Aryl-bromide reductive elimination from an isolated Pt(IV) complex[†]

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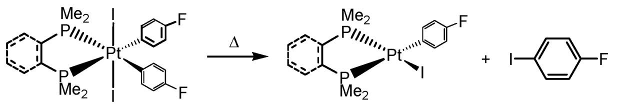
A Pt(IV) complex bearing two aryl and two bromo ligands, which undergoes selective elimination of a bromoarene molecule has been prepared and fully-characterized. The mechanistic studies of this reaction are presented.

Late transition metal-mediated formation of carbon–halogen bonds is becoming increasingly important for the design of new synthetic methods.[1] It is well established that a combination of a late transition metal center with a source of an electrophilic halogen can result in the catalytic halogenation of aromatic compounds that bear pendant chelating groups.[2,3] Only recently the examples of carbon–halogen bond formation from isolated metal complexes started to appear in the literature mostly involving palladium complexes.[4–7] Although Pt(IV) compounds have historically been crucial to the understanding of some mechanisms of transition metal-mediated C–X bond forming reactions, all examples reported thus far involved the formation of carbon–iodine bonds.[4,8] Herein, we report the first example of a far more challenging direct C–Br reductive elimination of an aryl bromide from an isolated diaryl dibromo Pt(IV) complex, a type of reaction that was previously presumed to be involved in brominolysis of some diaryl Pt(II) complexes.[9]

We recently reported octahedral Pt(IV) complexes bearing two aryl and two iodo ligands, the latter being in the mutual *trans*-position, that can undergo a selective C–I reductive elimination of an aryl iodide (Scheme 1).[10] The thermodynamically more stable *cis*-isomeric complexes undergo exclusive C–C reductive elimination reaction. Based on these results, we were interested in applying this strategy for C–X bond formation to significantly less reactive lighter halogens X. However, although the *trans*-dibromo analogues of the complexes shown in Scheme 1 could be prepared readily, they failed to exhibit the C–Br bond elimination reactivity.[9] To suppress the dominating undesired formation of C–C bonds and to increase the likelihood of the C–Br reductive elimination, we decided to replace one of the aryl ligands with C_6F_5, that forms stronger bonds to transition metal centers.[11] We also decided to utilize the commercially-available quinoxaline-based ligand—(*R*,*R*)-(−)-2,3-bis(*tert*-butylmethylphosphino)quinoxaline—that would decrease the electron density at the metal center and increase the steric strain while maintaining the necessary rigidity. Reacting this ligand with (COD)Pt(4-FC_6H_4)C_6F_5 (COD = 1,5-cyclooctadiene) cleanly produced the diaryl complex **1** (Scheme 2). As expected, the $^{31}P\{^1H\}$ NMR spectrum of **1** showed two signals at 28.72 (br m, J_{PtP} = 2441.9 Hz) and 31.19 (br d, J_{PtP} = 1649.6 Hz) due to two inequivalent phosphine ligands. Interestingly, the $^{19}F\{^1H\}$ spectrum of **1** showed five different signals due to the fluoro substituents in the pentafluorophenyl group, indicating restricted rotation around the metal–carbon bond. The X-ray structure of **1** showed the square planar arrangement around the Pt(II) center with the Pt–C bonds being nearly identical in length (2.082(9) Å). Both Pt–P distances were also found to be identical (2.281(2) Å).



Scheme 1

Complex **1** undergoes clean oxidative addition of Br_2 in CH_2Cl_2 solution to give the Pt(IV) complex **2**. Notably, this reaction is reversible in more polar solvents (*vide infra*). The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits two signals at −6.33 ppm (J_{PtP} = 929.1 Hz) and −4.34 ppm (J_{PtP} = 1404.9 Hz), which is more than thirty ppm upfield compared with **1**. The X-ray structure of **2**‡ shows that the two bromo atoms occupy the apical positions of the octahedron with the Pt–Br bonds being *ca.* 2.48 Å. Interestingly, although the Pt–C bond distances of *ca.* 2.113 Å remained fairly equal (albeit longer than in **1**), the Pt–P bonds are now inequivalent with the Pt–P4 (*trans* to the 4-FC_6H_4 group) bond being significantly longer than the Pt–P5 bond, 2.462(3) Å *vs.* 2.396(3) Å, respectively.

Importantly, heating **2** in CH_3CN for 24 h at 80 °C resulted in its complete conversion to the Pt(II) complex **3** with the concomitant formation of *p*-FC_6H_4Br as the major organic product (yield 80–90%) along with 10–20% of fluorobenzene (Scheme 2). The rate of disappearance of **2** followed first-order kinetics with $t_{1/2}$ being *ca.* 12 h at 70 °C, which corresponds to the Gibbs activation energy of 27.7 kcal mol^{-1}. To the best of our knowledge, this is the first example of a directly observed reductive elimination of a bromoarene from a Pt(IV) complex. The reaction rate was only slightly affected by light or presence of water additives. For example, a 50% conversion of **2** was observed after 5 h of reaction at 80 °C under bright light of a 100 W incandescent lamp *vs.* 40% conversion observed in the dark. Addition of 10% of water to an acetonitrile solution of **2** did not result in any significant increase in the reaction rate. Addition of 10 equiv. *n*-Bu_4NBr to the reaction mixture did

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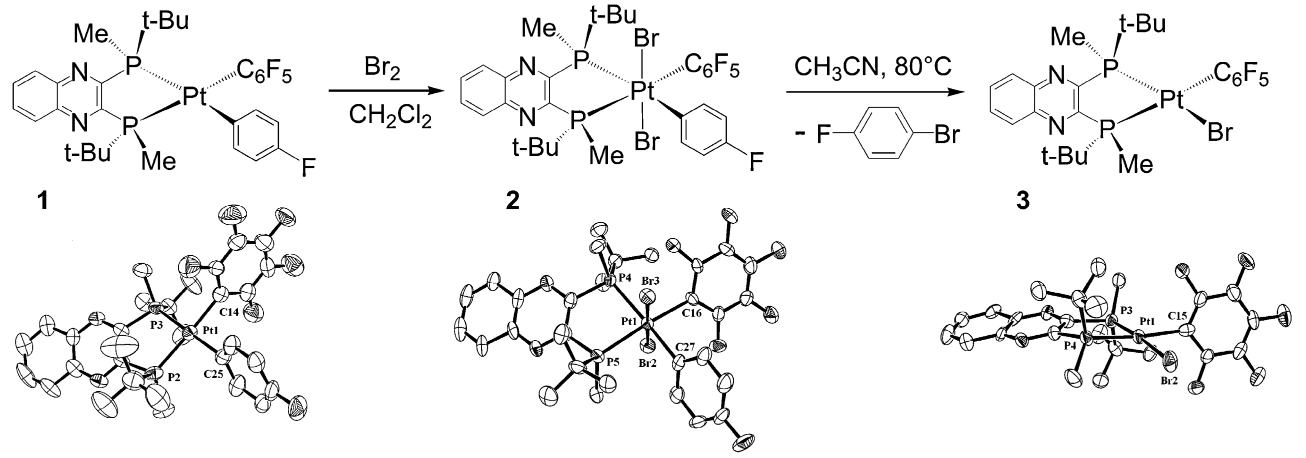
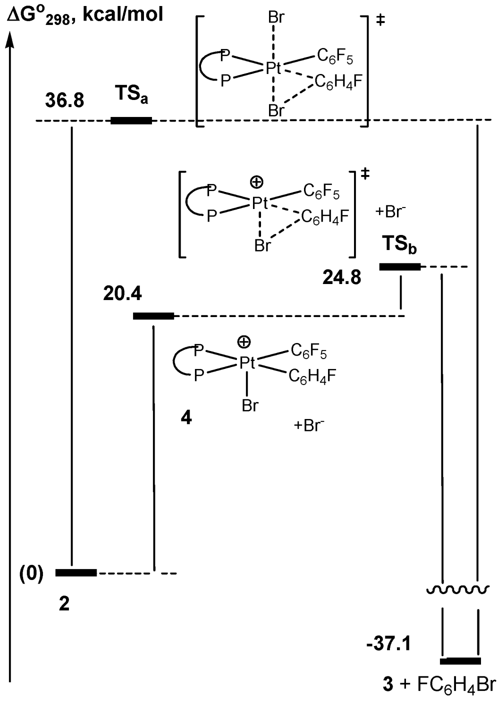


Scheme 2

not slow down the overall reaction rate significantly, although the fraction of *p*-FC_6H_4Br noticeably decreased whereas the amount of PhF, the C–H elimination byproduct, increased. Interestingly, performing the reaction in acetone, DMSO or NMP resulted in the unexpected reductive elimination of Br_2 and formation of **1**. Continued heating of those solutions led to the formation of complex **3**, *p*-FC_6H_4Br and substantial amounts of fluorobenzene, the C–H elimination product. The formation of some fluorobenzene byproduct in MeCN can be explained by partial elimination of Br_2 (*vide infra*), bromination of the reactive solvent (acetone, DMSO, NMP but not much so MeCN) to produce HBr and a subsequent reaction of the latter with complex **1** leading to PhF and complex **3**.

The possible mechanisms of the reactions described here were studied using the high-level DFT calculations. Two possible pathways were analyzed for the Ar–Br elimination in acetonitrile solutions (Scheme 3): the path a involving a concerted *p*-fluorophenyl and bromide ligands C–Br coupling from neutral species **2** *via* the transition state TS_a and the path b involving dissociation of one of the bromide ligands from **2** to form the cationic five-coordinate intermediate **4** along with a free bromide anion. The intermediate **4** undergoes a subsequent C–Br coupling *via* the transition state TS_b leading ultimately to complex **3** and *p*-FC_6H_4Br. The solvation of **2**, **4** and both transition states in acetonitrile was modeled using a Poisson–Boltzmann continuum solvation model (PBF) implemented in the Jaguar program[12] package. For bromide anion an experimental value of the Gibbs energy of solvation of -69.2 kcal mol^{-1} [13] was used (the calculated value is -75.0 kcal mol^{-1}). The results are presented in Scheme 3. The path a includes an ion-pair like transition state TS_a with both Pt–Br bonds being significantly stretched with the energy of 36.8 kcal mol^{-1}, which is noticeably higher than the experimental value of 27.7 kcal mol^{-1}. Note that a mechanism similar to the one in the path a was also studied computationally and was shown to be consistent with experimental observations in the case of an aryl C–I reductive elimination from *trans*-di-(*p*-fluorophenyl) diiodo Pt(IV) 1,2-bis(dimethylphosphino)benzene complex **5** (Fig. 1).[10] A concerted mechanism for C–Br elimination of vinyl bromides was also suggested previously for some octahedral dibromo Pd(IV) complexes **6** (Fig. 1).[14]



Scheme 3

The path b includes a pair of free ions, **4** and Br$^-$, with the Gibbs energy of 20.4 kcal mol^{-1} and the low energy transition state TS_b, 24.8 kcal mol^{-1}. Assuming that the solvation energy of cationic complex **4** is slightly overestimated by the PBF model as it is, for instance, in the case of bromide anion, the TS_b energy should be higher than 24.8 kcal mol^{-1} and, hence, more consistent with the experimental Gibbs activation energy value of 27.7 kcal mol^{-1}. A decrease of fraction of

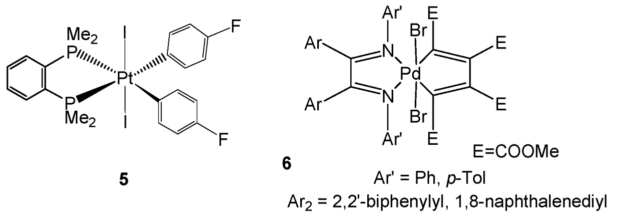


Fig. 1 d^6 Metal complexes undergoing concerted Ar–X reductive elimination.

p-FC_6H_4Br caused by n-Bu_4NBr additives is consistent with the path b,[15] whereas it is difficult to account for this effect in terms of the concerted mechanism in the path a. Interestingly, reductive elimination of an Ar–I from the iodo-analogue **5** in DMF solution was not sensitive to the presence of n-Bu_4NI suggesting that **5** reacts *via* a concerted path analogous to the path a.[10] Since formation of **1** from **2** was observed in some of our experiments, a computational analysis of the Ar–Br elimination from **1** as a result of a direct electrophilic attack of free Br_2 at an aryl carbon atom in **1** was attempted but no such reaction path could be found.

Finally, we also studied computationally Br_2 elimination from **2**. This reaction is only slightly uphill (Gibbs energy change is 1.7 kcal mol^{-1}). A homolytic loss of one of the bromine atoms from **2** is prohibitively endergonic with the reaction Gibbs energy of 39.8 kcal mol^{-1}. At the same time, a heterolytic mechanism with an intermediacy of **4** (and, possibly, a derived solvento complex) and Br^- favored by polar solvents and a subsequent virtually barrierless attack of Br^- at the bromo ligand in **4** allows one to account for facile formation of **1** and Br_2 elimination from **2** in acetone, DMSO or NMP and in the presence of additives of n-Bu_4NBr.[16]

In conclusion, we have demonstrated the first example of an aryl bromide C–Br reductive elimination from an isolated Pt(IV) complex. The reaction probably proceeds *via* the formation of a cationic five-coordinate Pt(IV) intermediate **4**.[17] This mechanism is different from the mechanism of concerted reductive elimination of aryl iodides from Pt(IV) center suggested by us previously for similar complex **5**. Interestingly, the pentacoordinate intermediate **4** also participates in the reductive elimination of Br_2, making the product distribution highly dependent on the reaction conditions.

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Notes and references

‡ X-Ray structure data for **2**: $C_{30}H_{32}Br_2F_6N_2P_2Pt$, $M = 951.43$, $0.3 \times 0.15 \times 0.15$ mm, orthorhombic, space group $P212121$, $a = 10.3414(2)$, $b = 12.3660(3)$, $c = 30.6670(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3921.75(15)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.611$ g cm^{-3}, $\theta_{max} = 27.70°$, Nonius KappaCCD, MoKα radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 110(2)$ K, 22 362 collected reflections, 8896 unique reflections ($R_{int} = 0.0760$). $R_1 = 0.0532$, $wR_2 = 0.1384$ for data with $I > 2\sigma(I)$, and $R_1 = 0.0884$, $wR_2 = 0.1524$ for all unique data. The lattice contains also severely disordered pentane solvent, as indicated by several residual electron-density peaks (within 1.0–1.7 e Å^{-3}) present in areas between molecules of the Pt-compound. The pentane solvent could not be modeled by discrete atoms, and was therefore excluded from the structural model.

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