Supporting Information

**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*

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I. General Information

All manipulations were performed under argon in a glovebox or using Schlenk techniques, unless noted otherwise. RuCl₃·xH₂O, PPh₃, and NaBH₄ were used as received. Anhydrous, oxygen-free hexane, benzene, benzene-d₆, toluene-d₈, THF, and THF-d₈ were obtained by distillation from Na/OCPh₂ under argon and stored over freshly activated 4 Å molecular sieves in an argon-filled glovebox. Ruthenium complexes [(Ph₃P)₃Ru(H₂)(H)] (1), [(Ph₃P)₄Ru(H)₂·0.5PPh₃·1.25C₆H₆ (3), [(Ph₃P)₃Ru(N₂)(H)] (4), and [(Ph₃P)₃RuCl₂]² were prepared by the literature procedures. For kinetic studies, 3 was additionally washed with hexanes and then with ether in the glovebox and dried under vacuum. The resultant complex had the composition [(Ph₃P)₄Ru(H)₂·0.5PPh₃·0.5hexane (NMR). NMR spectra were recorded on Bruker Avance Ultrashield 400 and 500 MHz spectrometers. Single-crystal X-ray diffraction studies were performed on Bruker FR591 and Apex DUO Kappa 4-axis diffractometers equipped with APEX II 4K CCD area detectors. An Agilent Technologies 7890A-5975C instrument was used for GC-MS analysis. Elemental analyses were performed by the Microanalysis Center at the Complutense University of Madrid.

As has been recently demonstrated,¹ complexes 1, 2, and 3 easily form solvates, and 3 can also contain lattice PPh₃. The composition of these materials may vary significantly depending on minor changes in crystallization conditions. It is therefore recommended that each batch of the complexes obtained be carefully analyzed by ′H and ³¹P NMR to determine the amount of cocrystallized solvents and/or PPh₃.

All experiments with air-sensitive Ru complexes were conducted in an argon rather than nitrogen atmosphere. Under N₂, solutions of both 1 and 3 gave rise to [(Ph₃P)₃Ru(N₂)(H)] (4) in various quantities, as can be easily detected by ′H and ³¹P NMR.¹ Even under argon containing adventitious N₂, solutions of 1 and 3 produced small yet NMR-detectable
quantities of 4 after a few hours. Contamination of the argon atmosphere with N₂ in a circulation glove-box can represent a serious problem when working with 1 and 3.

II. Ph-X Activation with 1/Styrene

A. Styrene (3.9 μL; 0.034 mmol) was added to a stirring mixture of [(Ph₃P)₃Ru(H₂)(H)] (1) (30 mg; 0.034 mmol), PhX (X = I, Br, or Cl; 0.034 mmol), and toluene (1 mL). The reaction mixture instantly turned dark and a deep purple precipitate was produced. After 10 min of agitation, hexane was added to complete precipitation of the resultant halo hydride, which was separated by filtration, washed with hexane (3 × 5 mL), and dried under vacuum. Analysis of the mother liquor by GC-MS indicated the formation of benzene. The yield of purple [(Ph₃P)₃RuH(X)] was 30 mg (88%), 29 mg (89%), and 22 mg (71%) for X = I (2-I), X = Br (2-Br), and X = Cl (2-Cl), respectively.

B. Styrene (2.9 μL; 0.025 mmol) was added to a stirring mixture of [(Ph₃P)₃Ru(H₂)(H)] (1) (22 mg; 0.025 mmol) and neat PhCl (1 mL) or PhX (X = I; 0.075 mmol or Br; 0.25 mmol) in toluene (1 mL). The reaction mixture instantly turned dark and a deep purple precipitate was produced. After 10 min of agitation, hexane was added to complete precipitation of the resultant halo hydride, which was separated by filtration, washed with hexane (3 × 5 mL), and dried under vacuum. The yield of purple [(Ph₃P)₃RuH(X)] was 22.5 mg (90%), 22 mg (92%), and 18 mg (79%) for X = I (2-I), X = Br (2-Br), and X = Cl (2-Cl), respectively.

2-I: ¹H NMR (CD₂Cl₂, 25°C), δ: -15.29 (q, J₃-P = 25.1 Hz, 1H, Ru-H), 6.99 (t, J₃-H = 7.7 Hz, 18H), 7.16-7.25 (m, 27H). ³¹P{¹H} NMR (CD₂Cl₂, 25°C), δ: 56.7 (br s).
2-Br: $^1$H NMR (CD$_2$Cl$_2$, 25°C), $\delta$: -17.16 (q, $J_{H-P} = 25.6$ Hz, 1H, Ru-H), 6.99 (t, $J_{H-H} = 7.6$ Hz, 18H), 7.16-7.25 (m, 27H). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 25°C), $\delta$: 56.9 (br s).

2-Cl: $^1$H NMR (CD$_2$Cl$_2$, 25°C), $\delta$: -18.23 (q, $J_{H-P} = 26.0$ Hz, 1H, Ru-H), 6.99 (t, $J_{H-H} = 7.6$ Hz, 18H), 7.16-7.25 (m, 27H). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 25°C), $\delta$: 57.0 (br s).

III. Preparation of 2-I for Kinetic Studies and [(Ph$_3$P)$_4$Ru$_2$I$_2$(μ-I)$_2$] (7)

[(Ph$_3$P)$_3$Ru(H)I] (2-I). In a glove-box, a solution of styrene (72 μL; 0.63 mmol) in THF (5 mL) was slowly added (5 min) via syringe to a stirring solution of [(Ph$_3$P)$_2$Ru(H$_2$)(H)$_2$] (1; 446 mg; 0.50 mmol) and PhI (70 μL; 0.63 mmol) in THF (50 mL). After 10 min, the deep purple reaction mixture was placed into a freezer at -30 °C for 1 day to complete precipitation of 2-I. The mixture was then reduced in volume to ca. 25 mL by evaporation with a flow of argon, the deep purple crystals of 2-I were separated, washed with Et$_2$O (3 × 5 mL), and dried under vacuum. A 100-mg portion of the thus obtained crude 2-I (430 mg) was dissolved in benzene at room temperature (30 mL) and filtered. Evaporation of the filtrate and drying under vacuum gave pure 2-I·3C$_6$H$_6$ in 69% yield (100 mg).

[(Ph$_3$P)$_4$Ru$_2$I$_2$(μ-I)$_2$] (7). In a glovebox, a 20-mL vial was charged with [(Ph$_3$P)$_3$Ru(H)$_2$]-0.5PPh$_3$-0.5hexane (3, 126 mg, 0.095 mmol), PhI (1 mL), and benzene (5 mL). The mixture was agitated first at 40 °C for 17 h, and then at 60 °C for 5 h. At that point, full conversion of 3 and intermediate 2-I was observed by $^1$H{$^{31}$P} NMR. The resultant dark brown solid was separated inside the glovebox, washed with benzene (3 × 2 mL), and dried under vacuum. The yield of 7 was 84 mg (100%). This solid appeared to be virtually insoluble in benzene, toluene, THF, dichloromethane, and DMF. It was found,
however, that 7 dissolves in DMSO to give a yellow solution that displayed only one signal in the $^{31}$P NMR spectrum, a singlet at -5.5 ppm, evidently from free PPh$_3$. Quantitative analysis in the presence of an internal standard (Ph$_3$PO) indicated that ca. 2 equiv. of PPh$_3$ had been released from each Ru atom. Anal. Calcd. for C$_{72}$H$_{60}$I$_4$P$_4$Ru$_2$: C, 49.2; H, 3.4. Found: C, 49.5; H, 3.5. To obtain X-ray quality crystals of 7, a solution of [(Ph$_3$P)$_3$RuCl$_2$] (50 mg) in deaerated C$_6$H$_6$ (10 mL) was treated, under argon, with a solution of NaI (2.0 g) in deaerated deionized water (5 mL). After 40 h, the organic phase was separated and layered with pentane to give X-ray quality crystals of 7.

IV. VT NMR Study of 3 in the presence of PhI (observation of 6)

A solution of 3 (ca. 7 mg; 0.006 mmol) and PhI (50 μL; 0.45 mmol) in THF-$d_8$ (0.6 mL) was placed in a 5-mm NMR tube, sealed with a rubber septum, and the sample was studied by VT $^1$H and $^{31}$P NMR. The spectra showing the formation of [(Ph$_3$P)$_3$Ru(H)$_2$(PhI)] (6) are presented in Figures S1 and S2.
Figure S1. VT $^1$H NMR spectra displaying the formation of 6 from 3 and PhI.
Figure S2. VT $^{31}$P{$^1$H} NMR spectra displaying the formation of 6 from 3 and PhI.
V. Kinetic Studies

**Determination of reaction orders for PhI activation with [(Ph₃P)₄Ru(H)]₂ (3).** In an argon-filled glovebox, iodobenzene was added to a solution of [(Ph₃P)₄Ru(H)]₂ (3) and PPh₃ in C₆D₆ in a 5-mm NMR tube. The reaction mixture was shaken, sealed with a rubber septum, and monitored to 5-15% conversion by ¹H{³¹P} NMR at 23 °C. See Table S1 for specifics. The data was analyzed in the assumption of the sum of concentrations of [(Ph₃P)₄Ru(H)]₂ and [(Ph₃P)₃Ru(H)I] in the presence of excess PPh₃ being constant and equal to the initial concentration of [(Ph₃P)₄Ru(H)]₂. For entries 8-11, additional correction of the initial concentrations of PPh₃ and the Ru complexes was made, taking into account the equilibrium between 3 and [(Ph₃P)₃Ru(H)₂(PhI)] (6). In all other runs, this correction was unnecessary because the amount of 6 present was estimated at <4% of the initial concentration of 3. The plots obtained are presented in Figures S3, S4, and S5.
Table S1. Determination of reaction orders for the reaction of [(Ph₃P)₄Ru(H)₂] with PhI by the method of initial rates.

| Entry | [(Ph₃P)₄Ru(H)₂]₀, M × 10⁻³ | [PhI]₀, M | [PPh₃]₀, M × 10⁻² | Initial rate, M/min × 10⁻⁷ | Amount of 6, (%) |
|-------|-------------------------|--------|------------------|-----------------|-----------------|
| 1     | 8.33                    | 1.49   | 8.33             | 9.11            | 3               |
| 2     | 6.67                    | 1.49   | 8.33             | 8.24            | 3               |
| 3     | 5.00                    | 1.49   | 8.33             | 6.15            | 3               |
| 4     | 3.33                    | 1.49   | 8.33             | 3.46            | 3               |
| 5     | 8.33                    | 1.12   | 8.33             | 7.55            | 2               |
| 6     | 8.33                    | 0.75   | 8.33             | 5.15            | 2               |
| 7     | 8.33                    | 0.37   | 8.33             | 2.15            | 1               |
| 8     | 8.33                    | 1.49   | 2.50             | 43.8            | 10              |
| 9     | 8.33                    | 1.49   | 3.17             | 32.5            | 8               |
| 10    | 8.33                    | 1.49   | 4.17             | 22.6            | 6               |
| 11    | 8.33                    | 1.49   | 5.83             | 13.6            | 4               |
| 12    | 8.33                    | 1.49   | 8.33             | 10.3            | 3               |
| 13    | 8.33                    | 1.49   | 10.0             | 9.65            | 3               |
| 14    | 8.33                    | 1.49   | 11.7             | 8.15            | 2               |
| 15    | 8.33                    | 1.49   | 13.3             | 4.90            | 2               |
| 16    | 8.33                    | 1.49   | 15.0             | 4.18            | 2               |
| 17    | 8.33                    | 1.49   | 16.7             | 3.85            | 2               |
**Figure S3.** Dependence of the initial rate on the initial concentration of $[(\text{Ph}_3\text{P})_4\text{Ru(H)}_2]$ in the reaction with PhI (1.49 M) in the presence of excess of PPh$_3$ (0.0833 M) at 23 °C.

**Figure S4.** Dependence of the initial rate on the initial concentration of PhI in the reaction with $[(\text{Ph}_3\text{P})_4\text{Ru(H)}_2]$ (0.00833 M) in the presence of excess of PPh$_3$ (0.0833M) at 23 °C.
Figure S5. Dependence of the initial rate on the initial concentration of PPh₃ (top) and on $1/\text{[PPh}_3\text{]}_{\text{init}}$ (bottom) in the reaction of [(Ph₃P)₄Ru(H)₂] (0.00833 M) with PhI (1.49M) at 23 °C.
**Determination of reaction orders for activation of PhI with [(Ph₃P)₃Ru(H)I] (2-I).**

In an argon-filled glovebox, PhI was added to a solution of [(Ph₃P)₃Ru(H)I]-3C₆H₆ (2-I), PPh₃, and cyclohexane (internal standard) in C₆D₆ in 5-mm NMR tube. The reaction mixture was shaken, sealed with a rubber septum, and monitored to 10-20% conversion by "H{³¹P} NMR at 23 ºC. See Table S2 for specifics. The plots are presented in Figures S6, S7, and S8.

**Table S2.** Determination of reaction orders for the reaction of [(Ph₃P)₃Ru(H)I] with PhI by the method of initial rates.

| Entry | [(Ph₃P)₃Ru(H)I]₀, M × 10³ | [PhI]₀, M | [PPh₃]₀, M × 10² | Initial rate, M/min × 10⁷ |
|-------|--------------------------|----------|------------------|-------------------------|
| 1     | 2.08                     | 1.49     | 0.63             | 15.9                    |
| 2     | 2.08                     | 1.49     | 1.33             | 8.27                    |
| 3     | 2.08                     | 1.49     | 2.40             | 4.85                    |
| 4     | 2.08                     | 1.49     | 4.17             | 3.07                    |
| 5     | 2.08                     | 1.49     | 0.98             | 11.3                    |
| 6     | 2.08                     | 1.49     | 1.69             | 6.86                    |
| 7     | 2.08                     | 1.12     | 0.63             | 13.3                    |
| 8     | 2.08                     | 0.75     | 0.63             | 7.49                    |
| 9     | 2.08                     | 0.37     | 0.63             | 3.51                    |
| 10    | 1.67                     | 1.49     | 0.63             | 14.3                    |
| 11    | 1.25                     | 1.49     | 0.63             | 8.90                    |
| 12    | 0.83                     | 1.49     | 0.63             | 8.52                    |
Figure S6. Dependence of the initial rate on the initial concentration of [(Ph₃P)₃Ru(H)] in the reaction with PhI (1.49 M) in the presence of PPh₃ (0.00625 M) at 23 °C.

Figure S7. Dependence of the initial rate on the initial concentration of PhI in the reaction with [(Ph₃P)₃Ru(H)] (0.00208 M) in the presence of PPh₃ (0.00625 M) at 23 °C.
Figure S8. Dependence of the initial rate on the initial concentration of PPh\(_3\) (top) and on 1/[PPh\(_3\)]\(_{\text{init}}\) (bottom) in the reaction of [(Ph\(_3\)P)\(_3\)Ru(H)(I)] (0.00208 M) with PhI (1.49 M) at 23 °C.
**Full kinetic profile of the reaction of [(Ph₃P)₄Ru(H)₂] with PhI.** In an argon-filled glovebox, [(Ph₃P)₄Ru(H)₂]-0.5PPh₃-0.5hexane (3; 13 mg; 0.01 mmol) was dissolved in C₆D₆ (2.0 mL). A 500-μL aliquot of the thus prepared solution, PhI (100 μL), and a flame-sealed capillary containing an external standard (dppf in CDCl₃) were placed in a 5-mm NMR tube. The tube was sealed with a rubber septum and the reaction was monitored by $^1$H{$^{31}$P} and $^{31}$P{$^1$H} IGD NMR at 25 °C. The data obtained were manually fitted to the model (Scheme S1) using the KINET³ and Tenua⁴ programs (See Table S3 for details and Figure S9).

**Scheme S1.**

\[
\begin{align*}
([\text{Ph}_3\text{P}]_4\text{Ru}(\text{H})_2) + \text{PhI} & \quad \overset{k_1}{\underset{k_1}{\rightleftharpoons}} ([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})_2) + \text{PPh}_3 & \\
& \quad [([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})_2) + \text{PhI}] \\
([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})_2\text{PhI}) & \quad \overset{k_2}{\rightarrow} ([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})) + \text{PhH} & \\
& \quad [([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})) + \text{PhI}] \\
([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})\text{PhI}) + \text{PhI} & \quad \overset{k_3}{\underset{k_3}{\rightleftharpoons}} ([\text{Ph}_3\text{P}]_2\text{Ru}(\text{I})(\text{PhI})) + \text{PPh}_3 & \\
& \quad [([\text{Ph}_3\text{P}]_2\text{Ru}(\text{I})(\text{PhI})) + \text{PPh}_3] \\
([\text{Ph}_3\text{P}]_2\text{Ru}(\text{I})(\text{PhI})) & \quad \overset{k_4}{\rightarrow} ([\text{Ph}_3\text{P}]_2\text{Ru}) + \text{PhH} & \\
& \quad [([\text{Ph}_3\text{P}]_2\text{Ru}) + \text{PhH}] \\
([\text{Ph}_3\text{P}]_2\text{Ru}) + \text{PPh}_3 & \quad \overset{k_5}{\rightarrow} ([\text{Ph}_3\text{P}]_3\text{Ru}) & \\
& \quad [([\text{Ph}_3\text{P}]_3\text{Ru}) + \text{PhH}] \\
([\text{Ph}_3\text{P}]_3\text{Ru}) + ([\text{Ph}_3\text{P}]_4\text{Ru}(\text{H})_2) & \quad \overset{k_6}{\rightarrow} 2([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})) + \text{PPh}_3 & \\
& \quad [2([\text{Ph}_3\text{P}]_3\text{Ru}(\text{H})) + \text{PPh}_3] \\
2([\text{Ph}_3\text{P}]_3\text{Ru}) & \quad \overset{k_7}{\underset{k_7}{\rightleftharpoons}} ([\text{Ph}_3\text{P}]_4\text{Ru}(\text{I})(\text{I})_2) + 2\text{PPh}_3 & \\
& \quad [([\text{Ph}_3\text{P}]_4\text{Ru}(\text{I})(\text{I})_2) + 2\text{PPh}_3]
\end{align*}
\]
Table S3. Parameters used in the simulation of the kinetic model presented in Scheme S1.

| Compound | Initial concentration, M |
|----------|--------------------------|
| A        | 4.2 × 10⁻³               |
| B        | 1.49                     |
| C        | 1 × 10⁻⁵                 |
| D        | 0                        |
| E        | 0                        |
| F        | 0                        |
| G        | 0                        |
| H        | 0                        |
| P        | 1 × 10⁻³                 |

| Rate constant | Value | Significant k and ΔG values |
|---------------|-------|----------------------------|
| κ₁            | 1.9 × 10² | $K_{eq}(1) = \frac{\kappa_1}{\kappa_{-1}} = 1.9 \times 10^3$ |
| κ₁⁻¹         | 1 × 10⁵  | ΔG = 3.7 kcal/mol           |
| κ₂            | 6.5 × 10⁻³| $k_1 = \kappa_2 \cdot \kappa_1 / \kappa_{-1} = 1.24 \times 10^5 \text{ min}^{-1}$ |
| κ₃            | 1 × 10²  | ΔG = 26.6 kcal/mol          |
| κ₄            | 6.8 × 10⁻¹| $k_2 = \kappa_4 \cdot \kappa_3 / \kappa_{-3} = 6.8 \times 10^6 \text{ min}^{-1}$ |
| κ₅            | 1 × 10³  | ΔG = 26.9 kcal/mol          |
| κ₆            | 5 × 10⁴  |                           |
| κ₇            | 1 × 10⁵  |                           |
| κ₋₇          | 1        |                           |

Figure S9. Plot of concentrations versus time for the reaction of [(Ph₃P)₄Ru(H)₂] (0.0042 M initial concentration) with PhI (1.49 M) at 25 °C monitored by $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Data points are from the experimental measurements. The curves are from the kinetic model.
VI. Comproportionation Reaction

Reaction of [(Ph₃P)₄Ru(H)₂] (3) with [(Ph₃P)₃RuCl₂] and NaI. In an argon-filled glove-box, a solution of [(Ph₃P)₄Ru(H)₂]-0.5PPh₃·0.5hexane in THF-δ₈ (0.005 M; 0.5 mL) and a solution of [(Ph₃P)₃RuCl₂] in THF-δ₈ (0.005 M; 0.5 mL) were added to NaI (40 mg; 0.27 mmol). Vigorous agitation of the reaction mixture at room temperature for 15 minutes produced a purple solution containing 2-I (ca. 70% yield; ¹H{³¹P} NMR: s, -15.15 ppm). In a separate experiment, it was shown that pregenerated 7 reacts with 3 only slowly, evidently because this reaction requires the formation of 8 via cleavage of the Ru-I bridge.

VII. General Equation for 2nd Order / 2nd Order Pre-equilibrium with Subsequent First Order Reaction

\[ A + B \xrightarrow{K_{eq}} C + D \]
\[ C \xrightarrow{k} E \]

Considering B is present in excess ([B] >> [A] + [C]),

\[ [A] + [C] = [A+C] \]
\[ K_{eq} = [C][D]/[A][B] \]
\[ [C] = [A+C] - [C][D]/K_{eq}[B] \]
\[ [C] + K_{eq}[B][C]/[D] = K_{eq}[A+C][B]/[D] \]
\[ [C] = K_{eq} \frac{[A+C][B]}{[D] \left(1 + K_{eq} \frac{[B]}{[D]}\right)} \]

\[ \frac{d[E]}{dt} = - \frac{d[A]}{dt} - \frac{d[C]}{dt} = k[C] \]
\[
\frac{d[E]}{dt} = k_{eq} \frac{[A + C][B]}{[D]\left(1 + K_{eq}\frac{[B]}{[D]}\right)} \quad (S1)
\]

If the pre-equilibrium is shifted to the right \(K_{eq}[B]/[D] \gg 1\), eq S1 can be simplified to:

\[
\frac{d[E]}{dt} = k[C] \quad (S2)
\]

If the pre-equilibrium is shifted to the left \(K_{eq}[B]/[D] \ll 1\) eq S1 can be simplified to:

\[
\frac{d[E]}{dt} = k_{eq} \frac{[A][B]}{[D]} \quad (S3)
\]

The values of \(k \times K_{eq}\) are \(k_1\) and \(k_2\) in the main text.

The value of \(k_1 = 1.24 \times 10^{-5} \text{ min}^{-1}\) is applied when the equilibrium between 3 and 6 is largely shifted toward 3. When the quantity of 6 is significant, the observable \(k_1\) value \(k_1'\) depends on the position of the equilibrium.

The value of \(k_1'\) for the kinetic experiment with PhI was derived from equation S1:

\[
k_1' = k_{eq} \frac{1}{\left(1 + K_{eq}\frac{[B]}{[D]}\right)} \quad (S4)
\]

Considering \([B] = [\text{PhI}] = 1.49 \text{ M}, [D] = [\text{PPh}_3] = 0.005 \pm 0.001 \text{ M}, k = k_2 = 6.5 \times 10^{-3}\), and \(K_{eq}(1) = 1.9 \times 10^{-3}\) (Figure S9, Table S3) gives \(k_1' = 7.8 \pm 0.6 \times 10^{-6} \text{ min}^{-1}\), even closer to the \(k_2 (6.8 \times 10^{-6} \text{ min}^{-1})\) than \(k_1\).
VIII. Derivation of Equation 4

**Scheme S2.** Mechanism of the autocatalysis in the formation of 2-I from 3 and PhI.

For the autocatalysis scheme above (Scheme S2),

\[
\frac{d[2-I]}{dt} = k_1[3][\text{PhI}][\text{PPh}_3]^{-1} - k_2[2-I][\text{PhI}][\text{PPh}_3]^{-1} + 2k_3[3][8]
\]

and

\[
\frac{d[8]}{dt} = k_2[2-I][\text{PhI}][\text{PPh}_3]^{-1} - k_3[3][8]
\]

Steady state approximation (\(\frac{d[8]}{dt} = 0\)) gives:

\[
\frac{d[2-I]}{dt} = k_1[3][\text{PhI}][\text{PPh}_3]^{-1} - k_2[2-I][\text{PhI}][\text{PPh}_3]^{-1} + 2k_2[2-I][\text{PhI}][\text{PPh}_3]^{-1}
\]

or

\[
\frac{d[2-I]}{dt} = k_1[3][\text{PhI}][\text{PPh}_3]^{-1} + k_2[2-I][\text{PhI}][\text{PPh}_3]^{-1}
\]

This is eq 4 in the main text.
IX. Computational Details

All calculations were run with Gaussian 03 Revision D.01\textsuperscript{5} with PCM solvent corrections run with Gaussian 09, Revision D.01.\textsuperscript{6} Geometry optimizations used the BP86 functional\textsuperscript{7,8} with Stuttgart relativistic ECPs and associated basis sets\textsuperscript{9} on Ru, P and I with additional polarization on P ($\zeta = 0.387$) and I ($\zeta = 0.289$)\textsuperscript{10} and 6-31G** all-electron basis sets\textsuperscript{11} on all other atoms (BS1). All stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. In one case the corrected free energy of the transition state (TS(7-8)) is actually slightly below that of the preceding intermediate (Int7) and this is due to the inclusion of zero-point energy corrections that have a greater effect on the minimum structure and so push it above the close-lying transition state.

The effects upon computed energies were assessed by adopting a selection of DFT methods, encompassing key developments in exchange-correlation functionals and dispersion correction schemes, on the BP86/BS1 optimized geometries with the same ECP/all-electron basis sets. These include: pure GGA functionals (BP86,\textsuperscript{7,8} BLYP,\textsuperscript{8,12} PBE\textsuperscript{13}); hybrid-GGA functionals (B3LYP,\textsuperscript{12,14} PBE0\textsuperscript{13,15}); pure and hybrid Minnesota functionals (M06\textsubscript{L},\textsuperscript{16} M06,\textsuperscript{17} M062X\textsuperscript{17}) which capture dispersion interactions through parameterization; pure and long range-corrected functionals adopting Grimme’s D2 dispersion correction (B97D,\textsuperscript{18} oB97XD\textsuperscript{19}); the addition of Grimme’s D3 dispersion corrections\textsuperscript{20} to pure and hybrid functionals (to give BP83-D3, B3LYP-D3, PBE-D3, PBE0-D3, B97D3) and the effect of Becke-Johnson damping,\textsuperscript{21} giving BP86-D3BJ. The effect of increasing basis set size was tested with the BP86 method (see Tables S4 and S5 below for details).
X. Alternative Mechanisms for 1st IPh Activation.

Two alternative C-I bond activation processes were characterized from 6 (Scheme S3). The first is a concerted oxidative addition via TS(6–Int1) at +31.3 kcal/mol and features elongation of the C-I bond with concomitant Ru-Ph and Ru-I bond formation. As this occurs a reductive coupling of the two hydride ligands is also seen and the species formed, Int1 (G = +1.4 kcal/mol), exhibits an elongated $\eta^2$-H$_2$ ligand (H···H = 1.34 Å) trans to iodide. Int1 can then readily undergo reductive elimination to form benzene and 2-I as products (G = -23.7 kcal/mol). The second alternative is related to previous work on the hydrodefluorination (HDF) of fluoroaromatics at Ru-NHC complexes, which showed how nucleophilic attack by a hydride ligand can induce C-X bond cleavage. A similar process was characterized here, where H-transfer onto the arene ring caused a concerted displacement of iodide directly onto the Ru via TS(6–2-I) at +32.0 kcal/mol. Both pathways in Scheme S4 entail barriers above 31 kcal/mol and so are significantly higher than both the formal oxidative addition barrier of 27.8 kcal/mol (see main text) and the value of 26.6 kcal/mol derived from experiment.

Scheme S3. Reaction pathway (BP86-D3(benzene), kcal/mol) for Ph-I activation at iodobenzene adduct 6 (P = PPh$_3$). All free energies are quoted relative to 3 + free PhI set to 0.0 kcal/mol; selected distances in Å and angles in degrees.
**XI. DFT Functional Testing**

**Table S4.** DFT functional dependency of PPh₃/IPh exchange and Ph-I activation.

| DFT Functional | PPh₃/IPh Exchange G(6)ᵃ | 1ˢᵗ Ph-I Activation G(TS(6-IPh-Int2))ᵇ | 2ⁿᵈ Ph-I Activation G(TS(Int6-Int7))ᵇ | Experiment |
|----------------|-------------------------|----------------------------------------|----------------------------------------|------------|
| BP86           | -10.1                   | +17.9                                  | +14.1                                  | +15.8      |
| BP86/BS2⁺      | -11.7                   | +19.0                                  | +17.8                                  | +16.3      |
| BLYP           | -13.3                   | +15.3                                  | +9.9                                   | +17.1      |
| B3LYP          | -11.8                   | +18.2                                  | +17.0                                  | +22.4      |
| PBE            | -6.2                    | +20.9                                  | +17.6                                  | +17.0      |
| PBE0           | -6.8                    | +22.8                                  | +24.1                                  | +22.6      |
| TPSS           | -9.7                    | +17.9                                  | +14.4                                  | +14.5      |
| M06            | +4.1                    | +26.5                                  | +28.3                                  | +23.8      |
| M06L           | +1.2                    | +21.4                                  | +19.8                                  | +21.4      |
| M062X          | 0.0                     | +22.3                                  | +30.6                                  | +30.8      |
| B97D           | +5.6                    | +22.6                                  | +19.0                                  | +25.6      |
| oB97xD         | +7.1                    | +30.1                                  | +34.1                                  | +33.4      |
| B97D3          | +10.8                   | +29.7                                  | +26.1                                  | +33.5      |
| BP86-D3        | +10.1                   | +27.8                                  | +25.6                                  | +27.3      |
| BP86-D3/BS2⁺   | +8.5                    | +28.9                                  | +29.3                                  | +27.8      |
| BP86-D3BJ      | +11.2                   | +30.4                                  | +28.1                                  | +30.6      |
| B3LYP-D3       | +5.5                    | +26.7                                  | +27.0                                  | +32.5      |
| PBE-D3         | +7.1                    | +28.9                                  | +26.1                                  | +24.4      |
| PBE0-D3        | +5.9                    | +29.9                                  | +32.0                                  | +30.0      |
| TPSS-D3        | +6.9                    | +26.9                                  | +24.3                                  | +23.8      |
| Experiment     | +3.8 ± 0.1              | +26.6                                  | +26.9                                  |            |

ᵃ Free energies, corrected for solvent (PCM, benzene) in kcal/mol with 3 + free IPh set to zero.
ᵇ As a with 2-I + free IPh set to zero.
ᶜ BS2: cc-PVTZ-PP pseudopotentials and associated basis sets on Ru and I and 6-311++G** basis sets on all other atoms.
**Table S5.** DFT functional dependency of comproportionation, phosphine addition and dimerization reactions of 8.

| DFT Functional | $\Delta G_f(2\text{-}I)^a$ | $\Delta G_f([\text{Ph}_3\text{P})_3\text{RuI}_2])^b$ | $\Delta G_f(7)^c$ |
|----------------|--------------------------|---------------------------------|-----------------|
| BP86          | -21.5                    | +16.1                           | +4.8            |
| BP86/BS2$^d$  | -20.6                    | +19.3                           | +5.5            |
| M06           | -17.8                    | -7.6                            | -9.2            |
| M06L          | -20.2                    | -6.7                            | -9.0            |
| M062X         | -24.2                    | -4.1                            | -7.1            |
| B97D          | -19.9                    | -9.1                            | -7.3            |
| oB97xD        | -20.0                    | -11.3                           | -10.4           |
| B97D3         | -23.0                    | -16.7                           | -12.9           |
| BP86-D3       | -19.6                    | -21.2                           | -16.6           |
| BP86-D3/BS2$^d$ | -18.7               | -18.0                           | -15.9           |
| BP86-D3BJ     | -23.6                    | -28.8                           | -23.1           |
| B3LYP-D3      | -23.1                    | -12.2                           | -11.2           |
| PBE-D3        | -17.5                    | -11.5                           | -11.9           |
| PBE0-D3       | -20.2                    | -13.4                           | -13.2           |
| TPSS-D3       | -18.7                    | -15.8                           | -14.9           |

$^a$ Free energy change for $\text{8} + \text{3} \rightarrow \text{2-}2\text{-I}$, corrected for solvent (PCM, benzene) in kcal/mol.

$^b$ Free energy change for $\text{8} + \text{PPh}_3 \rightarrow [(\text{Ph}_3\text{P})_3\text{RuI}_2]$, corrected for solvent (PCM, benzene) in kcal/mol.

$^c$ Free energy change for $\text{8} \rightarrow \frac{1}{2} \text{7}$, corrected for solvent (PCM, benzene) in kcal/mol.

$^d$ BS2: cc-PVTZ-PP pseudopotentials and associated basis sets on Ru and I and 6-311++G** basis sets on all other atoms.
XII. Computed Geometries

Geometries and BP86 energies (including thermal, solvation and D3 dispersion corrections) for computed species are given below. For 3D representations, H atoms are omitted from IPh and PPh₃ ligands for clarity.

Legend:

**First I-Ph Activation**

| BP86 Energy | -2902.3045307 |
| Enthalpy OK | -2901.217707 |
| Enthalpy 298K | -2901.145332 |
| Free Energy 298K | -2901.300085 |
| Lowest Frequencies | 14.6854 cm⁻¹ |
| PC(M(benzene)) Energy | -2902.31026179 |
| DFTD3 Corr. | -0.30030178 |

| C | 1.66988 | 1.95322 | 2.54995 |
| H | 1.88465 | 0.79939 | 3.32930 |
| C | 1.28670 | -0.99577 | 3.14664 |
| C | 2.86820 | 0.77299 | 4.32992 |
| H | 3.01288 | -0.14163 | 4.91374 |
| C | 3.66726 | 1.90409 | 4.56098 |
| H | 4.40452 | 1.88560 | 5.33666 |
| C | 3.46815 | 3.05967 | 3.78409 |
| H | 4.08195 | 3.95075 | 3.96150 |
| C | 2.47046 | 3.08821 | 2.79437 |
| H | 2.32523 | 4.00177 | 2.21219 |
| C | -1.13740 | 2.44774 | 2.43628 |
| H | -0.94340 | 2.82255 | 3.78363 |
| C | 0.05791 | 2.79366 | 4.22175 |
| C | -0.20248 | 3.23961 | 4.57369 |
| H | -1.85748 | 3.52485 | 5.61761 |
| C | -3.32253 | 3.29912 | 4.02937 |
| C | -4.16664 | 3.62535 | 6.4662 |
| C | -3.52454 | 2.93433 | 2.68819 |
| H | -4.52636 | 2.95981 | 2.24739 |
| C | -2.44123 | 2.50969 | 1.90473 |
| H | -2.61691 | 2.21164 | 0.86847 |
| C | 0.59548 | 3.61288 | 0.48477 |
| C | -0.02146 | 4.80539 | 0.91682 |
| H | -0.75887 | 4.78161 | 1.72354 |
| TS(6-IntI)       | BP86 Energy = | -2.4431 | 2.045967 | 2.65537 | 0.368594 | 0.14289 | 3.05356 | 0.231757 | 3.33237 | 0.301837 | 3.85023 | 2.95088 | 3.30145 | 2.43145 | 4.36017 | 3.05466 | -3.35676 | -0.85667 | 2.63683 | 3.65764 | 0.8646 | 1.32457 | 0.87456 | 2.34567 | 3.45678 | 4.56789 | 5.67890 | 6.78901 | 7.89012 | 8.90123 | 9.01234 | 10.12345 |
|------------------|----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| C -2.73138       | -4.12269      | -3.35332  | C -3.17082 | -3.78436 | -2.04443  | C -2.28493 | 3.20431  | -1.12304  | H 0.54332 | -3.17486  | -3.05092  | H -1.03770 | -4.14315 | -4.69337  | H -3.42341 | -4.57336 | -4.05461  | H -4.20953 | -3.96760  | -1.74899  | H -2.64991 | -2.39375  | -0.12623  | C -0.62011 | -4.44606  | 1.30011  | C -0.68086 | -5.21678  | 2.47322  | C -0.12815 | -4.73199  | 3.66901  | C 0.48034  | -3.46672  | 3.68542  | C 0.52590  | -2.68879  | 2.51775  | H -1.03805 | -4.84873  | 0.37326  | H -1.15438 | -6.20427  | 2.44580  | H -0.16784 | -5.33848  | 4.58042  | H 0.92570  | -3.07689  | 4.60667  | H 0.99714  | -1.70225  | 2.54457  | C 2.36659  | -4.08156  | -0.33286  | C 3.58240  | -4.59197  | -0.81608  | C 4.30262  | -3.89992  | -1.80334  | C 3.79681  | -2.69131  | -2.30707  | C 2.58356  | -2.17778  | -1.81873  | H 1.81272 | -4.63312  | 0.43793  | H 3.96764 | -5.53634  | -0.41567  | H 5.25253 | -4.29896  | -2.17518  | H 4.35034 | -2.13151  | -3.06797  | H 2.19895 | -1.23179  | -2.39924  | C 5.07459 | 0.95787  | -0.11620  | C 6.17863 | 1.02679  | -0.98025  | C 5.98688 | 1.10881  | -2.36977  | C 4.68327  | 1.11571  | -2.88794  | C 3.57880 | 1.03999  | -2.02125  | H 5.24141 | 0.89950  | 0.96350  | H 7.19201 | 1.01942  | -0.56426  | H 6.84943 | 1.16510  | -3.04247  | H 4.51796 | 1.17663  | -3.96905  | H 2.56809 | 1.01897  | -2.44125  | H 1.40408 | 3.10684  | 2.19221  | H 1.48978 | 4.36640  | 2.80542  | H 2.54942 | 5.23404  | 2.49616  | C 3.52326 | 4.82589  | 1.57351  | C 3.44872 | 3.55684  | 0.97349  | H 0.54938 | 2.45991  | 2.41161  | H 0.71288 | 4.67061  | 3.51495  | H 2.61072 | 6.22199  | 2.96500  | H 4.35049 | 5.49335  | 3.13009  | H 4.22321 | 3.26295  | 0.26055  | C 3.67921 | -1.27719  | 1.63289  | C 4.18405 | -2.08386  | 2.66473  | C 3.99672 | -1.71934  | 4.00760  | C 3.29973 | -0.53884  | 4.30996  | C 2.79639 | 0.27202  | 3.27815  | C 3.83816 | -1.57746  | 0.59363  | C 4.72365 | -3.00235  | 2.41137  | C 4.39543 | -2.34737  | 4.81140  | C 3.15508 | -0.23507  | 5.35262  | H 2.27349 | 1.19796  | 3.53365  | I -0.11226 | 0.43370  | -2.98645  | C -0.27704 | 2.49126  | -1.90044  | C 0.85946 | 3.32083  | -1.75486  | C 0.69793 | 4.71627  | -1.76402  | C -0.57566 | 5.29761  | -1.86969  | C -1.69752 | 4.45800  | -1.97222  | C -1.55665 | 3.06017  | -1.95571  | H 1.86583 | 2.90547  | -1.69567  | H 1.59134 | 5.34624  | -1.69342  | H -0.69113 | 6.38591  | -1.89002  | H -2.70179 | 4.88213  | -2.08364  | H -2.43710 | 2.42742  | -2.07503  |
### DFTD3 Corr. Energy

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| C    | -1.8549 | 4.7140 | -3.9605 |
| C    | 3.7262 | 5.5640 | -2.5246 |
| H    | 3.7698 | 4.9814 | -0.0840 |
| H    | 1.99320 | 3.5671 | 0.8959 |
| C    | -4.48916 | -0.95390 | 1.28594 |
| C    | 5.65498 | -0.37055 | -1.81143 |
| C    | -6.15182 | 0.82518 | -1.26924 |
| C    | 5.45950 | 1.44818 | -0.21304 |
| C    | 4.28521 | 0.87486 | 0.29239 |
| C    | 4.12659 | 1.89680 | -1.70888 |
| C    | -6.18113 | -0.86157 | -2.63744 |
| H    | -7.06808 | 1.27327 | -1.66774 |
| H    | -5.82522 | 2.39159 | 0.1920 |
| H    | 3.74917 | 1.38819 | 1.09715 |
| H    | 3.88416 | -3.43310 | 0.54400 |
| H    | 4.15445 | -4.80872 | 0.53132 |
| H    | 3.13555 | -5.72494 | 0.20801 |
| H    | -1.84491 | -5.25196 | -0.07448 |
| H    | -1.57571 | -3.87246 | -0.04321 |
| H    | -4.68786 | -2.73699 | 0.80075 |
| H    | 5.16547 | -1.65151 | 0.73871 |
| H    | 3.34852 | -6.79895 | 0.17643 |
| H    | -1.03744 | -5.94890 | -0.32526 |
| H    | -0.56396 | -3.52080 | -0.26525 |
| H    | -1.43501 | -1.50764 | 3.18000 |
| H    | -1.61627 | -1.62855 | 4.53637 |
| H    | -2.86170 | -1.33841 | 5.11687 |
| H    | -3.92762 | -0.94620 | 4.29387 |
| H    | -3.75135 | -0.83781 | 2.99619 |
| H    | -0.45737 | -1.73576 | 2.71487 |
| H    | -0.77717 | -1.95178 | 5.16171 |
| H    | -3.00165 | -1.42568 | 6.19956 |
| H    | -4.90807 | -0.72684 | 4.72946 |
| H    | -4.60281 | -0.54723 | 2.83836 |
| H    | 0.16662 | -1.47666 | -0.05405 |
| H    | 0.76761 | -0.25153 | -2.49335 |
| H    | 0.20894 | 0.44399 | -3.61915 |
| H    | -0.92473 | -0.02373 | -4.25979 |
| H    | -1.57539 | -1.19375 | -3.77105 |
| H    | -1.04627 | -1.91049 | -2.70901 |
| H    | 1.82104 | 0.06076 | -2.82376 |
| H    | 0.75346 | 1.30861 | -4.01212 |
| H    | -1.31636 | 0.49061 | -5.14335 |
| H    | -2.48559 | -1.55730 | -2.60177 |
| H    | -1.51041 | -2.85103 | -2.40182 |
| I    | 1.64145 | -3.29232 | -2.08607 |

### Int2

**BP86 Energy** = 2443.86772881

**Enthalpy 0K** = 2443.867728

**PCM(benzene) Energy** = 2443.87457851

**DFTD3 Corr. Energy** = -25940841

**Ru**

-0.00593 -0.28955 -0.14759
-0.04865 -0.08961 0.43072
0.17820 -1.76137 0.43965

**P**

-0.42393 2.17795 -0.25537
0.89741 3.32137 -0.96811
1.87592 2.78943 -1.30822

**C**

-0.824253 0.04795 3.36849
2.29349 -0.23995 0.57381
3.72905 -0.20686 -0.64067
2.79319 1.15776 1.74058
2.81756 -1.67431 1.69949
-2.19911 -1.09646 0.43144
-2.58984 -2.94475 0.25326
-2.49678 -1.09783 2.31210
-3.79066 -0.35139 -0.21531
3.91639 -1.52074 2.57617
4.33472 -5.27752 3.39927
3.66496 -3.81103 3.36399
2.57811 -3.97871 2.49389
2.16124 -2.91952 1.66943
4.44858 -0.56659 2.62763
5.18599 -2.43072 0.47286
3.98838 -4.63399 4.01034
2.04725 -4.93554 2.44969
1.32266 -3.06867 0.98481
1.91113 1.50531 2.78508
2.24832 2.50536 3.71238
3.48209 3.16809 3.61683
4.37704 2.81736 2.59342
4.03817 1.81945 1.66343
0.94534 0.99821 2.86755
1.53576 2.76704 4.50066
3.74521 3.95066 4.33643
5.34778 3.31934 2.51521
4.74753 1.56065 0.87272
3.86955 0.91530 -1.40055
4.90345 0.96825 -2.43840
5.80188 -0.10387 -2.56332
5.66048 -1.22725 -1.73366
4.63066 -1.28137 -0.78020
3.17828 1.76037 -1.39841
5.00083 1.85067 -3.07955
6.60531 -0.06563 -3.30655
6.35209 -2.07121 -1.82796
4.52742 -2.16490 -0.94467
1.45419 2.30867 2.38420
-1.85898 2.92134 3.58162
-1.62932 4.29122 3.78397

**H**

4.52742 -2.16490 -0.94467
1.45419 2.30867 2.38420
-1.85898 2.92134 3.58162
-1.62932 4.29122 3.78397

**S**

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TS(Int2-Int3)

BP86 Energy = -2443.86428253
Enthalpy OK = -2442.958046
Enthalpy 298K = -2442.896415
Free Energy 298K = -2443.058175

DFTD3 Corr. = -0.25561652
Ru 0.04310
DFTD3 Corr. = -0.25561652

Lowest Frequencies = 292888 cm^{-1}

PCM(benzene) Energy = -2443.87596952
### Int4

**BP86 Energy** = -2443.90822993

**Enthalpy 0K** = -2443.000321

**Enthalpy 298K** = -2442.938091

**Free Energy 298K** = -2443.103837

**Lowest Frequencies** = 5.8904 13.2983 cm⁻¹

**PCM(benzene) Energy** = -2443.91613322

**DFTD3 Corr.** = -0.2538310

| C       | H       | C       | H       | C       | H       | C       | H       | C       | H       | C       | H       | C       | H       | C       | H       | C       | H       |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| -1.45735 | 4.49133 | -2.96955 |
| -0.56041 | 4.25020 | -4.02129 |
| 0.49622  | 3.34551 | -3.83332 |
| 0.64711  | 2.67688 | -2.60882 |
| -2.00020 | 4.05282 | -0.92658 |
| -2.27977 | 5.20351 | -3.09698 |
| -0.67964 | 4.76855 | -4.97875 |
| 1.207286 | 3.15122 | -4.64286 |
| 1.48661  | 1.99126 | -2.47407 |
| 2.42811  | 2.29901 | 1.64973 |
| 3.58478  | 2.93110 | 2.13252 |
| 4.05282  | 4.10379 | 1.52016 |
| 3.35421  | 4.63732 | 0.42523 |
| 2.18807  | 4.01315 | -0.04804 |
| 2.07249  | 1.38709 | 2.13329 |
| 4.12107  | 2.49471 | 2.98192 |
| 4.95671  | 4.59862 | 1.89126 |
| 3.71124  | 5.55038 | -0.06326 |
| 1.64702  | 4.45284 | -0.89006 |
| -2.45267 | 2.81347 | 1.20704 |
| -3.32993 | 3.57423 | 1.99699 |
| -2.83159 | 4.88765 | 2.83016 |
| -1.45130 | 4.83939 | 2.85655 |
| -0.57416 | 4.08786 | 2.05681 |
| -2.86343 | 2.03727 | 0.55727 |
| -4.40388 | 3.36432 | 1.95831 |
| -3.51327 | 5.17740 | 3.45210 |
| -1.04775 | 5.62875 | 3.49595 |
| 0.49585  | 4.30729 | 2.08856 |
| 4.70723  | 0.76380 | -0.38063 |
| 5.59252  | 1.54228 | -1.14318 |
| 5.38166  | 1.71833 | -2.51899 |
| 4.26237  | 1.12558 | -3.12226 |
| 3.36373  | 0.36067 | -2.35986 |
| 4.89887  | 0.63551 | 0.68645 |
| 6.45317  | 2.00952 | -0.65285 |
| 6.80037  | 2.31636 | -3.11369 |
| 4.07826  | 1.25592 | -4.19431 |
| 2.17652  | -0.06911 | -2.84009 |
| 4.20239  | -0.01326 | 0.96111 |
| 1.20627  | -0.02050 | 1.26634 |
| 3.13378  | -0.92292 | 2.85393 |
| 5.00798  | -2.22758 | 0.30601 |
| 6.52584  | -2.73496 | 2.19581 |
| 5.88456  | -2.09823 | 4.53686 |
| 3.69142  | -0.04856 | 4.94339 |
| 2.17516  | -0.44546 | 3.06157 |
| 2.18281  | -3.72882 | 0.02883 |
| 2.27187  | -0.53610 | -0.46801 |
| 2.79023  | -5.26525 | -1.75632 |
| 3.21141  | -4.17782 | -2.53364 |
| 3.11390  | -2.86526 | -0.03785 |
| 1.80926  | -3.56760 | 1.04655 |
| 1.96131  | -5.87727 | 0.15797 |
| 2.86588  | -6.28556 | -2.14662 |
| 3.61868  | -4.34262 | -3.53678 |
| 3.45752  | -0.03478 | -2.65769 |
| -0.10073 | 0.63553 | 2.22824 |
| -0.09592 | 0.45238 | 3.14586 |
| -0.10756 | 0.28141 | 4.55382 |
| -0.13491 | -1.00188 | 5.10925 |
| -0.16453 | -2.10557 | 4.24272 |
| -0.14947 | -1.91853 | 2.85071 |
| -0.09685 | 1.48270 | 2.78209 |
| -0.09748 | 1.16856 | 5.18955 |
| -0.14279 | -1.13905 | 6.19580 |
| -0.19696 | -3.12425 | 4.64731 |
| -0.16823 | -2.82438 | 2.22954 |
| -0.14823 | -0.76617 | -2.82220 |
**TS(int4-2-I)**

| PCM(benzene) Energy | Free Energy 298K | BP86 Energy | Enthalpy OK | Enthalpy 298K |
|---------------------|------------------|-------------|-------------|---------------|
| -2443.89702075      | -2443.909785     | -2443.89702075 | -2443.909785 | -2443.89702075 |

**DFTD3 Corr.**

| Ru -0.06880 | -0.50465 | 0.24560 |
|-----------------|-----------------|-----------------|
| H -0.28005 | -2.06198 | 0.11247 |
| P 0.37320 | -1.37122 | 1.45575 |
| C 0.25660 | 2.10131 | -0.06531 |
| C 0.91300 | 3.30620 | -1.80815 |
| C 1.89159 | 2.81889 | 0.54139 |
| C 0.22157 | 2.81851 | -1.80379 |
| P -2.47633 | -0.84436 | -0.07924 |
| C -3.52392 | 0.29909 | -1.15912 |
| C -2.83166 | -2.50961 | -0.88262 |
| C -3.60703 | -0.97276 | 1.42405 |
| P 2.31964 | -1.09596 | 0.16705 |
| C 3.30425 | -1.25541 | 1.77659 |
| C 2.53677 | -2.89752 | -0.36225 |
| C 3.57279 | -0.18509 | -0.90436 |
| C -4.38275 | -2.60969 | 1.73945 |
| C -5.24578 | -2.04729 | 2.84997 |
| C -5.34889 | -0.90248 | 3.65263 |
| C -4.13870 | 1.31782 | -1.80815 |
| C -3.72008 | 0.22151 | 2.23666 |
| H -4.32271 | -2.95813 | 1.11751 |
| H -5.84334 | -2.93758 | 3.07988 |
| H -6.02045 | -0.89414 | 4.51788 |
| H -4.64977 | 1.12257 | 3.96216 |
| C -3.11975 | 1.10732 | 2.01344 |
| C -2.29173 | -3.68067 | -0.30873 |
| C -2.55593 | -4.90483 | -0.86464 |
| C -3.35674 | -5.05078 | -2.01315 |
| C -3.89772 | -3.89285 | -2.59041 |
| C -3.64475 | -2.63131 | -2.02588 |
| H -1.65152 | -3.67092 | 0.57654 |
| H -2.12671 | -5.83674 | -0.40377 |
| H -3.55337 | -6.03279 | -2.45603 |
| H -4.51382 | -3.96413 | -3.48996 |
| H -4.07109 | -1.73971 | -2.49228 |
| C -2.93824 | 1.02537 | -2.21657 |
| C -3.72479 | 1.85045 | -3.03798 |
| C -5.10574 | 1.96241 | -2.81617 |
| C -5.69312 | 1.24134 | -1.76702 |
| C -4.91682 | 0.41568 | -0.94042 |
| H -1.86585 | 0.92953 | -2.41070 |
| H -3.34999 | 2.40909 | -3.84712 |
| H -5.71775 | 2.60737 | -3.45603 |
| H -6.77668 | 1.31788 | -1.58509 |
| H -5.39383 | -0.14164 | -0.13316 |
| C -0.66229 | 3.84348 | -2.20131 |
### 2-I-benzene

**BP86 Energy** = $-2443.9184967$  
**Enthalpy OK** = $-2443.008275$  
**Enthalpy 298K** = $-2442.946340$  
**Free Energy 298K** = $-2443.109976$

**Lowest Frequencies** = 8.0583 19 3.3842 cm⁻¹  
**PCM(benzene) Energy** = $-2443.9259567$  
**DFTD3 Corr.** = $-0.24852044$

| Ru | 0.01564 | -0.32390 | 0.13025 |
|---|---|---|---|
| H | -0.04777 | -1.90689 | 0.27048 |
| H | 0.47425 | -0.03800 | 1.82788 |
| P | 0.21008 | 2.20846 | 0.02245 |
| C | 1.13395 | 3.32040 | 0.77806 |
| C | 1.63976 | 2.92852 | 0.94740 |
| C | 0.40724 | 3.06941 | -1.64068 |
| P | -2.34751 | -0.85611 | -0.19396 |
| C | -3.48981 | 0.02847 | -1.41964 |
| C | -2.48728 | -2.63101 | -0.81215 |
| C | -3.57246 | -0.89960 | 1.25101 |
| P | 2.28583 | -1.08300 | 0.13556 |
| C | 2.93440 | -1.55894 | 1.84395 |
| C | 2.62143 | -2.70295 | -0.77015 |
| C | 3.71632 | -0.06455 | -0.55987 |
| C | -4.16929 | -2.07457 | 1.75131 |
| C | -5.14251 | -2.00925 | 2.76487 |
| C | 5.54416 | -0.77143 | 3.28462 |
| C | -4.95564 | 0.40530 | 2.79503 |
| C | -3.97470 | 0.33905 | 1.79587 |
| C | -3.98870 | -0.03461 | 1.33845 |
| C | -5.59540 | -2.93593 | 3.13421 |
| C | -6.31169 | -0.72267 | 4.06636 |
| C | -5.25790 | 1.38139 | 3.19009 |
| C | -3.52882 | 1.26537 | 1.42312 |
| C | -1.98334 | -3.67505 | -0.00401 |
| C | -2.07447 | -5.01367 | -0.41825 |
| C | -2.64843 | -5.32951 | -1.66133 |
| C | -3.13281 | -4.29795 | -2.47884 |
| C | -3.06018 | -2.95929 | -2.05603 |
| C | -1.51557 | -3.43702 | 0.95749 |
| C | -1.69116 | -5.80882 | 0.23330 |
| C | -2.71347 | -6.37221 | -1.99005 |
| C | -3.56954 | -5.42924 | -3.45618 |
| C | -3.44171 | -2.17002 | -2.70845 |
| C | -2.99315 | 0.97716 | -2.33591 |
| C | -3.85797 | 1.62476 | -3.23625 |
| C | -5.22941 | 1.32990 | -3.23695 |
| C | -5.73515 | 0.38402 | -2.32924 |
| C | -4.87420 | -0.25843 | -1.42663 |
| C | -1.92177 | 1.19615 | -2.36530 |
| C | -3.44805 | 2.35890 | -3.93764 |
| C | -5.90214 | 1.85318 | -3.93986 |
| C | -6.80443 | 0.14612 | -2.31893 |
| C | -5.28885 | -0.98716 | -0.72045 |
| C | -0.37234 | 4.17194 | -2.04901 |
| C | -0.16321 | 4.77025 | -3.30312 |
| C | 0.83697 | 4.28808 | -4.16137 |
Second I-Ph Activation

Int5

BP86 Energy = -1753.29174928
Enthalpy OK = -1753.660031
Enthalpy 298K = -1753.748679
Free Energy 298K = -1753.748679
Lowest Frequencies = 13.9998 17.2745 cm⁻¹
PCM(benzene) Energy = -1753.29966278
DFTD3 Corr. = -0.16373406
Ru -0.15181 -0.38200 -0.37365
H 0.25684 0.12868 -1.83685
P -0.07015 1.76711 0.22706
C -1.73647 2.40512 0.84664
C 1.05721 2.18530 1.66690
C 0.36084 3.10266 -1.03110
P 2.04900 -0.96693 -0.31586
C 2.07111 -2.43447 -1.48668
C 3.36640 0.16135 -1.02933
C 2.89284 -1.65356 2.10411
C -0.00932 2.90934 -2.37808
C 0.21678 3.90880 -3.37711
C 0.82108 5.12059 -2.96346
C 1.18565 5.32887 -1.62416
C 0.95216 4.33098 -0.66269
H -0.46945 1.96036 -2.67240
H -0.07907 3.73832 -4.37784
H 1.00382 5.89935 -3.71151
H 1.65245 6.27225 -1.32101
H 1.23169 4.51326 0.37899
C 2.42948 2.44870 1.45529
C 3.28537 2.68110 2.54331
C 2.78770 2.64483 3.85603
C 1.42685 2.37625 4.07497
C 0.56564 2.14924 2.98934
H 2.83282 2.47606 0.43893
H 4.34508 2.86737 2.36022
C 3.45706 2.82545 4.70371
H 1.02789 2.34650 5.09445
H -0.92629 1.94328 3.17345
C -2.56508 1.54788 1.60302
C -3.78634 2.01228 2.11830
C -4.20331 3.33058 1.87448
C -3.39019 4.18440 1.11260
H -2.16361 3.72811 0.60299
H -2.25707 0.51050 1.78225
H -4.41366 1.33260 2.70427
H -5.15892 3.68974 2.27155
H -3.70807 5.21309 0.91046
H -1.54308 4.40871 0.01416
C 3.81205 -2.72075 1.11178
C 4.45340 -3.20406 2.26174
C 4.18338 -2.62591 3.51477
C 3.26822 -1.56536 3.61098
C 2.62013 -1.08297 2.46310
H 0.02379 -3.17836 0.14029
H 5.16094 -4.03614 2.18156
H 4.67955 -3.00725 4.41371
H 3.04317 -1.11740 4.58416
H 1.88759 -0.27618 2.54671
C 2.75902 -2.41036 -2.71808
C 2.68609 -3.50733 -3.59203
C 1.92765 -4.63790 -3.24885
C 1.24485 -4.67114 -2.02164
C 1.31090 -3.57774 -1.14441
C 3.35792 -1.53750 -2.99372
C 3.22875 -3.47692 -4.54312
H 1.87079 -5.49098 -3.93393
H 0.65330 -5.54972 -1.74301
H 0.76803 -3.60705 -0.19245
C 3.03880 0.99758 -2.11785
C 4.00220 1.84974 -2.69030
C 5.30507 1.88351 -2.15684
C 5.64000 1.05481 -1.07399
C 4.67972 0.19626 -0.51388
H 2.08121 0.98516 -2.51191
H 3.72707 2.49509 -3.52093
H 6.05514 2.55401 -2.58970
H 6.65391 1.07377 -0.65992
H 4.95219 -0.44486 0.32903
I -0.91606 -2.01350 1.75888
I -2.52104 -0.46442 -1.72934
C -4.36733 -1.06689 -0.74079
C -4.43238 -2.32258 -0.12020
C -5.63691 -2.70076 0.50022
C -6.74448 -1.83796 0.49255
C -6.65368 -0.58322 -1.13377
C -5.45624 -0.18315 -0.75104
H -3.56247 -2.98348 -0.10293
H -5.70040 -3.67661 0.99283
H -7.67877 -2.14247 0.97535
H -7.51417 0.09442 -0.13818
H -5.37840 0.79862 -1.22697

TS(Int5–Int6)

BP86 Energy = -1753.27454674
Enthalpy OK = -1753.642886
Enthalpy 298K = -1753.597165
Free Energy 298K = -1753.727015
Lowest Frequencies = 118.0027 14.1249 cm⁻¹
PCM(benzene) Energy = -1753.28199689
DFTD3 Corr. = -0.17733142
Ru 0.03235 -0.72495 0.00040
H 0.07397 -0.60093 1.57621
P 1.72134 0.76884 0.15278
C 3.36662 0.18024 -0.60165
C 1.56723 2.47510 -0.65632
C 2.30938 1.26517 1.88222
P -1.76335 0.66929 0.16268
C -3.30456 -0.34728 0.32514
C -1.86465 1.78441 1.67901
C -2.32586 1.80624 -1.22560
H 2.23177 0.31191 2.91818
H 2.74921 0.59045 4.19278
C 3.34928 1.83268 4.45293
C 3.43834 2.78773 3.43060
C   2.59025  1.05055  4.10200
C   2.08510  0.61546  2.86476
H   0.09295
DFTD3 Corr. =
Lowest Frequencies =
Enthalpy 298K =
H   0.42930
H
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8-benzene

BP86 Energy = -1753.31102098
Enthalpy 0K = -1752.6753106
Enthalpy 298K = -1752.629011
Free Energy 298K = -1752.759620

Lowest Frequencies = 17.5944 25.6147 cm⁻¹

PCM(benzene) Energy = -1753.32013728

DFTD3 Corr. = -0.17784185
Ru -0.09323 -0.63138 -0.49662
H 0.12485 -1.47845 1.24836
P 1.92929 0.37262 0.14005
C 3.16933 -0.93153 -0.39918
C 2.69131 1.91028 -0.62386
C 2.34689 0.64175 1.39979
P -1.63932 0.73119 0.46865
C -3.31855 0.87296 -0.37381
C -2.11724 0.16674 2.19684
C -1.32103 2.57437 0.71105
C 2.37258 -0.45276 -1.33642
C 2.63034 -0.25431 4.21729
C 2.84871 1.04100 4.71554
C 2.81513 2.13416 3.83604
C 2.57237 1.93831 2.46620
H 2.19450 -1.46865 2.48766
H 2.66058 -1.11782 4.89029
H 3.04866 1.19570 5.78099
H 2.98988 3.14789 4.21198
H 2.56723 2.79855 1.73099
H 1.93643 3.09546 -0.72731
H 2.51938 4.26713 -1.23491
H 3.85735 4.26555 -1.65946
H 4.61249 3.08635 0.15699
H 4.03653 1.91499 -1.04839
H 0.88975 3.10419 -0.42028
H 1.91556 5.17753 -1.30674
H 4.30833 5.17739 -2.06514
H 5.65630 3.07227 -1.89730
H 4.63972 1.00578 -0.98088
C 2.97775 -1.52973 -1.66702
C 3.86232 -2.51794 -2.12792
C 4.95136 -2.91683 -1.33595
C 5.16071 -2.31328 -0.80500
C 4.27760 -1.32566 0.38265
C 2.14029 -1.21788 -2.30154
C 3.69296 -2.97496 -3.10747
C 5.63839 -3.69055 -1.69440
H 6.01649 -2.60780 0.53198
H 4.45674 -0.85881 1.35536
C -0.86523 3.13024 1.92394
C -0.64485 4.51406 2.03550
C -0.87999 5.36046 0.94151
C -1.34003 4.81589 -0.26967
C -1.55648 3.43461 -0.38720
H -0.69981 2.49500 2.79725
H -0.29391 4.92853 2.98852
H -0.71500 6.43914 1.03376
H -1.53457 5.46603 -1.12912
H -1.90688 3.01976 -1.33642
C -4.26380 1.77838 0.16723
PCM(benzene) Energy =

Lowest Frequencies =

Free Energy 298K =

Enthalpy 298K =

Enthalpy 0K =

BP86 Energy =

Enthalpy OK =

Free Energy 298K =

Lowest Frequencies =

PCM(benzene) Energy =

Enthalpy 0K =

Enthalpy 298K =


ew Energy =

Enthalpy OK =

Free Energy 298K =

Enthalpy 0K =

Enthalpy 298K =


ew Energy =

Enthalpy OK =

Free Energy 298K =

Enthalpy 0K =

Enthalpy 298K =

BP86 Energy =
| C   | 2.85700 | 5.43053 | 1.98736 |
|-----|---------|---------|---------|
| H   | 2.85700 | 5.43053 | 1.98736 |
| H   | 2.85700 | 5.43053 | 1.98736 |
| C   | 3.51193 | 0.93894 |         |
| C   | 3.80120 | 2.60028 |         |
| C   | 4.05068 | 3.57811 |         |
| H   | 4.25379 | 4.61292 |         |
| H   | 4.22969 | 4.00955 |         |
| C   | 3.51193 | 0.93894 |         |
| C   | 3.80120 | 2.60028 |         |
| C   | 4.05068 | 3.57811 |         |
| H   | 4.25379 | 4.61292 |         |
| H   | 4.22969 | 4.00955 |         |
| C   | 3.51193 | 0.93894 |         |
| C   | 3.80120 | 2.60028 |         |
| C   | 4.05068 | 3.57811 |         |
| C   | 4.05068 | 3.57811 |         |
| H   | 4.25379 | 4.61292 |         |
| H   | 4.22969 | 4.00955 |         |

**IPh**

**SCF Energy** = -243.097817108

**Enthalpy OK** = -243.010398

**Enthalpy 298K** = -243.003386

**Free Energy 298K** = -243.041645

**Lowest Frequencies** = 145.4995 212.0747 cm⁻¹

**PCM(benzene) Energy** = -243.099316319

**DFTD3 Corr.** = -0.00906004

I 0.0000 0.0000 1.58620
C 0.0000 0.0000 -0.57664
C 0.0000 1.22487 -1.26093
C 0.0000 1.21416 -2.66632
C 0.0000 -1.21416 -2.66632
C 0.0000 -1.24478 -1.26093
H 0.0000 2.17030 -0.71242
H 0.0000 2.16642 -3.20713
H 0.0000 0.0000 -4.46510
H 0.0000 -2.16642 -3.20713
H 0.0000 -2.17030 -0.71242

**HPh**

**SCF Energy** = -232.242069561

**Enthalpy OK** = -232.144358

**Enthalpy 298K** = -232.138882

**Free Energy 298K** = -232.137190

**Lowest Frequencies** = 397.3897 397.4287 cm⁻¹

**PCM(benzene) Energy** = -232.243152781

**DFTD3 Corr.** = -0.00593486

C -0.70236 1.21651 0.0000
C -1.40487 0.0000 0.0000
C -0.70236 -1.21651 0.0000
C 0.70239 -1.21651 0.0000
C 1.40480 0.0000 0.0000
C 0.70239 1.21651 0.0000
H -1.24998 2.16513 0.0000

S49
| H  | -2.50020  | -0.00000  | 0.00000   |
| H  | -1.24998  | -2.16513  | 0.00000   |
| H  | 1.25002   | -2.16515  | 0.00000   |
| H  | 2.50013   | 0.00000   | 0.00000   |
| H  | 1.25002   | 2.16515   | 0.00000   |

**PPh$_3$**

SCF Energy = -701.502627402

Enthalpy 0K = -701.237103

Enthalpy 298K = -701.219662

Free Energy 298K = -701.284090

Lowest Frequencies = 22.5487 24.2082 cm$^{-1}$

PCM(benzene) Energy = -701.505260493

DFTD3 Corr. = -0.03544293

P  
-0.00001  
-0.00001  
-1.25105

C  
-0.32759  
1.64441  
-0.41602

C  
-1.26033  
-1.10582  
-0.41588

C  
1.58790  
-0.53853  
-0.41603

C  
2.79466  
-0.15148  
-1.04074

C  
4.03390  
-0.51881  
-0.49489

C  
4.08450  
-1.29538  
0.67482

C  
2.89103  
-1.69727  
1.29603

C  
1.64965  
-1.32060  
0.75658

H  
2.75973  
0.43893  
-1.96398

H  
4.96050  
-0.20764  
-0.98922

H  
5.05082  
-1.59166  
1.09654

H  
2.92424  
-2.30698  
2.20566

H  
0.72294  
-1.63894  
1.24489

C  
-1.52960  
-2.34387  
-1.04120

C  
-2.46717  
-3.23344  
-0.49506

C  
-3.16368  
-2.88954  
0.67558

C  
-2.91389  
-1.65556  
1.29745

C  
-1.96717  
-0.76883  
0.75770

H  
-1.00184  
-2.60838  
-1.96314

H  
-2.66187  
-4.19104  
-0.98988

H  
-3.90328  
-3.57827  
1.09756

H  
-3.45748  
-1.37994  
2.20784

H  
-1.77858  
0.19246  
1.24650

C  
0.32038  
2.08990  
0.75536

C  
0.02573  
3.35328  
1.29479

C  
-0.92079  
4.18486  
0.67484

C  
-1.56959  
3.75177  
-0.49364

C  
-1.26791  
2.49495  
-1.03952

H  
1.06074  
1.44728  
1.24268

H  
0.53836  
3.68768  
2.20345

H  
-1.14751  
5.16983  
1.09656

H  
-2.30376  
4.39782  
-0.98698

H  
-1.76304  
2.16875  
-1.96180
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