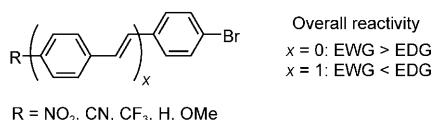


A Coordination Controlled Aryl–Halide Oxidative Addition to Platinum

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Aryl–halide bond activation and coordination of unsaturated substrates are key steps in many metal-mediated carbon–carbon bond-forming reactions.^[1,2] Numerous experimental and computational studies have been reported on these processes.^[3] The electronic nature of the reactants is known to affect both steps. In particular, an electron withdrawing group (EWG: e.g., CF₃, CN, NO₂) makes the C_{aryl}–halogen bond more ionic, weakens this bond, and therefore increases the rate of the bond activation (Scheme 1, $x=0$).^[4]



Scheme 1. Overall reactivity trend of aryl–bromides with zero valent platinum complexes. EWG = electron withdrawing group, EDG = electron donating group.

Such EWGs strengthen metal–olefin bonds by increasing the π -backbonding between the metal center and the carbon–carbon double bond of the substrate.^[5] How would the activation of aryl–halide bonds be affected if the same substrate also contains a carbon–carbon double bond capable of interacting with a metal center (Scheme 1, $x=1$)? We have shown that halogenated arylarenes are versatile sys-

tems ideal for studying coordination chemistry coupled with aryl–bond activation. For instance, the reaction of M(PEt₃)₄ (M = Ni, Pt) with a halogenated substrate results in η^2 -coordination to a -C=C- or -N=N- moiety, followed by “ring-walking” of the metal center, yielding the product of aryl–halide oxidative addition.^[6–8] However, partially fluorinated substrates kinetically prefer aryl–halide bond activation.^[9] Thus, the metal center can be selectively directed to a specific site by varying the electronic properties of the reactants.

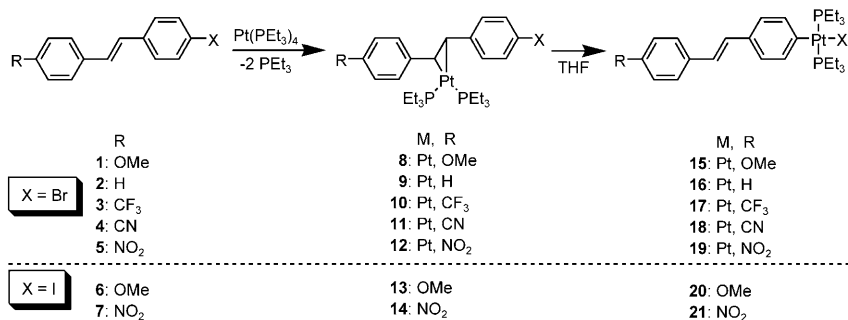
We observe in the stilbene systems presented here that η^2 -coordination of the platinum center to a -C=C- unit is kinetically preferable over metal insertion into the carbon–halide bond regardless of the electronic properties of the substrate (Schemes 1 and 2). Nevertheless, the substituents of the stilbenes play a dominant role in the overall process. The reactivity trend is opposite from that of other aryl halides: The substrates with electron-deficient substituents are transformed much slower in the products of aryl–bromide activation than in those with electron-donation groups (EDGs). The overall reactivity is controlled by the coordination of the ligand to the metal center, whereas the activation of the aryl–Br bond is the rate-determining step. These findings are in good agreement with DFT calculations.

A series of reactions with stilbenes **1–7** and Pt(PEt₃)₄ were used to explore the role of substrate coordination on aryl–halide activation. Reaction of a stoichiometric amount of Pt(PEt₃)₄ with a stilbene (**1–7**) in THF results in the formation of complexes **8–14**, respectively, by η^2 -coordination of the metal center to the central carbon–carbon double bond (see the Supporting Information for details). No products indicative of aryl–halide bond activation were observed by ¹H and ³¹P{¹H} NMR spectroscopy prior to the formation of these complexes. The complexes **8–14** were characterized by NMR spectroscopy. In addition, complexes **9–12** and **14** were isolated and characterized by elemental analysis (C, H) and/or mass spectrometry. Nearly identical spectroscopic properties were reported for structurally related stilbazole complexes.^[6,7,10] Prolonged reaction times and elevated temperatures resulted in the quantitative formation of com-

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Scheme 2. Selective formation of platinum (**8–14**) complexes by η^2 -coordination of compounds **1–7** followed by metal insertion into the aryl–halide bond (**15–21**).

CF₃ > CN > NO₂. The rate-determining step involves the aryl–halide unit. The iodo derivatives (**13**, **14**) of complexes **8** and **12** react significantly faster to afford complexes **20** and **21**, respectively (e.g., $k_I/k_{Br} \approx 60$ at 341 K for the transformations: **14**→**21** and **12**→**19**). The electronic effect of the halide (Br vs. I) on the η^2 -coordination is small (σ_p : I=0.18, Br=0.23)^[13] and, therefore, it is

plexes **15–21**, as judged by ¹H and ³¹P{¹H} NMR spectroscopy. These thermodynamically preferred products were isolated and characterized by a combination of ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹⁹⁵Pt{¹H} NMR spectroscopy, elemental analysis (C, H) and mass spectrometry. Complexes **10** and **17** were previously reported by us.^[11]

The X-ray structure of complex **12**, shown in Figure 1, confirms the η^2 -coordination of the central carbon–carbon double bond of the stilbene (**5**) to the metal center. The structural features are typical for Pt⁰-olefin complexes.^[12]

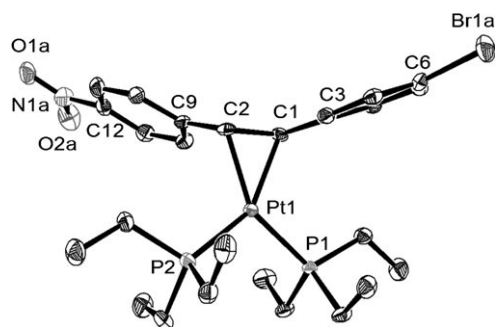


Figure 1. ORTEP diagram of complex **12** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity (CCDC 738014). Selected bond lengths [Å] and angles [°]: Pt1–C1 2.111(3), Pt1–C2 2.125(3), Pt1–P1 2.2663(8), Pt1–P2 2.2703(8), C1–C3 1.467(4), C2–C9 1.469(4), Br1a–C6 1.932(3), C12–N1a 1.443(7), N1a–O1a 1.199(7), N1a–O2a 1.270(9), C1–C2 1.456(5), C1–Pt1–C2 40.21(12), C1–Pt1–P1 106.45(9), C1–Pt1–P2 147.71(9), C2–Pt1–P1 145.96(9), C2–Pt1–P2 108.28(9), P1–Pt1–P2 105.59(3).

Follow-up ³¹P{¹H} NMR experiments in THF were used to derive the rate constants, k , at 58 °C for the transformations: **8–12**→**15–19** (Figure 2A). The reactivity differences are substantial: The stilbene complex (**8**), having a MeO substituent, reacts ≈ 70 times faster than the analogous system having a NO₂ unit (**12**) under identical reaction conditions. The reactivity trend for these stilbene complexes is opposite that known for *para*-substituted aryl-bromides.^[4] Apparently, the here observed η^2 -coordination dominates the rate of product formation because it follows the order: MeO > H >

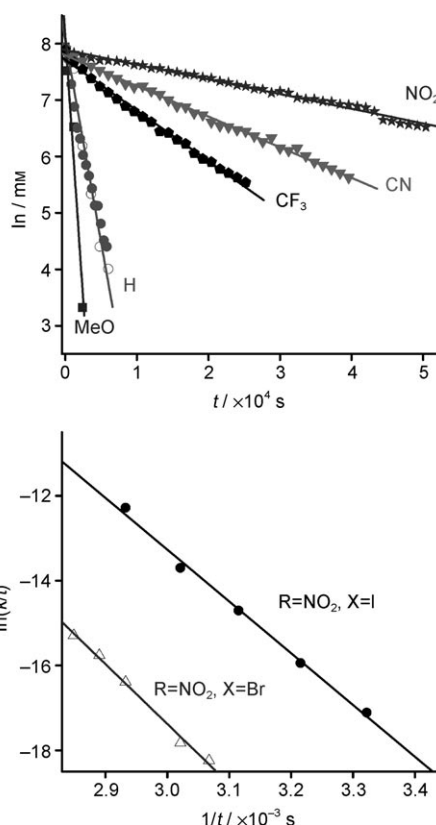


Figure 2. A) In situ ³¹P{¹H} NMR follow-up measurements of the quantitative conversion of **8–12** to **15–19**, respectively, in THF with a concentration of 28 mM. The lines are linear fits with $R^2=0.957$ – 0.995 . B) Eyring plot of the conversion of **12**→**19** (R=NO₂, X=Br, $R^2=0.994$; $\Delta G^\ddagger_{298\text{K}}=27.4 \pm 1.2$ kcal mol⁻¹, $\Delta H^\ddagger=28.1 \pm 1.2$ kcal mol⁻¹, $\Delta S^\ddagger=2.4 \pm 3.6$ e.u.) and **14**→**21** (R=NO₂, X=I, $R^2=0.995$; $\Delta G^\ddagger_{298\text{K}}=24.5 \pm 1.0$ kcal mol⁻¹, $\Delta H^\ddagger=24.1 \pm 1.0$ kcal mol⁻¹, $\Delta S^\ddagger=-0.9 \pm 3.0$ e.u.). The follow-up ³¹P{¹H} NMR data are presented in Figure S1.

not expected to drastically affect the overall process. The same reactivity order MeO \gg NO₂ was observed with the iodo derivatives (**13**, **14**). The activation parameters for the transformation **12**→**19** and **14**→**21** derived from Eyring plots (Figure 2B) indicate similar reaction pathways for the bromo and iodo systems. The near-zero entropy values

argue against a metal–ligand dissociation process as the rate-determining step.

A good linear correlation was observed between the rates of these transformations (**8–12**→**15–19**) and the electronic properties of the substituent of the stilbenes (**1–5**): The plot of $\log k_X/k_H$ versus σ_p shows that the reaction rates progressively decrease as the electron-withdrawing ability of the substituents (σ_p)^[13] increase (Figure 3, red line). The linear

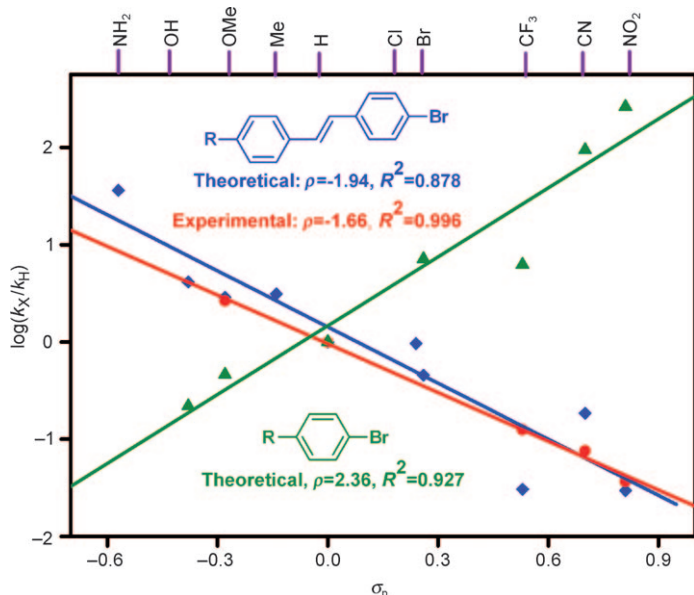


Figure 3. Hammett correlation plots for the reactions of a series of substituted aryl-bromides (theoretical: green line) and stilbenes (theoretical, blue line; experimental, red line). $\text{Pt}(\text{PH}_3)_2$ was used for the theoretical systems.

dependence indicates that the mechanism underlying all these reactions is very similar. DFT calculations at the PBE0/SDB-cc-pVDZ//PBE0/SDD level of theory showed that the potential energy surface (PES) for the transformation: **8–12**→**15–19** is comparable to that of a related system described elsewhere by us.^[6,7] Computational details are provided in the Supporting Information. Figure 3 also shows a good correlation between the measured and calculated rates (the reaction constants, ρ , are -1.7 and -1.9 , respectively). A similar linear trend was calculated for iodo derivatives (Figure S2). The theoretical activation energy for the aryl–halide oxidative addition process is taken as the difference in Gibbs free energy ($\Delta G_{298\text{K}}^\ddagger$) between the transition state of the metal insertion into the aryl–halide bond and the local minimum corresponding to $\text{Pt}(\text{PH}_3)_2$ η^2 -coordinated to the central carbon–carbon double bond of the stilbene (Table S1). This reveals that the substituent predominantly affects the stability of the η^2 -coordination complexes **8–12**, and not the $\Delta G_{298\text{K}}$ values of the transition state associated with the actual aryl–halide bond cleavage and its products (**15–19**). This is in agreement with the $^{195}\text{Pt}\{^1\text{H}\}$ NMR data of complexes **15–19**, which show a noticeable, but relatively small, substituent effect (see below). An EWG lowers the

energy of the π^* orbital (providing better overlap for back bonding), thereby stabilizing the pre-reaction complex such as **8–12** relative to the transition state for aryl–halide bond activation. Likewise, an EDG destabilizes the pre-reaction complex, resulting in a lower barrier for the overall process. In contrast, the relative energy of the oxidative addition transition state of substituted bromobenzene with platinum is reduced according to the electron accepting strength of the substituent. The theoretical plots of $\log k_X/k_H$ versus σ_p for such substrates in Figure 3 clearly shows the generally expected trend.

Complexes **15–19** exhibit long-range communication between the metal center and the substituent. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectroscopy for these complexes shows a triplet resonance within a rather small range of only $\delta = -4471$ – -4485 ppm with $^1J(\text{Pt},\text{P}) \approx 2750$ Hz.^[14] Apparently, these interactions are weak and this also explains why the aryl–halide bond activation step is not much influenced by the various substituents. Linear correlations were observed between the $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts of the *ipso*-carbon σ -bound to the metal center, the $^{195}\text{Pt}\{^1\text{H}\}$ NMR data, and the Hammett σ_p values of the various substituents (Figure 4). Van Koten showed that the slope of the linear

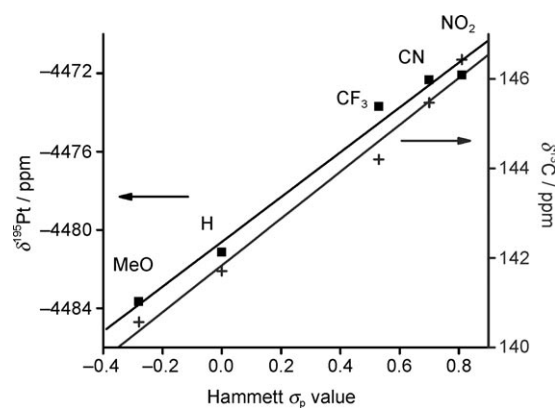


Figure 4. Linear correlations between the $^{13}\text{C}\{^1\text{H}\}$ (+, $R^2=0.986$), $^{195}\text{Pt}\{^1\text{H}\}$ (■, $R^2=0.986$) chemical shifts of the σ bound $\text{Pt}-\text{C}_{\text{aryl}}$ unit of complexes **15–19** and their corresponding Hammett substituent constants (σ_p).

correlation between the $^{195}\text{Pt}\{^1\text{H}\}$ NMR data and the Hammett σ_p values of the substituents of structurally related stilbenoid-pincer Pt^{II} complexes is ≈ 2 times steeper.^[14] Moreover, the range is ≈ 3.5 times larger. This demonstrates that the level of sensitivity towards variations of the electronic properties of the ligand system is controllable while maintaining the intramolecular distances (≈ 13 Å) between the metal center and the substituent nearly identical.

In summary, we observed relatively fast and selective η^2 -coordination of the stilbene-based substrates to the zero valent metal center regardless of the electronic nature of the system. This kinetically preferred process is followed by a slower metal insertion into the aryl–halide (Br, I) bond. The kinetics of the overall process is controlled by the substitu-

ent (i.e., MeO, H, CF₃, CN, or NO₂), resulting in a trend opposite what is generally observed for the activation of substituted aryl-halides by late transition metals.^[4] The DFT calculations showed that the η²-coordination of the central carbon-carbon double bond is much more affected by the electronic nature of the substituent than the actual metal insertion into the aryl-halide (halide = Br, I) bond. Therefore, the observed trend follows the expected order of metal binding interactions of olefins;^[5] however, the aryl-halide bond activation process is the rate-determining step. This demonstrates that substrate coordination can play an important role in oxidation addition processes. This can be utilized, for instance, for the selective activation of relatively strong aryl-Br bonds in the presence of much weaker aryl-I bonds,^[6] or in cross-coupling reactions.^[15,16]

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Keywords: aryl-halide activation • bond activation • olefin coordination • platinum • substituent effects

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