

Reversible insertion of Ir into arene ring C-C bonds with improved regioselectivity at a higher reaction temperature

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ABSTRACT: Regioselective metal insertion into aromatic C-C bonds is a long-standing problem critical for development of new arene functionalizations and cleaner conversion of fossil fuel into value-added chemicals. We report reversible insertion of iridium into the aromatic C-C bonds of η^4 -bound methyl arenes to give eight-membered diiridium metallacycles with yields up to 99%. While at 50-100 °C the reaction yields a mixture of isomers corresponding to iridium insertion in both unsubstituted and Me-substituted ring C-C bonds, at 150 °C a single isomer dominates. Kinetic and DFT studies suggest that at 150 °C insertion of iridium is reversible, allowing equilibration of the metallacycle products via a diiridium arene sandwich complex. The selectivity of metal insertion is determined by the relative stabilities of isomeric metallacycles governed by steric repulsion between methyl groups of the hydrocarbon chain of the cleaved arene and the Cp* ligands.

1. INTRODUCTION

Metal insertion into aromatic C-C bonds is a key step for the generation of higher value chemicals from coal and petroleum by breaking down large aromatic molecules into smaller synthetically useful units, and for developing efficient methods of arene functionalization via ring expansion.¹ The high bond dissociation energy of the arene C-C bond, however, makes such insertion kinetically challenging. As a result, standard industrial heterogeneous catalysts for arene C-C scission require temperatures >350 °C.^{1a-c,2} Few examples of soluble metal complexes capable of breaking of an arene ring C-C bond at 25-150 °C have been reported.³ In most cases weaker C-H bonds were activated first, which triggered ring isomerization or dehydrogenation, followed by metal insertion, usually with low overall yields.³⁻⁴ Recently we showed that undesired competing C-H activation can be suppressed by exploiting metal-induced arene ring strain⁵ that enables high-yield direct insertion of iridium into the aromatic ring.⁶ However, the problem of regioselective metal insertion into the specific aromatic C-C bonds, which is critical for designing further synthetic applications, has yet to be addressed.

Herein we describe the first example of selective, reversible insertion of metal into the aromatic ring of methyl arenes. The insertion occurs in simple iridium arene complexes with higher regioselectivity at a higher reaction temperature (150 °C). Experimental and computational data indicate that the selectivity of insertion at 150 °C is governed by the relative stability of the resulting metallacycles that are equilibrated under the reaction conditions.

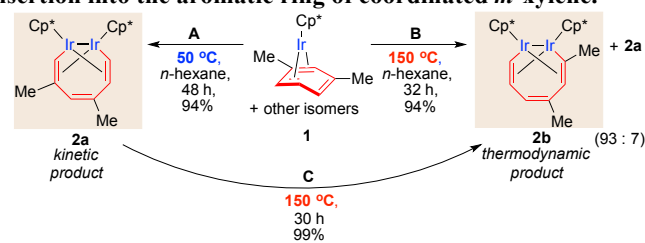
2. RESULTS AND DISCUSSION

Temperature-switchable regioselectivity of arene ring C-C cleavage in *m*-xylene

Previously we reported that heating η^4 -*m*-xylene iridium complex **1** in hexane at 50 °C gave dinuclear metallacycle **2a**

and one equivalent of free arene as the only products (Scheme 1, path A). Metallacycle **2a** resulted from selective insertion of two Ir atoms into the least hindered arene ring C-C bond.⁶ In the current study we found that heating of the same complex **1** at 150 °C yields only traces of **2a** (7%), while the main product is regioisomer **2b** (93%) formed via insertion of iridium into the second least hindered C-C bond of the arene (Scheme 1, Path B). Isomer **2a** produces an identical mixture of the two isomers, **2a** and **2b** (7:93) upon heating at 150 °C for 32 h (Scheme 1, Path C). The composition of this mixture does not change on further heating to 200 °C, suggesting that the equilibrium is reached and the more stable thermodynamic product **2b** dominates. Note that such a complete reversal of a reaction regioselectivity upon changing the reaction temperature is rare in organic chemistry and unprecedented in metal-mediated C-C activation.⁷

Scheme 1. Temperature-switchable regioselectivity of Ir insertion into the aromatic ring of coordinated *m*-xylene.



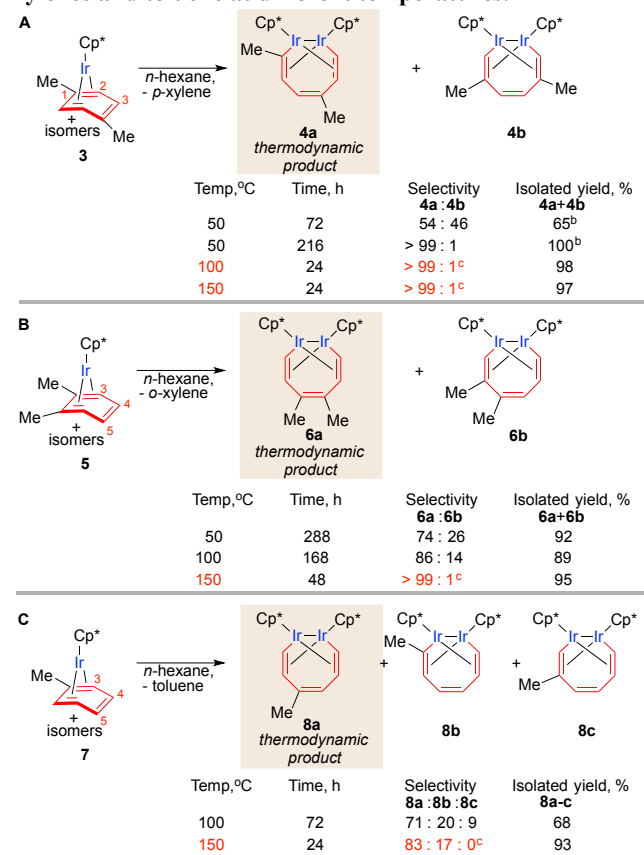
Temperature-controlled regioselectivity of arene ring C-C cleavage in other BTX methyl arenes

We next examined thermolysis of the *p*-xylene, *o*-xylene and toluene analogs of **1** at different temperatures (Scheme 2). Although in all cases the insertion occurred slower than that in **1**, it proceeded with improved selectivity at a higher reaction temperature.

Thus, thermolysis of η^4 -*p*-xylene complex **3** at 50 °C for 3 days gave a nearly equal ratio of two isomeric metallacycles **4a** and **4b** at 65% conversion, but further heating for 6 days

yielded **4a** as the only product (Scheme 2A). Reactions at 100 °C, 150 °C and 200 °C gave metallacycle **4a** as a single observable product in quantitative yields within 24 h. Similarly to the cleavage of *m*-xylene, the kinetic product **4b** corresponds to insertion of iridium into the least sterically hindered ring C-C bond (C2-C3), whereas thermodynamic product **4a** results from cleavage of the most sterically hindered bond (C1-C2) (Scheme 2A). Conversely, the thermodynamic products of thermolysis of *o*-xylene and toluene complexes **5** and **7** corresponded to Ir insertion into the least sterically hindered C-C bond (Scheme 2B-C). Thus, heating η^4 -*o*-xylene complex **5** at 50 °C for 12 days gave a mixture of **6a** and **6b** in a 74:26 ratio with the 92% total yield (Scheme 2B). At 100 °C the ratio improved to 86:14 and at 150 °C, **6a** was isolated as the only product in a 95% yield after 48 h. Thermolysis of toluene complex **7** yielded regioisomer **8a**, resulting from Ir insertion into the least sterically hindered bond C3-C4, as the main product, regardless of the reaction temperature (Scheme 2C). At 100 °C the insertion gave **8a** with 71% regioselectivity along with two minor isomers **8b** and **8c**,⁶ at 150 °C **8c** converts to **8a** improving the regioselectivity to 83%, whereas the fraction of **8b** remains temperature-independent.

Scheme 2. Ir insertion into the coordinated *p*- and *o*-xylenes and toluene at different temperatures.^a



^aReactions were conducted with 0.1 mmol of an η^4 -arene complex and 0.8 mL of *n*-hexane under Ar. ^bConversion of **3**. ^cNo change in the ratio after heating at 200 °C (in *n*-dodecane) for 24 h.

Regioselectivity of the C-C cleavage and relative stability of the metallacycles

The observed regioselectivity of arene scission does not correlate with the steric accessibility of the ring C-C bonds. However, to utilize the observed arene ring scission for synthetic functionalizations, a straightforward rule predicting the regioselectivity is required (Fig. 1).

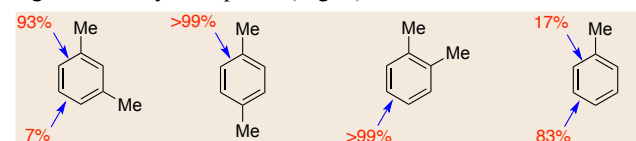


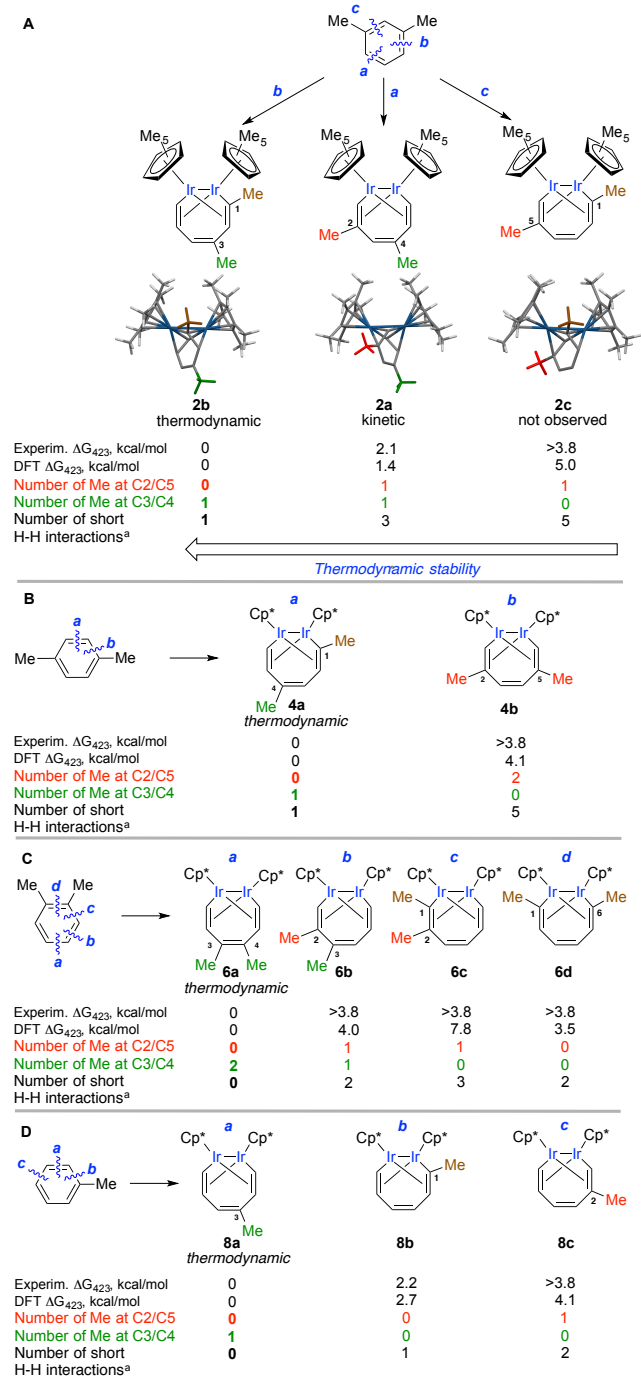
Figure 1. Regioselectivity of the Ir insertion under thermodynamic conditions.

Because the regioselectivity under thermodynamic control is determined by the relative stabilities⁸ of the isomeric metallacycles, we calculated free energies of all isomers of the products of Ir insertion in *m*-, *p*- and *o*-xylene and toluene by DFT (Scheme 3). For calculations we used the B3LYP functional and a mixed basis set of LanL2DZ on Ir and 6-31G(d) on the other atoms.⁹ For each arene our calculations correctly identified the observed minimum energy metallacycle and the relative stability of the detected isomers (Scheme 3). Examination of the obtained structures revealed that the relative stabilities are mainly governed by steric factors and follow a common trend (Fig. 2): Me groups at the C3, C4 positions of a metallacycle are least destabilizing while those at C2, C5 are most destabilizing. The reason is that a methyl group at C2 or C5 directly faces a Cp* group, producing short H-H contacts of <2.4 Å, whereas a methyl group at C3 or C4 is free from the unfavorable contacts.¹⁰ That is, the most stable metallacycles have the maximum number of methyl groups at the C3/C4 positions, and minimum number of methyl groups at C2/C5, which minimizes the number of unfavorable repulsive H-H interactions (Scheme 3).¹¹

Scheme 4 shows how this rule accurately predicts the observed regioselectivity of Ir insertion into all xylenes and toluene, including the seemingly counterintuitive cleavage of the more substituted C-C bonds in *m*- and *p*-xylene. In all cases iridium inserts in the ring C-C bond so as to avoid locating Me groups in the most unfavorable C2 or C5 position of the hydrocarbon chain in the resulting metallacycle, while placing at least one Me group at a C3 or C4 position.

One of the unusual aspects of the described chemistry is the increasing reaction selectivity with increasing temperature. The opposite is often observed in chemistry as temperature decreases the effect of barrier-height differences on the reaction rates leading to leveling of selectivities.¹² In the present case the relatively poor regioselectivity at lower temperatures reflects a small difference in the relative rates of direct C-C scission in η^4 -complexes to give different isomeric metallacycles (i.e., under kinetic control). Higher temperatures enable isomerization of the metallacycles, yielding a thermodynamic mixture of isomers, where one isomer dominates because it is substantially more stable than the rest (Scheme 3).

Scheme 3. Relative stability of metallacycles derived from *m*-xylene (A), *p*-xylene (B), *o*-xylene (C) and toluene (D).



(a) See Figs. S1-S12 for more details.

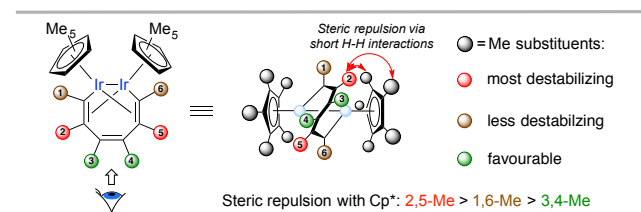
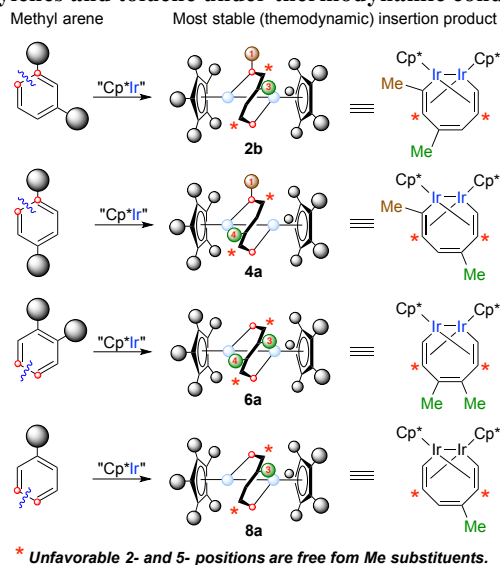


Figure 2. General structure of the metallacycles resulted from Iridium insertion into the arene ring.

Scheme 4. Model for regioselectivity of the insertion of Ir into xylenes and toluene under thermodynamic conditions.



Mechanistic studies

Because the isomerization of the metallacycles determines the product distribution at higher temperatures, we probed the mechanism of conversion of **2a** into **2b** by conducting kinetic and DFT studies (Fig. 3A). Kinetics was measured in d_3 -THF at 120, 130, 140 and 150 °C by ^1H NMR spectroscopy. The time-dependent intensity of the peaks at 7.71 and 7.63 ppm, corresponding to metallacycle **2a** and of the equivalent resonance of **2b** at 7.54 ppm, followed the reversible first order rate law, $\ln[(A_t - A_{eq})/(A_0 - A_{eq})] = -(k_f + k_r)t$, where A_0 , A_t , and A_{eq} are integrated intensities before heating, at reaction time t , and at equilibrium (the end of measurement), respectively;¹³ and k_f , k_r are rate constants for **2a**→**2b** and **2b**→**2a** conversions (Fig. 3B). From the observed rate ($k_{\text{obs}} = k_f + k_r$) and equilibrium ($K = k_f/k_r$, Table S5) constants, we estimated k_f and k_r at each temperature and derived the activation and reaction enthalpies and entropies of **2a**→**2b** isomerization of $\Delta H_f^\ddagger = 31 \pm 2$ kcal/mol, $\Delta S_f^\ddagger = 0 \pm 5$ cal/(mol·K) and $\Delta G_f^\ddagger = 31 \pm 2$ kcal/mol¹⁴ from the Eyring plot (Fig. 3C).¹⁵ The small activation entropy agrees with a unimolecular reaction. The isomerization likely proceeds without dissociation of *m*-xylene because heating **2a** in the presence of a 4-fold excess of d_3 -*m*-xylene produced no detectable incorporation of D in the complexes (Scheme S1).

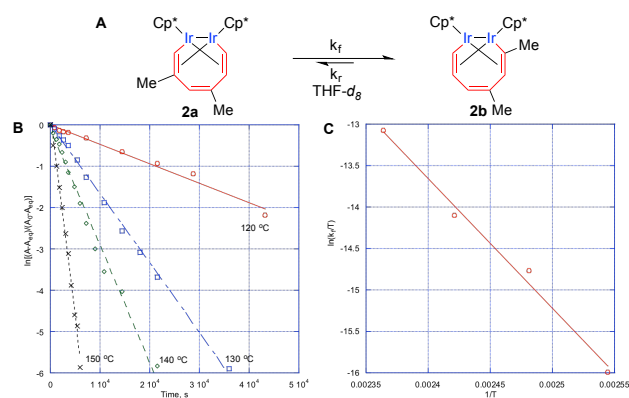


Figure 3. Kinetic investigation of isomerisation **2a** into **2b** (A); reversible first order kinetic plot (B); Eyring plot (C).

We calculated the mechanism of interconversion of the three isomers of **2**: **2a**, **2b** and experimentally unobserved **2c** with the B3LYP-D3 and M06-L functionals for geometry optimizations and frequencies, and single-point energy calculations, respectively⁹ (Fig. 4). The calculations showed that the isomerization occurs via diiridium bridging arene complexes **2a-c_arena**. Although such iridium complexes are not known, their Cp cobalt and rhodium analogues were described.¹⁶ The isomerization starts with partial decoordination of the bridging hydrocarbon chain in **2a** from one Ir atom. This hapticity change from μ -(η^3, η^3) to μ -(η^3, η^2) triggers dissociation of the Ir-Ir single bond in the resulting **2a_int1** to give a dinuclear μ -(η^4, η^4) Ir(II) intermediate **2a_int2**. The latter undergoes a binuclear C-C bond forming reductive elimination to form *m*-xylene sandwiched between two Ir(I) centers (**2a_arena**).¹⁷ Fast rotation of the bridging arene ring leads to **2b_arena** in which the μ -(η^4, η^2)-coordinated *m*-xylene ring is non-planar

(Fig. 4; the bending angle between the planes C1-C2-C3-C4 and C4-C5-C6-C1 is 40 °). The resulting ring strain promotes exergonic oxidative addition of the arene ring C-C bonds to both Ir(I) centers to give dinuclear Ir(II) metallacycle **2b_int2**. The subsequent rate-determining Ir-Ir bond formation with the free energy barrier of 31.7 kcal/mol and the hapticity change of the bridging hydrocarbon chain affords the thermodynamic product **2b**. Unobserved isomer **2c** is both the least thermodynamically stable and separated from the reactant by the highest activation barrier. The excellent agreement of the computed and measured free energy difference of isomers **2a** and **2b** (-3.2 kcal/mol vs. -2.1±0.1 kcal/mol) and the activation free energy of **2a** → **2b** isomerization (31.7 kcal/mol vs. 31 ± 2 kcal/mol, all at 150 °C), give credence to the calculated mechanism. To the best of our knowledge, the reversible formation/cleavage of an arene ring that enables this isomerization has not been described in the literature.

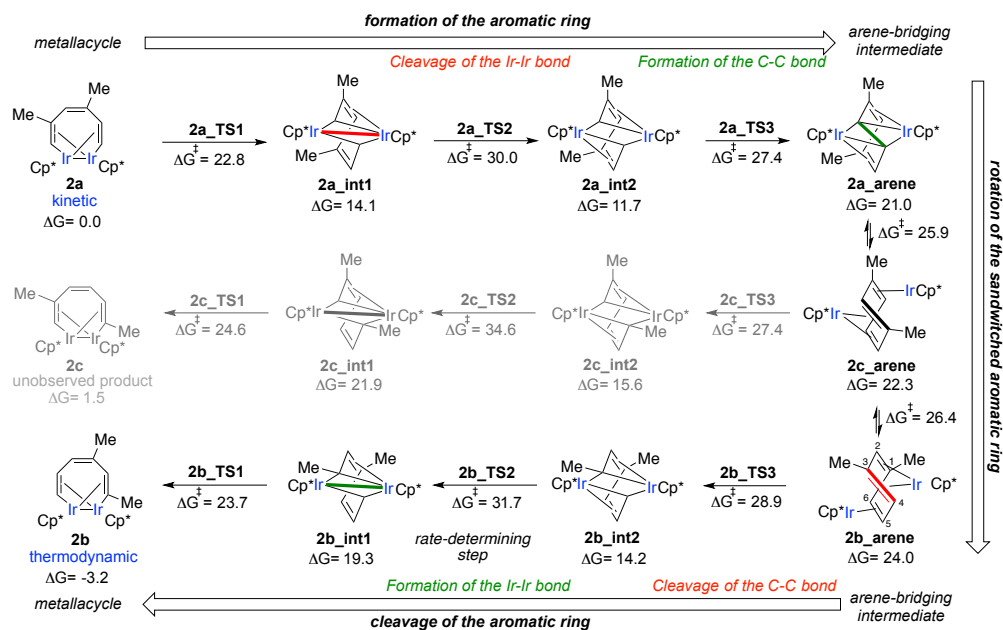


Figure 4. Proposed mechanism for isomerization of **2a** via reversible arene ring scission with the calculated free energies in kcal/mol in *n*-hexane at 423 K.

CONCLUSIONS

We report an unprecedented reversible insertion of iridium into the aromatic ring C-C bonds of alkyl arenes to give dinuclear metallacycles. The regioselectivity of the insertion increases with the reaction temperature to exceed 93% in 3 out of 4 substrates. This regioselectivity does not correlate with the steric accessibility of the C-C bonds in arenes but results from facile equilibration of isomeric metallacycles at 150 °C. The isomerization occurs via a diiridium arene sandwich complex and requires a sequential formation and cleavage of the arene ring C-C bonds as well as cleavage and rate-determining formation of the Ir-Ir bond. A simple empirical rule based on steric interactions of methyl groups on the backbone of the cleaved arene ring and Cp* ligands in the metallacycle products predicts the reaction selectivity. For all arene cleavages, even at 150 °C the free energy difference between the most and second-most stable isomers is large enough that a single isomer dominates. Detailed investigations of the mechanism of direct iridium insertion into the arene ring in Cp*Ir(η^4 -arene) complexes are ongoing in our laboratory.

ASSOCIATED CONTENT

Experimental protocols, characterization data and computational details (list of coordinates of all calculated species in xyz files). The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no conflicting financial interests.

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- (12) In the simplest case of two competing paths of the same molecularity, each yielding different products, the ratio of the competing reaction rates depends exponentially on ΔΔH/RT, where ΔΔH is the difference of the (total) activation enthalpies of the two paths. As the temperature increases the exponent, and hence the rate ratio, approaches 1, i.e., the contribution of the two paths becomes more similar, which decreases the selectivity.
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