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Exceedingly Facile Ph–X Activation (X = Cl, Br, I) with Ruthenium(II): Arresting Kinetics, Autocatalysis, and Mechanisms**

Fedor M. Miloserdov, David McKay, Bianca K. Muñoz, Hamidreza Samouei, Stuart A. Macgregor,* and Vladimir V. Grushin*

Abstract: $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{L})(\text{H})_2]$ (where $\text{L}=\text{H}_2$ (**1**) in the presence of styrene, Ph_3P (**3**), and N_2 (**4**)) cleave the Ph–X bond ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) at RT to give $[(\text{Ph}_3\text{P})_3\text{RuH}(\text{X})]$ (**2**) and PhH. A combined experimental and DFT study points to $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{H})_2]$ as the reactive species generated upon spontaneous loss of L from **3** and **4**. The reaction of **3** with excess PhI displays striking kinetics which initially appears zeroth order in Ru. However mechanistic studies reveal that this is due to autocatalysis comprising two factors: 1) complex **2**, originating from the initial PhI activation with **3**, is roughly as reactive toward PhI as **3** itself; and 2) the Ph–I bond cleavage with the just-produced **2** gives rise to $[(\text{Ph}_3\text{P})_2\text{RuI}_2]$, which quickly comproportionates with the still-present **3** to recover **2**. Both the initial and onward activation reactions involve PPh_3 dissociation, PhI coordination to Ru through I, rearrangement to a η^2 -PhI intermediate, and Ph–I oxidative addition.

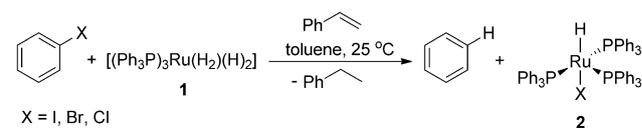
Efficient activation of inert bonds is a major goal of organometallic chemistry and catalysis with metal complexes.^[1] The C–X ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) bond of unactivated haloarenes is especially targeted because of their key role in organic synthesis. Most economically attractive aryl chlorides

are particularly challenging substrates because of the strength and low reactivity of the Ar–Cl bond.^[2] High-cost bulky, electron-rich phosphine ligands are usually required for Ar–Cl oxidative addition to Pd^0 , which is most widely used in cross-coupling reactions.^[2,3] Activation of chloroarenes as well as aryl bromides and iodides with metals besides Pd and Ni are rare.^[2,4,5]

By far the lowest-cost platinum-group metal, ruthenium, is highly attractive for Ar–X activation. However, examples of such reactions are rare, especially under mild conditions. Carbonyl- and PPh_3 -ligated Ru complexes can cleave the less inert C–X bonds of iodo- and bromobenzene and -toluene, but only at 125 °C.^[6] With bulky electron-rich Cy_3P co-ligands, Ru can activate the Ph–I bond at ambient temperature,^[7a,b] but the Ar–Cl bond requires 80 °C.^[7c] In general, ruthenium-catalyzed arylation reactions with chloroarenes occur only at 120–150 °C.^[8] Herein we report unprecedentedly facile (room temperature) activation of iodo-, bromo-, and even chlorobenzene with simple PPh_3 -based Ru complexes, with no need to employ electron-rich bulky phosphine ligands. The Ph–I bond cleavage reaction displays striking apparent zero-order kinetics that we show to arise from a masked autocatalysis. We detail a combined experimental and computational mechanistic study of this unconventional Ph–X bond activation, which is expected to be significant for future progress in the area.

Adding 1 equiv of styrene to a mixture of $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{H}_2)(\text{H})_2]$ (**1**) and PhX ($\text{X}=\text{I}, \text{Br}, \text{Cl}$) in toluene at room temperature resulted in instantaneous reaction that produced $[(\text{Ph}_3\text{P})_3\text{RuH}(\text{X})]$ (**2**) and benzene (GC-MS). The Ru product precipitated out and was isolated in ca. 90%, 90%, and 70–80% yield for $\text{X}=\text{I}$ (**2-I**), Br (**2-Br**), and Cl (**2-Cl**), respectively (Scheme 1). The structures of **2-I-CH}_2\text{Cl}_2**, **2-Br-2 THF**, and **2-Cl-C}_6\text{H}_6** were confirmed by single-crystal X-ray diffraction.^[9]

Such facile Ph–X ($\text{X}=\text{Cl}, \text{Br}$) bond cleavage with a simple PPh_3 -stabilized Ru^{II} species is unprecedented. Free radicals are unlikely to be involved in this transformation, as no bibenzyl was seen in reactions performed in toluene and deuterium incorporation into the benzene product was insignificant (< 4%, GC-MS) with $[\text{D}_8]\text{THF}$ used as solvent.



Scheme 1. Room-temperature Ph–X activation with 1–styrene.

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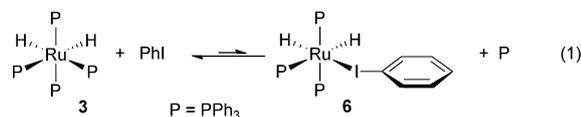
[**] We thank Prof. Alan S. Goldman, Prof. Vladimir I. Bakhmutov, Prof. Juan A. Casares, Prof. Michael K. Whittlesey, and Prof. Sylviane Sabo-Etienne for helpful discussions, and Dr. Jordi Benet-Buchholz, Dr. Eduardo C. Escudero-Adán, Dr. Marta Martínez Belmonte, and Dr. Eddy Martin for X-ray studies. The ICIQ Foundation and The Spanish Government (Grant CTQ2011-25418 and the Severo Ochoa Excellence Accreditation 2014-2018 SEV-2013-0319) are thankfully acknowledged for support of this work. F.M.M. is grateful to the Government of Spain (MICINN) for the FPI Ph.D. Scholarship (BES-2012-054922). S.A.M. and D.M. thank the EPSRC for support through award EP/J010677/1.

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In the absence of styrene, **1** reacted sluggishly even with PhI: after 1 day at 40 °C in toluene, the conversion of **1** was only 35%. Both $[(\text{Ph}_3\text{P})_4\text{Ru}(\text{H})_2]$ (**3**) and $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{H})_2(\text{N}_2)]$ (**4**) reacted more readily to give 2-I. Deliberately added PPh_3 slowed down these processes. These data suggested that the Ph–X bond was activated by the same reactive species, likely $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{H})_2]$ (**5**) produced upon removal of L from $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{L})(\text{H})_2]$, where L = H_2 (**1**), PPh_3 (**3**), or N_2 (**4**). Complex **5** has been convincingly proposed as a reactive intermediate in various transformations but never unambiguously characterized in the solid state or in solution.^[10] Attempts to detect **5** by VT ^1H and ^{31}P NMR spectroscopy upon generation from **1** and styrene in $[\text{D}_8]\text{THF}$ at -78°C were unsuccessful. We therefore sought mechanistic data on Ph–X activation at **3** through kinetic and computational studies, focusing on the most reactive substrate, PhI.

A critical observation was made during a VT NMR study of **3** in the presence of PhI (75 equiv) in $[\text{D}_8]\text{THF}$ or $[\text{D}_8]\text{toluene}$.^[11] A new species, **6**, (15%) in equilibrium with **3** was detected (-90 to $+25^\circ\text{C}$) and identified as *mer*- $[(\text{Ph}_3\text{P})_3\text{Ru}(\text{H})_2(\text{PhI})]$ [Eq. (1)]. The best resolved $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum (-40°C) displayed two 1:1 doublets from **6** (-8.56 and -16.14 ppm) with $J(\text{H}-\text{H}) = 7.1$ Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at the same temperature exhibited a doublet (57.1 ppm) and a triplet (52.7 ppm) in a 2:1 integral ratio with $J(\text{P}-\text{P}) = 17$ Hz. The formation of **6** was accompanied by the formation of 1 equiv of free PPh_3 (-5.5 ppm). Neither **6** nor its analogues were observed in the absence of PhI or upon its replacement with PhBr or PhCl. These observations along with the formation of **6** in toluene indicate that PhI in **6** is coordinated to Ru through the iodine atom, not the π -system of the aromatic ring.^[12] Small amounts of 2-I owing to Ph–I activation were observed in these experiments only above -40°C .



The reaction of **3** with PhI in large excess (300 equiv) occurring in $[\text{D}_6]\text{benzene}$ at 25°C with ca. 95% selectivity to 2-I was monitored to more than 95% conversion (^1H NMR) to reveal a stunning linear dependence: the rate of disappearance of **3** and the formation of 2-I appeared to be concentration independent, that is, zeroth order. As surprisingly, after its nearly quantitative formation in a seemingly zeroth order process, 2-I decayed exponentially (Figure 1). As 2-I disappeared, its deep purple color vanished and the reaction mixture turned brown. In parallel, the broad $^{31}\text{P}\{^1\text{H}\}$ NMR signal at 57.1 ppm from 2-I was replaced with a broad resonance at 69.9 ppm, and the peak from free PPh_3 at -5.5 ppm grew in intensity to 2 equiv per Ru at full conversion of 2-I. The Ru product of the onward reaction appeared to be $[(\text{Ph}_3\text{P})_4\text{Ru}_2\text{I}_2(\mu-\text{I})_2]$ (**7**), which was formed quantitatively and structurally characterized (Figure 2).^[9,11] Therefore, 2-I produced in the first step reacted with PhI still present in excess to give **7** along with PhH and one equiv of PPh_3 (Scheme 2).

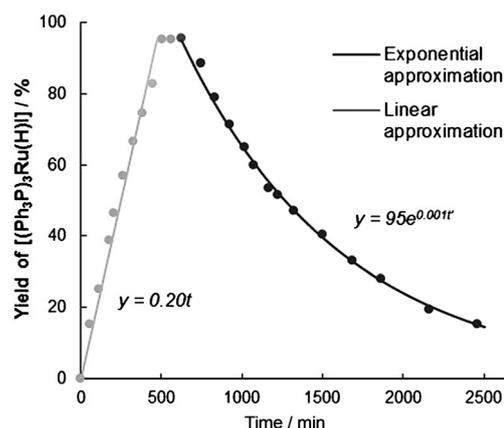


Figure 1. Kinetic profile of the reaction of **3** (0.0051 M) with PhI (1.49 M) at 25°C (^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR).

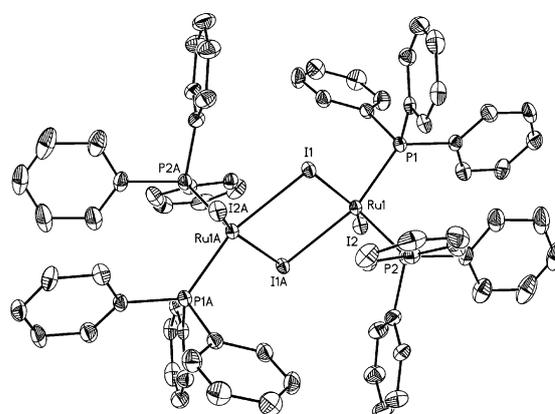
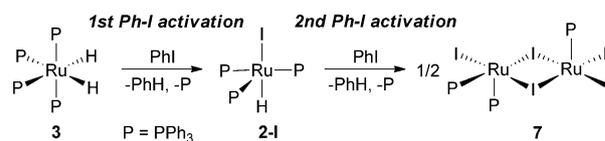


Figure 2. ORTEP of $[(\text{Ph}_3\text{P})_4\text{Ru}_2\text{I}_2(\mu-\text{I})_2]$ (**7**) with all H atoms omitted for clarity and ellipsoids set to 50% probability.



Scheme 2. Initial and onward reactions of **3** with PhI (25°C).

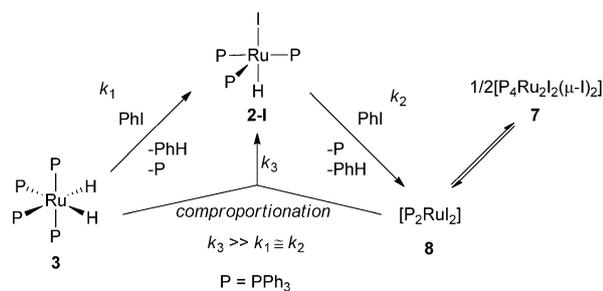
The method of initial rates was used to determine reaction orders for the first and second Ph–I activations. Each process is positive first order in both PhI and the metal complex (**3** or 2-I) and negative first order in PPh_3 [Eqs. (2) and (3)]. Although Equation (2) was consistent with PPh_3 predissociation from **3** to give **5** (see above), which reacted with PhI in a bimolecular fashion, it could not account for the apparent zeroth order behavior. Furthermore, Scheme 2 and Equations (2) and (3) were fully consistent with the observed stoichiometry of the reaction sequence involving stepwise formation of first 2-I and then **7** from **3** and PhI. However, none of the conventional kinetic schemes for two consecutive reactions could fit the highly reproducible, but peculiar kinetic profile (Figure 1). The seeming zeroth order of

appearance of **2-I** and the apparent lack of its transformation to **7** until its nearly quantitative formation seemed inexplicable, given similar reaction rates for both steps.

$$d[2-I]/dt = k_1[3][PhI][PPh_3]^{-1} \quad (2)$$

$$-d[2-I]/dt = k_2[2-I][PhI][PPh_3]^{-1} \quad (3)$$

We suspected that autocatalysis^[13] might account for this kinetic discrepancy [Figure 1 versus Eqs. (2) and (3)], and that **2-I** does in fact react with PhI once it is formed in the first step. The negative first order in PPh₃ [Eq. (3)] suggests PPh₃ predissociation from **2-I** prior to Ph-I activation. Consequently, the Ru product of the C-I cleavage is most likely four-coordinate [(Ph₃P)₂RuI₂] (**8**) that dimerizes to give **7**. We proposed, however, that **8** comproportionates with the as yet unreacted starting dihydride **3** to revive **2-I** in a reaction that is much faster than both that between PhI and **3** and the dimerization leading to **7** (Scheme 3).



Scheme 3. Autocatalysis in the reaction of **3** with PhI.

This mechanistic proposal was confirmed by generating **8** in situ from [(Ph₃P)₃RuCl₂] and NaI in the presence of **3** in THF and observing the formation of **2-I** within the time of mixing.^[11,14] Although k_3 (Scheme 3) could not be accurately determined experimentally, this instantaneous formation of **2-I** indicated that the comproportionation reaction is much faster than both Ph-I activation processes and therefore the condition for the proposed autocatalysis ($k_3 \gg k_2$) is met. Furthermore, if $k_1 \approx k_2$ and changes in [PhI] and [PPh₃] are negligible during the process, the general kinetic equation for the first step in Scheme 2 (Eq. (4), as derived from the steady-state approximation for **8**) is transformed to Equation (5) accounting for the apparent zeroth order behavior observed (Figure 1).^[11,15]

$$d[2-I]/dt = k_1[3][PhI][PPh_3]^{-1} + k_2[2-I][PhI][PPh_3]^{-1} \quad (4)$$

$$d[2-I]/dt = k'([3] + [2-I]) = \text{const.} \quad (5)$$

To our delight, the model presented in Scheme 3 gave an excellent fit to the full kinetic profile of the reaction (Figure 3).^[11] Although the starting complex **3** equilibrates with **6** ($K_{\text{eq}} = 1.7 \pm 0.3 \times 10^{-3}$), this equilibrium [Eq. (1)] establishes within the time of mixing and is therefore much faster than the rate determining steps of both Ph-I activation

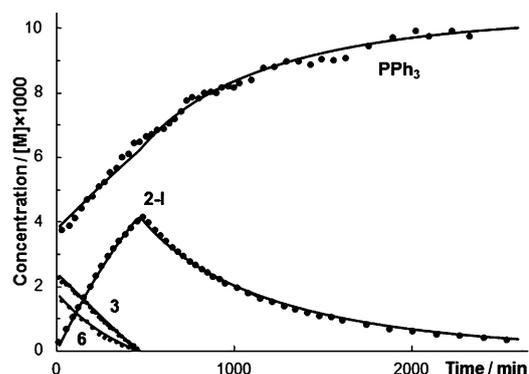
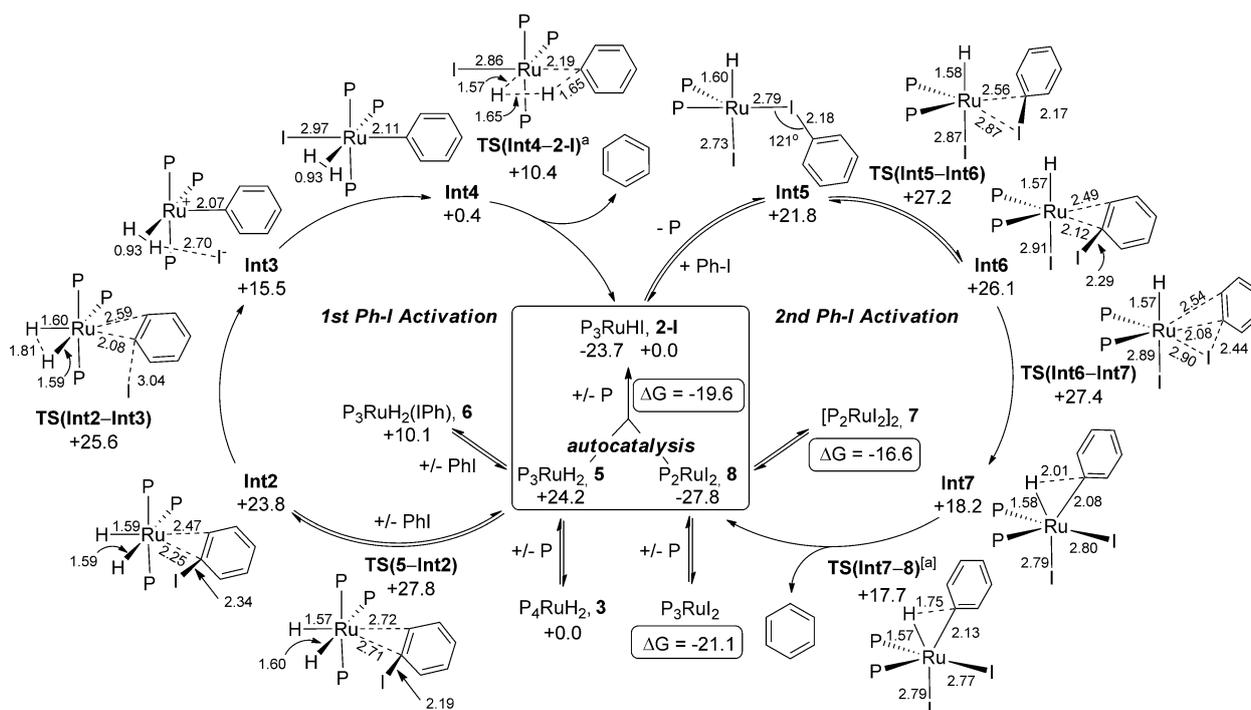


Figure 3. Plot of concentrations versus time for the reaction of **3** (0.0042 M) with PhI (1.49 M) at 25 °C. Data points are from the experimental measurements. The curves are from the kinetic model based on Scheme 3.^[11]

reactions. The similarity of $k_1 = 1.24 \times 10^{-5} \text{ min}^{-1}$ (first step)^[15] and $k_2 = 6.8 \times 10^{-6} \text{ min}^{-1}$ (second step) at 25 °C fulfills the above-described condition for the approximate zero-order decay of **3** and formation of **2-I**.^[11]

DFT calculations were used to probe the mechanisms of Ph-I bond activation at **3** and **2-I** using a BP86-D3(benzene) procedure, as in previous related studies.^[16] Profiles for the first and second Ph-I activations are shown in Scheme 4. Starting with **3** (0.0 kcal mol⁻¹), PPh₃/PhI substitution leads, via five-coordinate **5**, to **6** (+10.1 kcal mol⁻¹) in which PhI binds through iodine. Species **6** is more stable than alternative σ -(C,H) and π -bound adducts, consistent with experimental observations favoring such an I-bound form. To access the Ph-I activation, **6** must first isomerize (via **5**) to π -bound **Int2** (+23.8 kcal mol⁻¹); **TS(5-Int2)**, the TS for PhI binding, lies at +27.8 kcal mol⁻¹. **Int2** features an asymmetrically bound arene (Ru-C_{ipso} = 2.25 Å, Ru-C_{ortho} = 2.47 Å), and an elongated C-I bond (2.34 Å cf. 2.14 Å in free PhI). C-I bond cleavage can therefore readily occur, via **TS(Int2-Int3)** at +25.6 kcal mol⁻¹. This nucleophilic displacement of I⁻ by the Ru center leads to **Int3** (+15.5 kcal mol⁻¹), a cationic Ru-Ph species that also features an η^2 -H₂ ligand (H-H 0.93 Å) formed via the reductive coupling of the two hydrides. The displaced I⁻ in **Int3** is loosely associated with the H₂ ligand (H...I = 2.70 Å), but moving the anion *trans* to the Ph ligand gives a more stable species, **Int4** (+0.4 kcal mol⁻¹). Facile hydrogenolysis of the Ru-Ph bond then occurs via **TS(Int4-2-I)** at +10.4 kcal mol⁻¹. The overall rate-limiting TS for the first Ph-I activation is **TS(5-Int2)** at +27.8 kcal mol⁻¹.^[17]

Once formed, **2-I** can effect the second Ph-I activation (Scheme 4, right, where the energy of **2-I** is reset to 0.0 kcal mol⁻¹). This process again shows an inverse dependence on [PPh₃], consistent with initial PPh₃/PhI exchange to form **Int5** (+21.8 kcal mol⁻¹) as an I-bound adduct. **Int5** isomerizes to **Int6** (+26.1 kcal mol⁻¹) in which the major interaction is with the *ipso* carbon (Ru-C_{ipso} 2.12 Å) and significant C-I bond lengthening is again seen (2.29 Å). **Int6** undergoes facile three-centered oxidative addition via **TS(Int6-Int7)** at +27.4 kcal mol⁻¹ and forms **Int7** (+18.2 kcal mol⁻¹), which has an unusually short C_{ipso}...H non-bonded contact of 2.01 Å. **Int7** could therefore be viewed as an



Scheme 4. Reaction pathways [BP86-D3(benzene), kcal mol⁻¹] for Ph-I activation at **3** and **2-I**, respectively. P = PPh₃, selected distances in Å. For the first Ph-I activation (left), free energies are quoted relative to **3** + free PhI set to 0.0 kcal mol⁻¹; for the second Ph-I activation (right), **2-I** + free PhI are then reset to 0.0 kcal mol⁻¹. Boxed data indicate the free-energy changes associated with the reactions of **8**. [a] Reductive elimination involves an intermediate C,H-bound C₆H₆ σ-complex.^[11]

“elongated benzene σ-complex”, with a square-pyramidal Ru, an axial PPh₃ ligand, and “C₆H₆” occupying a basal position *trans* to I⁻. Facile Ph–H reductive elimination then forms [(Ph₃P)₂RuI₂], **8**, plus free benzene at –27.8 kcal mol⁻¹.

The overall computed barriers for C–I activation at **3** (27.8 kcal mol⁻¹) and **2-I** (27.4 kcal mol⁻¹) are in good agreement with experiment (26.6 and 26.9 kcal mol⁻¹ respectively) and reiterate the similar barriers for these two processes (that is, $k_1 \approx k_2$; Scheme 3). In both cases the energy surface around PhI association to form a π-bound adduct and the subsequent C–I activation is very flat; for **3** the highest point is for association (TS(5–Int2)), whereas for **2-I** it corresponds to C–I cleavage (TS(Int6–Int7)). The nature of the C–I bond cleavage also differs in the two systems: nucleophilic (S_N-type) displacement of I⁻ by Ru in TS(Int2–Int3) and a more conventional concerted oxidative addition in TS(Int6–Int7). The greater steric bulk around Ru in TS(Int2–Int3) explains why I⁻ is initially expelled from the inner coordination sphere, whereas the Ru center in TS(Int6–Int7) (with only two PPh₃ ligands) permits the formation of new Ru–Ph and Ru–I bonds. Nonetheless, both C–I activations are formally oxidative additions with transfer of two electrons from Ru^{II} to the π-bound PhI. The implied oxidation to Ru^{IV} is mitigated by either the simultaneous reductive coupling of two hydrides (in Int3, first C–I activation) or the unusually short Ph···H non-bonding contact (in Int7, second C–I activation).

The comproportionation mechanism likely involves facile PPh₃ dissociation^[10] from 18-electron **3** to form **5**. H/I exchange with [(Ph₃P)₂RuI₂], **8**, produced in the second C–I activation (Scheme 3), could then occur, most likely via an I-

and H-bridged intermediate, [(Ph₃P)₃Ru(H)(μ-H)(μ-I)(I)Ru(PPh₃)₂], which then collapses in the presence of PPh₃ to two molecules of **2-I**. Whereas the BP86-D3(benzene) procedure gave good agreement between the experimental and computed barriers, this approach is less successful in describing these ligand exchange processes. For example [(Ph₃P)₃RuI₂] is predicted to form in preference to [(Ph₃P)₄Ru₂I₂(μ-I)₂], **7** (boxed data in Scheme 4) and the experimental K_{eq} for Ph₃P/PhI exchange in **3** to give **6** is overestimated ($\Delta G_{calc} = +10.1$ kcal mol⁻¹ cf. $+3.8 \pm 0.1$ kcal mol⁻¹ from experiment). Extensive functional testing^[11] indicates that the M06 functional performs well for such processes, but then this approach fails to capture the similar barriers for two C–I activation processes. This complementarity of different DFT approaches will be addressed in a future report.

Experimentally, both PhBr and PhCl in excess also react with **3** at 50–55 °C to give first **2-Br** and **2-Cl** in more than 95 % and about 70 % yield, respectively. While the onward reaction of PhBr leads cleanly to stable [(Ph₃P)₃RuBr₂] in equilibrium with small quantities of the dimer [(Ph₃P)₄Ru₂Br₂(μ-Br)₂], that of PhCl is less selective. Details of these studies will be reported separately.

In conclusion, it has been found, for the first time, that Ru^{II} complexes devoid of electron-rich bulky phosphines can efficiently cleave the Ph–X (X = Cl, Br, I) bond under exceedingly mild conditions. The mechanism of this unusual Ph–X bond activation at Ru has been elucidated. In the reaction of [(Ph₃P)₄Ru(H)₂] with PhI (or PhBr), a well-masked autocatalysis is involved, which has been recognized, thoroughly studied by experimental and computational

means, and understood in considerable detail. Novel results of the current study contribute to basic knowledge for further progress in the area of inert bond activation, catalysis, and reaction mechanisms.

Keywords: Ar-X activation · autocatalysis · DFT calculations · kinetics · ruthenium

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