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Formation of Fluorinated Platinum−Stilbazole Complexes: Aryl−Halide Oxidative Addition vs η^2-Coordination of a Carbon−Carbon Double Bond

André C. B. Lucassen,[†] Linda J. W. Shimon,[‡] and Milko E. van der Boom*,[‡]

Department of Organic Chemistry and Chemical Research Support Unit,
Weizmann Institute of Science, Rehovot, 76100, Israel

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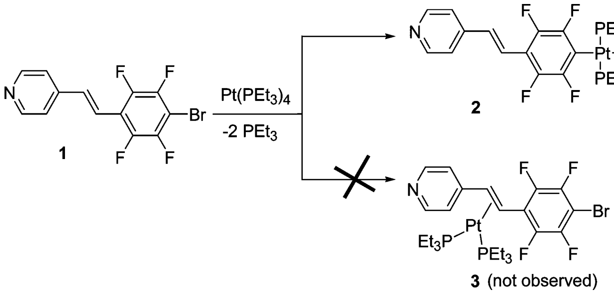
Summary: Reaction of a zerovalent platinum complex with a partially fluorinated stilbazole ligand results in direct Ar_f*−Br oxidation addition. The exclusive formation of the* Ar_f*−*Pt^{II}*−Br complex does not proceed via* η^2*-C═C coordination on the reaction coordinate or as a side-equilibrium prior to the observed C−Br bond activation.* Ar_f*−Br activation by* Pt^0 *is the kinetically and most probably also the thermodynamically favorable process independent of the reaction temperature and solvent polarity. This is in stark contrast with the reactivity of isostructural nonfluorinated stilbazole systems, where there is a lower barrier for* η^2*-C═C coordination than for Ar−Br oxidative addition with* Pt^0*.*

Scheme 1. Direct Generation of Complex 2 without Parallel Formation and/or Intermediacy of the Postulated Complex 3; Ar_f-Br Oxidative Addition Is Kinetically Preferred over η^2-C═C Coordination



Competitive olefin coordination and aryl−halide oxidative addition to low-valent late transition metals are key steps in several homogeneous catalytic processes,[1,2] including synthetically important cross-coupling reactions. Furthermore, metal-mediated synthesis often involves the use of substrates having both carbon−carbon double bonds and aryl−halides. Numerous studies have been devoted to the design of sophisticated task-specific, platinum group metal catalysts in parallel to the utilization of phosphine metal complexes in organic synthesis.[1,2] A better fundamental understanding of coordination and oxidative addition chemistry may open up practical routes for the formation of new organic products.[3,4] We reported recently that the reaction between a zerovalent platinum phosphine complex and a halogenated vinylarene resulted in η^2-C═C coordination of the zerovalent metal center prior to Ar−Br oxidative addition.[4] Upon heating, either in solution or in the solid state, the metal center "walks" around the π-system from the bridging C═C double bond to the C−Br bond. We demonstrate here that Ar_f−Br oxidative addition with an analogous fluorinated stilbazole substrate by $Pt(PEt_3)_4$ is kinetically favorable over π-coordination of a C═C double bond.

The reaction of 4′-bromo-2′,3′,5′,6′-tetrafluorostilbazole (**1**)[5] with a stoichiometric amount of $Pt(PEt_3)_4$[6] in dry THF or toluene at room temperature under nitrogen resulted in rapid formation of the new complex **2** by selective oxidative addition of the Ar_f−Br moiety to the d^{10} metal center (Scheme 1).

Complex **2** was formed quantitatively with concurrent formation of 2 equiv of PEt_3, as judged by $^{31}P\{^1H\}$ NMR spectroscopy. The product was isolated as white crystals formed overnight from a saturated solution of hexane/toluene (10:1 v/v) at −30 °C in 81% yield and was fully characterized by ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, and mass and single-crystal X-ray crystallography (Figure 1).[7] The X-ray analysis reveals a square-planar geometry around the Pt(II) center having mutually *trans* phosphines with a P−Pt−P angle of 174.3(6)° and a C−Pt−Br angle of 176.5(2)°. The dihedral angle between the aromatic rings is 11.4°; however, the pyr−C, Ar_f−C, and C═C bonds lengths of 1.55(3), 1.53(3), and 1.38(3) Å, respectively, are not affected by formation of the strong M−Ar_f σ-bond.

Monitoring the reaction of $\mathbf{1} + Pt(PEt_3)_4 \rightarrow \mathbf{2} + 2\ PEt_3$ in THF-d_8 as shown in Scheme 1 by variable-temperature ^1H, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy in the temperature range from −75 to +25 °C did not reveal formation of any η^2-C═C coordination complexes such as the postulated complex

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* To whom correspondence should be addressed. E-mail: milko.vanderboom@weizmann.ac.il.

[†] Department of Organic Chemistry.

[‡] Chemical Research Support Unit.

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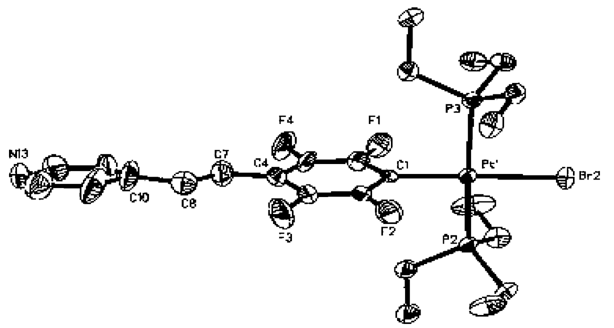
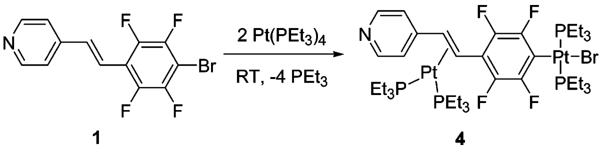


Figure 1. ORTEP diagram of complex **2** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Pt(1)−Br(2) 2.4925(10), Pt(1)−C(1) 2.006(7), C(4)−C(7) 1.53(3), C(7)−C(8) 1.38(3), C(8)−C(10) 1.55(3), Pt(1)−P(2) 2.301(19), Pt(1)−P(3) 2.304(18); C(1)−Pt(1)−P(3) 90.8(19), C(1)−Pt(1)−P(2) 92.6(19), P(2)−Pt(1)−P(3) 174.3(6), C(1)−Pt(1)−Br(2) 176.5(2), P(2)−Pt(1)−Br(2) 88.05(5), P(3)−Pt(1)−Br(2) 88.8(5).

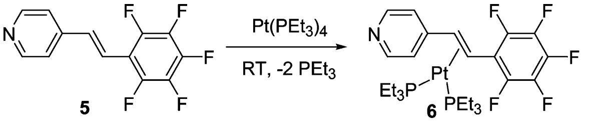
3 in parallel or prior to the observed product of Ar_f−Br oxidative addition (**2**). An intermediate complex having two magnetically different *cis* PEt_3 ligands in a 2:1 ratio was observed in the temperature range from −75 to −35 °C, which may be a cationic Ar_f−Pt(II) complex.[9,10] No reaction occurred at lower temperatures; only signals attributed to $Pt(PEt_3)_4$ were observable in the $^{31}P\{^1H\}$ NMR spectra. It is likely that unsaturated platinum complexes are initially formed, which in principle can undergo η^2-C═C coordination and/or Ar_f−Br oxidative addition. $Pt(PEt_3)_4$ is known to undergo reversible PEt_3 dissociation in solution to form the 16-electron complex $Pt(PEt_3)_3$.[11,12] This equilibrium is clearly visible in the variable-temperature $^{31}P\{^1H\}$ NMR spectra in the absence of substrate **1**. However, formation of $Pt(PEt_3)_3$ was not observed during the course of the reaction with **1**, indicating that PEt_3 dissociation is a relative slow process in comparison with the subsequent reaction of **1** with platinum. $Pt(PEt_3)_3$ can undergo both associative and dissociative ligand exchange.[12] A kinetically significant amount of unobserved $Pt(PEt_3)_2$ might be present in the system, which undergoes a selective reaction with the Ar_f−Br unit. However, other mechanistic routes are also possible.[13] Heating the reaction mixture to 60 °C for 1 h in a sealed vessel after consumption of the starting materials also did not result in the formation of η^2-C═C coordination complexes.

Substrate **1** was reacted with 2 equiv of $Pt(PEt_3)_4$ in dry THF at room temperature to verify that platinum coordination to the carbon−carbon double bond is not prohibited due to steric hindrance or is energetically unfavorable in the presence of PEt_3. This reaction resulted in the quantitative formation of the new bimetallic complex **4** (eq 1). This compound was isolated as a white solid in 82% yield and fully characterized by ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, and mass spectrometry.[7] The $^{31}P\{^1H\}$ NMR spectrum shows the signals both for Ar_f−Br oxidative addition and for η^2-C═C coordination of the partially fluorinated stilbazole ligand in a 1:1 ratio. Apparently, metal coordination to the carbon−carbon double bond of complex **1** is not hampered. The formation of the formally mixed-valence Pt^0/Pt^{II} complex **4** clearly demonstrates that there is a fine balance between η^2-coordination of the −C═C− moiety and Ar_f−Br oxidative addition, as both processes can occur under identical reaction conditions at room temperature.



(1)

To further elucidate the mechanism of the formation of complex **2** (Scheme 1), pentafluorostilbazole **5**[5,15] was also reacted with an equimolar amount of $Pt(PEt_3)_4$ in THF-d_8 at −70 °C followed by stepwise warming of the reaction mixture to room temperature in the NMR probe (eq 2). This process resulted in the exclusive formation of the η^2-C═C coordination complex **6** and free PEt_3. Complex **6** was fully characterized by the same means as for **2**.[7] Single-crystal X-ray diffraction analysis of **6** reveals a trigonal coordination environment (Figure 2).[14] The η^2-C═C bond length of 1.451(6) Å is relatively long due to back-bonding from the metal center into the olefin π^*-orbitals.[16] Olefins with electron-withdrawing substituents are often strongly bound to Pt^0.[17]



(2)

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(7) See Supporting Information for complete experimental details and characterization data for complexes **2**, **4**, and **6**. The crystal structures of complexes **2** and **6** have been deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 271980 and CCDC 271981, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

(8) X-ray crystal data for **2**. Crystal data: $C_{22}H_{41}NF_4P_2BrPt+C_6$, colorless, prism, 0.2 × 0.2 × 0.2 mm^3, monoclinic, $P2(1)/c$ (no.14) a = 19.737(4) Å, b = 10.879(2) Å, c = 16.287(3) Å, β = 91.12(3)° from 20 degrees of data, T = 120(2) K, V = 3496.5(12) Å^3, Z = 4, fw = 804.56, D_c = 1.528 Mg·m^{-3}, μ = 5.285 mm^{-1}. Data collection and processing: Nonius KappaCCD diffractometer, Mo Kα, λ = 0.71073 Å, graphite monochromator, $-23 \leq h \leq 23$, $0 \leq k \leq 13$, $0 \leq l \leq 19$, frame scan width = 1.0°, scan speed 1.0° per 30 s, typical peak mosaicity 0.56°, 29 478 reflections collected, 8383 independent reflections (R_{int} = 0.086). The data were processed with Denzo-Scalepack. Solution and refinement: Structure solved by Patterson method with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97 348 parameters with 0 restraints, final R_1 = 0.0474 (based on F^2) for data with $I > 2\sigma(I)$ and, R_1 = 0.0663 on 6373 reflections, goodness-of-fit on F^2 = 1.104, largest electron density peak = 2.049 e·Å^{-3}. Note: There is a partially disordered hexane solvent molecule, which has been modeled with only the carbon atoms.

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(10) δ = 19.46 (d, 2P, $^1J_{Pt,P}$ = 2268 Hz, $^3J_{P,P}$ = 19.4 Hz), 16.07 (t, 1P, $^1J_{Pt,P}$ = 3466 Hz, $^3J_{P,P}$ = 19.4 Hz). Formation of a similar complex was observed by $^{31}P\{^1H\}$ NMR upon treatment of complex **2** at room temperature with $AgBF_4$ and PEt_3 in dry THF with the exclusion of light.

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(14) X-ray crystal data for **6**: Crystal data: $C_{25}H_{36}NF_5P_2Pt$, colorless, prism, 0.1 × 0.1 × 0.1 mm^3, triclinic, $P\bar{1}$ (no. 2), a = 8.792(2) Å, b = 11.444(2) Å, c = 14.941(3) Å, α = 109.00(3)°, β = 93.03(3)°, γ = 106.96(3)° from 20 degrees of data, T = 120(2) K, V = 1341.3(5) Å^3, Z = 2, fw = 702.58, D_c = 1.740 Mg·m^{-3}, μ = 5.399 mm^{-1}. Data collection and processing: Nonius KappaCCD diffractometer, Mo Kα λ = 0.71073 Å, graphite monochromator, $-11 \leq h \leq 11$, $-14 \leq k \leq 13$, $0 \leq l \leq 19$, frame scan width = 2.0°, scan speed 1.0° per 90 s, typical peak mosaicity 0.82°, 27 559 reflections collected, 6089 independent reflections (R_{int} = 0.056). The data were processed with Denzo-Scalepack. Solution and refinement: Structure solved by Patterson method with SHELXS-97. Full matrix least-squares refinement based on F^2 with SHELXL-97, 349 parameters with 92 restraints, final R_1 = 0.0307 (based on F^2) for data with $I > 2\sigma(I)$ and R_1 = 0.0404 on 6085 reflections, goodness-of-fit on F^2 = 1.038, largest electron density peak = 1.832 e·Å^{-3}.

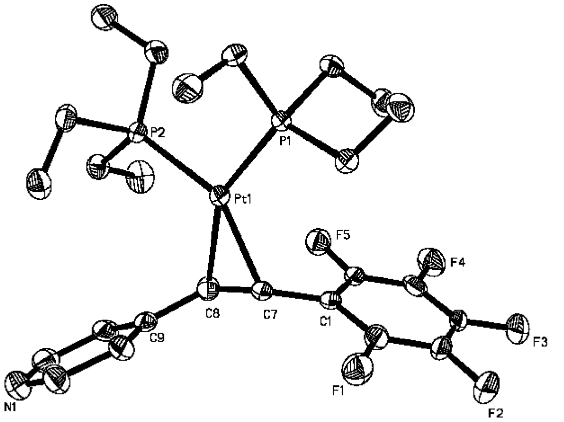

Figure 2. ORTEP diagram of complex **6** (thermal ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Pt(1)−C(7) 2.105(4), Pt(1)−C(8) 2.114(4), C(1)−C(7) 1.482(5), C(7)−C(8) 1.451(6), C(8)−C(9) 1.475(6); C(1)−C(7)−C(8) 123.5(4), C(7)−C(8)−C(9) 122.8(4), C(7)−Pt(1)−C(8) 40.23(16), C(7)−C(8)−Pt(1) 69.5(2), C(8)−C(7)−Pt(1) 70.2(2), P(1)−Pt(1)−P(2) 102.18(4).

In contrast to the stoichiometric reaction of **1** with Pt(PEt$_3$)$_4$: (i) no intermediate complexes were observed by in situ ^{31}P{^{1}H} NMR follow-up measurements during the formation of complex **6**, and (ii) no complexation of **5** with platinum was observed at temperatures below −50 °C for ∼4 h, while a significant amount of the 16-electron complex, Pt(PEt$_3$)$_3$, was present in the reaction mixture. Relatively slow conversion of **5** and Pt(PEt$_3$)$_3$ into complex **6** and PEt$_3$ was observed at −50 °C with $t_{1/2} \approx 15$ h. The coordination complex **6** was observed only at temperatures ∼20 °C higher than the formation of complex **2** via Ar$_\mathrm{f}$−Br oxidative addition. This unambiguously demonstrates that Ar$_\mathrm{f}$−Br oxidative addition is the kinetically preferred process for substrate **1**. In full agreement with the above-mentioned findings, reaction of the model complex **6** with an equimolar amount of **1** in the presence of 2 equiv of PEt$_3$ at room temperature in dry THF resulted in the relatively slow formation of complex **2** ($t_{1/2} \approx 2.5$ h), further ruling out the possibility that the direct formation of complex **2** as shown in Scheme 1 proceeds via a bimolecular process involving the unobserved complex **3**.

In summary, the exclusive formation of the Pt$^{\mathrm{II}}$ complex **2** does not proceed via η^2-C=C coordination of the partially fluorinated stilbazole ligand **1** on the reaction coordinate or as a side-equilibrium prior to the observed C−Br bond activation. Ar$_\mathrm{f}$−Br activation is the kinetically and most probably also the thermodynamically favorable process independent of the reaction temperature and solvent polarity. This is in stark contrast with the previously reported η^2-C=C coordination vs Ar−Br oxidative addition with isostructural nonfluorinated stilbazole systems, where there is a lower barrier for η^2-C=C coordination than for Ar−Br oxidative addition with platinum.[4] Oxidative addition of the nonfluorinated substrate involves an intermediate η^2-C=C complex (akin to the postulated complex **3**, Scheme 1), and this coordination complex rearranges to the oxidative addition product via an unimolecular “ring-walking” process.[4,18] The here-presented observations are a clear example that the mechanistic route toward Ar−Br activation can be significantly different for corresponding fluorinated substrates. Furthermore, the kinetic balance of olefin coordination vs Ar−Br oxidative addition can be inverted upon fluorination of the aromatic system. It is known that the rate of Ar−halide oxidative addition increases by placing electron-withdrawing groups on the arene.[2] Nevertheless, it is remarkable that insertion of a zerovalent late-transition metal center into a carbon−halide bond can be kinetically favorable over η^2-coordination to a carbon−carbon double bond.[19] The implementation of these findings with respect to other metal complex precursors and substrates is under investigation, as it might lead to selective chemical transformations with high kinetic control over the reaction outcome.

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Supporting Information Available: Complete experimental details and characterization data for complexes **2**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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