands.[11]

The observed P3-Pd-P1 angle (170.48(4)°) is slightly distorted from linearity, as compared with perfectly linear P-Pd-P angles reported for the few other structurally characterized 14 e Pd^0 complexes,[12] except when steric factors are involved.[12e] The distance between the metal centers of 3.0389(11) Å in **3** seems too long for a Pd–Pd bond, although there are instances where Pd–Pd separations of approximately 3.0 Å are treated as bonding.[13] This distance, together with the slight distortion from linearity of the Pd^0 moiety, which is pointed towards the Pd^{II} atom, might indicate a weak electronic interaction between the metal centers which might provide additional stabilization to the butterfly environment of the Pd^{II} center.

Complex **3** is significantly less thermally stable than **1**, undergoing decomposition in aromatic solvents within hours at room temperature. Heating **3** in NMP (*N*-methylpyrrolidone) up to 140 °C led to a mixture of products, in contrast to **1** which shows exceptional thermal stability.

Although mechanistic studies were not performed, a possible scenario for formation of **3** might include a single electron transfer from sodium to Pd^{II} with precipitation of NaX and formation of a tri-coordinate Pd^I intermediate which is likely to undergo dimerization, subsequent disproportionation to Pd^0 and Pd^{II}, and rearrangement involving the pincer ligands.

If complex **3** is involved in the Heck reaction catalyzed by **1**, following a classical Pd^{II}/Pd^0 mechanism, then **3** should be at least as active as **1**. However, the dinuclear complex **3** exhibits lower activity. Using Heck coupling of iodobenzene and methyl acrylate as an example, under the reported conditions,[3a] after 60 h a turnover number (TON) of 142 900 and quantitative conversion were obtained with **1** while a TON of 54 300 (based on Pd atom) and 38 % yield were obtained with **3**. This result indicates that **3** is not an intermediate in the catalysis by **1**. Moreover, formation of biphenyl (approximately one equivalent relative to **3**) was observed in the reaction catalyzed by **3**, unlike when **1** was the catalyst.[3a]

When complex **3** was treated with an excess of benzyl chloride, quantitative formation of the monomeric PCP-Pd-Cl complex was observed within minutes. A corresponding amount of dibenzyl was detected by GC. Similarly, adding iodobenzene to a THF solution of complex **3** led to formation of the PCP-Pd-I complex and biphenyl but at a much slower reaction rate. These reactions indicate electron transfer from the Pd^0 center to the organic halide.[14] Supporting the electron-transfer reaction, addition of two equivalents of AgOTf to a THF solution of **3** resulted in immediate and clean formation of the monomeric PCP-Pd-OTf complex as well as silver metal. This complex was independently prepared by addition of an equimolar amount of AgOTf to a THF solution of complex **2**. The relatively high catalytic activity of the binuclear **3** in Heck reactions is probably based on formation of the corresponding monomeric PCP-Pd-I complex upon reaction with iodobenzene. Indeed, when an NMP solution of **3** was heated for several minutes before the olefin and iodobenzene were added, the catalytic activity dramatically decreased, owing to the thermal instability of **3** under the reaction conditions. These results are in line with a mechanism of the Heck catalysis by $PCP\text{-}Pd^{II}$ which might be different than the traditional Pd^0/Pd^{II} catalytic sequence.

In summary, reduction of a PCP-type palladium(II) complex results in an unprecedented process leading to a novel dinuclear complex **3**, incorporating a very rare, diamagnetic nonplanar "butterfly" type palladium(II) moiety and a 14 e Pd^0L_2 unit. This process can be reversed upon mild oxidation, regenerating the PCP system. The Pd^{II}–Pd^0 complex **3** is unlikely to be an intermediate in the Heck catalysis by the more active Pd^{II} pincer complex **1**. Thus, despite the high thermal stability of pincer systems they may not retain their structural integrity under reducing conditions and can open up, giving rise to unusual structures, and can be regenerated upon reaction with potential oxidants, including organic halides, which are often used as substrates in catalytic reactions.

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