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Unprecedented 1,3-migration of the aryl ligand in metallacyclic aryl α-naphthyl Pt(IV) difluorides to produce β-arylnaphthyl Pt(II) complexes[†]

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Electrophilic fluorination of aryl α -naphthyl Pt(II) complexes leads to an unprecedented 1,3-migration of the aryl ligand to the β -position of the naphthyl group. The reaction proceeds *via* the initial oxidative addition of two fluoro ligands to the Pt center followed by C(sp²)–C(sp²) coupling and aryl migration.

Electrophilic fluorination of the platinum group organometallic complexes is a rapidly developing area of research.^{1,2} Typically, the initially formed high-oxidation state species can react further leading to the formation of new bonds, particularly C-C or C-F bonds,³⁻⁵ with the reaction outcome depending on the nature of the ligands, geometry of the metal complex and the source of the electrophilic fluorine. For example, Gagné and co-workers used Selectfluor[®] for fluorination of cationic trisphosphine aryl Pt(II) complexes to produce the corresponding arylfluorides, whereas the use of XeF₂ was less efficient.⁶ On the other hand, the reaction of cyclometallated Pt(II) complexes with XeF2 can lead to benzylic C-H fluorination, whereas the use of the cationic N-fluorocollidinium salt as a fluorinating agent resulted in the C(sp²)-C(sp²) bond formation with subsequent cyclometallation of the resulting biphenylylphosphine (Scheme 1).⁷ Similarly, competitive C(sp²)-H and C(sp³)-H activation at the Pt(II) center in the products resulting from the C-C reductive elimination from the Pt(IV) precursor was reported very recently by Crespo et al.⁸ In all these cases, the newly formed C-X bond resulted from a classical C-X reductive elimination at the high valent metal center. Herein, we report the first example of the $C(sp^2)-C(sp^2)$ coupling of metallacyclic aryl α-naphthyl Pt(w) difluorides including an unprecedented 1,3-aryl migration from the Pt center to the β -carbon of the naphthyl fragment.





The naphthalene-based ligand 1 was designed and prepared to explore the possibility of the benzylic C-H bond functionalization under the electrophilic fluorination conditions. In this ligand, both C(sp³)-H and C(sp²)-H bonds may be involved in cycloplatination after the initial coordination of the phosphine 1 to a $Pt(\pi)$ center. In practice, only cyclometallated $Pt(\pi)$ -aryl complex 2 was obtained upon the reaction with (COD)PtCl₂ (Scheme 2). Complex 2 can be readily converted to the diaryl derivatives 3a-d by the action of the corresponding Grignard reagents in the presence of pyridine. The X-ray structure of 3a (see ESI⁺) confirms the formation of a square-planar Pt(II) complex with the aryl ligands cis to each other.⁹ The reaction of 3 with XeF₂ in CH₂Cl₂ or CH₃CN leads to the formation of moderately unstable Pt(IV) difluorides 4a-d (Scheme 3). Complexes 4a-d exhibit the characteristic multiplets in the ${}^{19}F_1^{1}H$ NMR spectra between -200 and -230 ppm due to two inequivalent fluoro ligands at the Pt(v) center. The ${}^{31}P{}^{1}H$ NMR spectra of complexes 4 show the signal at \sim 75 ppm with a Pt-P coupling constant of ca. 2900 Hz. In the case of the 3,5-difluorophenyl complex 3b Pt(IV) difluoride 4b could be prepared in a pure form and characterized using single crystal X-ray diffraction (Scheme 3). The platinum atom in 4b has an octahedral environment with both fluoro



Scheme 2 Synthesis of the Pt(II) diaryl complexes 3

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Scheme 3 Electrophilic fluorination of Pt(II) diaryl complexes 3.



Scheme 4 Aryl migration to the 7 position of the naphthalene ligand core. See ESI† for X-ray structures of 5a and 5c.

ligands *trans* to the aryl ligands, which is typical for the difluoro diaryl platinum complexes bearing chelating donors. The Pt–F distances of 2.043(4) Å and 2.071(4) Å are within the typical range for the Pt($_{IV}$) complexes.^{6,10}

Intriguingly, the aryl α -naphthyl Pt(π) difluorides 4a-d dissolved in MeCN or CH2Cl2 reacted at 20-60 °C to form cyclometallated Pt(II) complexes 5a-d (>90% NMR vield), the products of the unprecedented $C(sp^2)-C(sp^2)$ coupling of the phenyl and the naphthyl groups, which includes the 1,3-aryl migration between the Pt center and the β -carbon of the naphthyl fragment (Scheme 4). The structures of complexes 5a-d have been established unequivocally using single crystal X-ray diffraction. The reactions are fast enough already at 20 $^\circ\mathrm{C}$ for the electron-rich 4c,d but require heating at 40-60 °C for the electron-poor 4a,b. The ³¹P{¹H} NMR spectra of complexes 5 exhibited one signal at ~88 ppm (J_{PtP} ~ 2100-2500 Hz) whereas the ¹H NMR spectra were consistent with the presence of Pt-bound aryl groups derived from the original naphthyl and phenyl ligands in 4. In turn, the ¹⁹F{¹H} spectrum of 5b showed two broad singlets due to two non-equivalent carbon-bound fluorine atoms and no Pt-bound fluorides.



Fig. 1 Proposed structure of complex 6 and X-ray structure of the derived Pt(v) monofluoride, 6b'.

Noteworthily, transient platinum phosphine complex 6 (Fig. 1a) having the metal-coordinated HF₂⁻ ligand¹¹ was observed almost in all the cases during the conversion of 4 to 5. The fraction of complex 6 in such solutions depends on the aryl substituent, solvent and the reaction time. The addition of (i-Pr)2EtN or pyridine to a solution containing 6b in CH₃CN leads to the disappearance of the signal of the coordinated HF2⁻ in the ¹⁹F NMR spectrum and formation of the Pt(IV) monofluoride **6b**' having the cyclometallated *tert*-butyl group (Fig. 1b). The addition of bases led to the complete suppression of the $C(sp^2)$ - $C(sp^2)$ coupling suggesting that 6 is not an intermediate of the reaction in Scheme 4. In the case of the perfluorophenyl complex 3e no 4e was observed upon treatment of 3e with XeF₂. Instead, the intermediate 6e was detected which decomposed very slowly to form several products including the crystallographically characterized 7 in which the initially cyclometallated *tert*-butyl group is coupled to the α -naphthyl group (Fig. 1c).

To get further insight into the unprecedented C–C coupling of **4** leading to the formation of the 7-aryl-1-naphthylphosphine core present in **5**, transformation of the representative 3,5-difluorophenyl Pt(v) complex **4b** was studied using the DFT calculations.¹² In these calculations acetonitrile was modeled as the reaction medium; the Gibbs energies for the gas phase reactions are also provided. The reaction sequence that we considered is presented in Scheme 5. Pyridine dissociation from **4b** to form **8** and subsequent isomerization of **8** lead to the formation of a relatively low-energy five-coordinate transient **9** with the coordination vacancy *trans* to the phenyl ligand, which is required for facile C–C coupling¹³ of the phenyl and the α -naphthyl ligands. Interestingly, the C–C coupling of **9** is thermodynamically unfavorable. The coupling product **10** is a



Scheme 5 DFT-calculated Gibbs energy profile for reaction of **4b** in acetonitrile solution and gas phase to form the 7-aryl-1-naphthyl-bis(*tert*-butyl)phosphine core present in **5**.



Pt(II) σ-complex derived from the 8-aryl-1-naphthyl-bis(tert-butyl)phosphine where the newly formed C-C bond is coordinated to the Pt(II) center. The biaryl unit in 10 is heavily distorted due to the rigidity of the Pt-coordinated 8-arylnaphthylphosphine and its inability to accommodate the agostic C-C bond perpendicular to the Pt(II) coordination plane. These geometric constraints make the C-C coupling of 9 unfavorable, whereas, typically, the C-C coupling of Pt(IV) diaryl complexes is exothermic.¹⁴ The reaction coordinate analysis shows that the C-C reductive coupling of 9 to form 10 involves the low-lying transition state TS_{Pt-C8}. Subsequent isomerization of 10 via another low energy transition state $TS_{\sigma-\pi}$ produces the highly geometrically distorted π -complex **11**. Interestingly, the transient 11 undergoes a cleavage of the C-C bond formed initially at the C-C coupling step to form a moderately stable Pt(II) carbene complex 12. This reaction includes migration of a formally carbanionic aryl from the C8 to the C7 position of the naphthalene fragment *via* the transition state TS_{C8-C7} . As a result, the geometric distortion of 11 is relieved and the planarity of the Pt(II)-naphthylphosphine fragment is regained thus contributing to the exothermicity of this transformation. The formation of 12 from 11 may, formally, be compared with pinacol rearrangement in organic chemistry (Scheme 6).¹⁵

The **11** to **12** transformation is the rate limiting step of the whole reaction sequence in Scheme 6, both in MeCN solution and in the gas phase.¹⁶ The aromaticity of the former naphthalene fragment present in **12** is restored and complex **13** is formed as a result of an intramolecular low-barrier proton transfer from the C7 position of the naphthalene fragment to the fluoride ligand *cis*- to the naphthyl ligand. The elimination of HF from **13** allows production of a C–H agostic transient **14** required for the cycloplatination of the 7-aryl-1-naphthylphosphine residue. The cycloplatination leads to a Pt(rv) hydride intermediate **15** *via* the transition state **TS**_{CH-Pt}. Finally, the observed reaction product **5b** results from the reductive elimination of HF from **15** and the formation of a pyridine–(HF)₂ adduct.

In summary, we have discovered an unprecedented 1,3-aryl migration in aryl α -naphthyl Pt(v) complexes. The reaction produces unexpected C(sp²)–C(sp²) coupling products containing the aryl β -naphthyl rather than the expected aryl α -naphthyl fragment. Based on the results of the experimental study and the DFT modeling the reaction mechanism was proposed that includes a tandem C–C coupling of Pt(v) aryl naphthyl complexes, a 1,2-aryl shift in the naphthalene ring to produce a

stabilized Pt(n) naphthylidene transient and deprotonation of the latter carbene complex leading to the restoration of the naphthalene aromatic system. These results also point to the high potential for discoveries of new reactions induced by sterically bulky and/or rigid ligands present in a transition metal coordination sphere.¹⁷

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