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Aryl-Halide versus Aryl−Aryl Reductive Elimination in Pt(IV)−Phosphine Complexes

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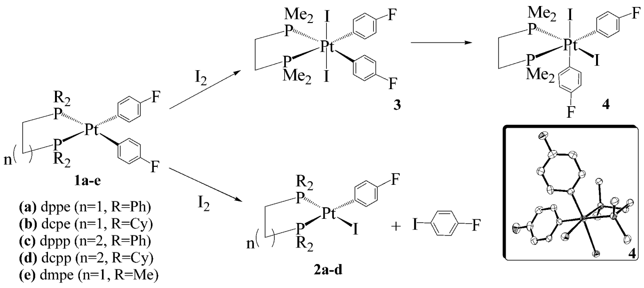
Oxidative addition of C−X (X = halide) bonds to late transition metal centers is a well-studied process, yet its microscopic reverse, carbon-halide reductive elimination, is extremely rare.[1] Being thermodynamically uphill, this reaction, nevertheless, often plays an important role in catalysis, as illustrated in the Monsanto methanol carbonylation process.[2] Since the formation of a carbon−halogen bond is usually suppressed when alternative pathways, such as C−C reductive elimination, are available, very few examples of the C−X reductive elimination from the high oxidation state metal centers have been reported, with most of them restricted to the sp^3 C−X bond-forming reactions.[3−5] In these reactions, the C−X reductive elimination can be viewed as the reverse step of the S$_N$2 oxidative addition mechanism.[3,6] With sp^2 and sp-hybridized carbon substituents, the C−X reductive elimination is generally not observed, the C−C reductive elimination being by far the dominant pathway.[7] This paper reports the competitive aryl−halide and aryl−aryl reductive elimination from a series of (P−P)Pt(IV) complexes that show a remarkable selectivity dependence on the ligand's bite angle.

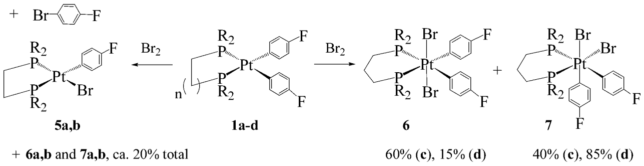
We recently reported that the addition of XeF$_2$ to Pt(II) diaryl complexes bearing the chelating phosphine ligands (dcpp, dppp, or dppe) instantaneously produced the difluoro Pt(II) complexes together with the product of C−C reductive elimination.[8a] As the same reaction with the Pt(II) complexes bearing monodentate phosphines gave stable Pt(IV) difluoro complexes,[8b] we considered that, in the former case, the C−C reductive elimination might have occurred from a cationic Pt(IV) intermediate, at a step prior to the formation of the difluoro complexes. Since little information is available with regard to the formation of (P−P)Pt(Ar)$_2$X$_2$ complexes, we sought to study the mechanism of dihalogen oxidative addition to square planar Pt(II) diaryl complexes.

Upon the addition of a solution of I$_2$ to a series of the chelating Pt(II) diaryl complexes **1a**−**d**, facile formation of the aryl iodo Pt(II) complexes **2a**−**d** was observed, and aryl iodide was obtained as an organic product. The reaction proceeded smoothly, even at very low temperatures, in different solvents, and no competition from C−C reductive elimination was observed. These results contrast with the exclusive C−C reductive elimination observed for the vinyl−vinyl (sp^2−sp^2)[9] and ethynyl−ethynyl (sp−sp)[10] Pt(IV) systems, where no C−I reductive elimination was detected and no such pathway was calculated in the DFT studies.[9b−d] It is noteworthy that only when the small dmpe ligand was used was the formation of a stable *trans*-Pt(IV) complex **3** observed at room temperature.[11] The ^{31}P NMR spectrum showed a characteristic signal at −24.37 ppm (about 40 ppm upfield from the starting material) with a very low J_{PtP} of 1200 Hz.[12] At 50 °C in benzene this compound underwent smooth conversion into the more stable *cis*-product **4** (Scheme 1). These observations suggest that the trans complex, such as **3**, is the kinetic product of the X$_2$ oxidative addition to (P−P)Pt(Ar)$_2$ and results from the S$_N$2-type mechanism involving cationic Pt(IV) intermediates.

Scheme 1



Scheme 2



Heating **4** at 90 °C for days gave the C−C reductive elimination products.

Considering, however, the high kinetic lability and often unpredictable behavior of iodides in organometallic chemistry,[13] we decided to investigate the reactivity of complexes **1a**−**e** with Br$_2$. Surprisingly, upon the addition of bromine to solutions of **1a** or **1b** in different solvents (THF, toluene, acetone, or CH$_2$Cl$_2$), instantaneous aryl-bromide reductive elimination was observed together with the formation of dppePt(Ar)Br (**5a**) and dcpePt(Ar)Br (**5b**), respectively (Scheme 2). Small amounts of the Pt(IV) oxidative addition products (both *trans*- and *cis*-isomers, **6a**,**b** and **7a**,**b**, respectively, in an approximately 1:2 ratio depending on the conditions), as well as Pt(II) dibromide (**8a**,**b**, the product of the reaction between **5a**,**b** and Br$_2$) were also observed. No biaryl formation was detected in these reactions. On the other hand, the addition of 1 equiv of Br$_2$ to either **1c** or **1d** gave stable Pt(IV) complexes (**6c**,**d** and **7c**,**d**), which showed no Ar−Br reductive elimination at room temperature or below (Scheme 2). The ratio between the isomers varied slightly depending on the solvent, with the polar solvents (THF vs CH$_2$Cl$_2$ or benzene) giving higher percentage of the *trans*-product.[14] When these complexes were heated for several hours in benzene or THF, only aryl−aryl reductive elimination was observed, and the corresponding Pt(II) dibromides (**8c**,**d**) were obtained as the metal-containing species. The reaction was significantly faster in the more polar solvent THF. Addition of an excess of tetrabutylammonium bromide (TBA-Br) to solutions of **6c**,**d** and **7c**,**d** in toluene or THF significantly slowed the reductive elimination reaction (Figure 1), suggesting that initial Pt−Br bond cleavage facilitates this reaction. Unlike the sp^3 system,[3b] the direct anion attack at an sp^2 carbon atom is not possible, and aryl bromide formation is not aided by the presence of TBA-Br. Similar to the reaction with I$_2$, **1e** reacted with Br$_2$ to

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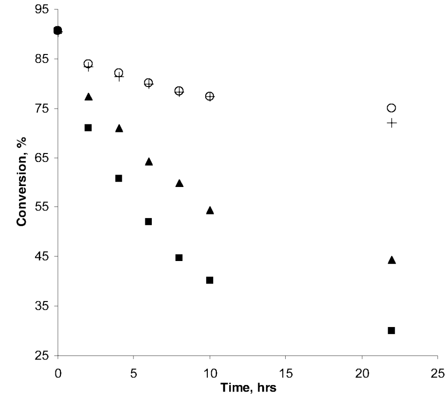
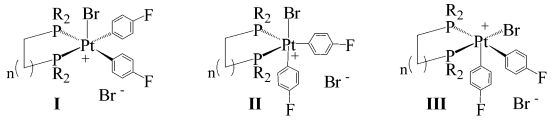


Figure 1. Rates of C−C reductive elimination from **7d** at 80 °C in THF (■), benzene (▲), THF with 10 equiv TBA-Br (+), and benzene with 10 equiv TBA-Br (○).

Chart 1



give a stable *trans*-Pt(IV) complex **6e**, which upon prolonged heating at 90 °C in THF converted to the *cis*-**7e**.

These results show that the bite angle plays a crucial role in determining the outcome of the reductive elimination reactions in Pt(IV) diaryl systems. Both steric bulk (with small dmpe as the notable exception) and electronic properties of the substituents at the phosphorus atoms appear to be of a lesser importance. Although dppe and dcpe differ significantly in their steric and electronic properties, they both favor the C−Br reductive elimination, while dppp and dcpp favor C−C reductive elimination from isolated Pt(IV) complexes. The importance of the bite angle in organometallic transformations is well-known, primarily with regard to its influence on the reaction rates.[15] In our case, a complete change in the reaction pathways is obtained upon a slight change in the diphosphine backbone.

To explain this phenomenon, we propose that the product distribution in the reported reaction is primarily dependent on the stability of the cationic intermediates produced during the oxidative addition reaction (Chart 1). In the S_N2-type mechanism, the square pyramidal cation **I** is initially formed. This cation can either undergo C−Br reductive elimination, react with the anion to give the *trans* oxidative addition product or rearrange to the more stable square pyramidal intermediate **III**. The last pathway is followed by the reaction with the anion to give the *cis* oxidative addition product. The rearrangement of **I** to **III** should be favored by the ligands with the propane backbone (larger bite angles), because it is accompanied by an increase in the P−Pt−P angle (cation **II** as a putative intermediate).[16]

Interestingly, when a mixture of **5a** with small amounts of **6a** and **7a** (from the original reaction of **1a** with Br_2) was heated for several hours at 70 °C, the Pt(IV) complexes gradually disappeared to give more **5a** and a small amount of the (dppe)PtBr_2 (**8a**). The equivalent amounts of the bromoarene and biaryl were also observed, showing that, at high temperatures, both C−C and C−Br reductive elimination reactions can proceed in the same system. In an attempt to trap **I** *prior* to the C−Br reductive elimination step, we reacted **1a**,**b** with Br_2 in the presence of 10 equiv of TBA-Br. Under these conditions, **6a** and **6b** were obtained as the major species (90 and 60%, respectively).[17] Upon heating with TBA-Br, these complexes underwent C−C reductive elimination to give the biaryl and **8a**,**b**. Thus, the added bromide shuts the regeneration of **I** from **6**, shifting the reaction from the C−Br to the C−C elimination.[18]

Although the detailed mechanistic studies are still underway, it is clear that the aryl-halide reductive elimination can compete favorably with the more common C−C reductive elimination. The reaction course appears to be extremely sensitive to even minor changes in the ligand's structure and reaction media.

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Supporting Information Available: Experimental details and characterization of complexes **2**−**7**. Crystallographic information for complex **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Although we observed no changes in the NMR spectra upon the addition of TBA-Br to complexes **1a**−**e**, the possibility of Br^- precoordination to the Pt(II) center before the reaction with Br_2 cannot be excluded.

(18) In the presence of TBA-Br, the biaryl formation from **6a**,**b** might occur via the direct elimination or chelate ring-opening. Ion-pair rearrangement mechanisms also cannot be ruled out at this stage.

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