Chemical
Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2026, **17**, 664

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 21st October 2025
Accepted 31st October 2025

DOI: 10.1039/d5sc08107f

rsc.li/chemical-science

Transient π-coordination enables nucleophilic borylation of simple arenes

Yuichiro Mutoh, *[a] Relam Khalaf,[ab] Sobi Asako [a] and Laurean Ilies *[a]

Borylation of an arene typically proceeds *via* transition-metal-catalyzed C–H activation. We report here that transient π-coordination to chromium activates 1 equiv. of a simple arene towards nucleophilic borylation with $B_2(pin)_2$ in the presence of an additive such as K_2CO_3 or KF. The transient activation of the substrate is achieved *via in situ* ligand exchange with a naphthalene chromium complex, followed by borylation of the resulting arene chromium complex. Electron-rich and sterically hindered arenes, challenging substrates for transition-metal-catalyzed C–H borylation, react well under these conditions. Mechanistic studies support an anionic mechanism, where a borate species undergoes nucleophilic addition to the arene chromium complex, followed by hydride migration.

Introduction

Functionalization of the C–H bond in an arene enables rapid construction of molecular complexity.[1–3] For these reactions to proceed efficiently, specialized substrates such as arenes bearing a directing group,[4] and/or complex catalysts are often required.[5] π-Coordination of a metal fragment is known to decrease the electron density of an arene and has been often used in organic synthesis,[6–11] but applications to the C–H functionalization of arenes remain scarce.[12,13] Recently, Larossa and others showed that palladium-catalyzed C–H arylation of arenes with aryl halides can be enhanced by π-coordination of the arene substrate to chromium or ruthenium (Fig. 1B).[14–25] However, these reactions require the synthesis and isolation of the arene metal complex as a starting material, typically using an excess amount of arene; to the best of our knowledge, there is only one example of generation of an arene chromium complex through arene exchange, followed by one-pot palladium/silver-catalyzed C–H arylation.[20] We report here that 1 equiv. of a simple arene can be borylated with $B_2(pin)_2$ in the presence of a base such as K_2CO_3 or KF, upon transient activation through *in situ* arene exchange with a π-arene chromium complex precursor (Fig. 1C). Mechanistic studies suggest that the reaction proceeds through nucleophilic attack of a borate species to the arene activated by π-coordination, followed by hydride migration.

Results and discussion

Reaction development: a model study

Transition-metal-catalyzed borylation of an arene is one of the most widely utilized C–H functionalization reactions,[26–29] because it proceeds without the need of directing groups, and the boroester group can be easily converted to valuable functionality (Fig. 1A).[30] Iridium has been the mostly used catalyst to date,[31–33] and because oxidative addition is typically the turnover-limiting step, the reactions proceed the best for electron-deficient arenes. We envisioned that transient π-coordination of an arene to a metal fragment such as tricarbonylchromium through arene exchange with an appropriate precursor would decrease its electron density and enable efficient borylation, even for electron-rich substrates (Fig. 1C).

To achieve this scenario, we first studied a model reaction of a xylene chromium complex (**1a-Cr**) with $B_2(pin)_2$ (Table 1). We initially investigated several catalysts often used for C–H borylation such as iridium[24,31–33] or cobalt,[34,35] but a control experiment showed that in the presence of an additive such as K_2CO_3, the reaction proceeds well without the need of the catalyst (entry 1). This result is intriguing, because borylation of an arene without the requirement of a transition metal catalyst has been achieved to date[36] by using electrophilic borylating reagents,[37,38] frustrated Lewis pairs,[39] deprotonative[40] or photochemical conditions.[41] A brief screening of additives (entries 1–7) revealed a puzzling trend: K_2CO_3 and Na_2CO_3 were the most efficient, while Li_2CO_3, KF and KOMe also gave moderate yields (entries 3, 4, and 7). CsF and KO*t*-Bu were largely ineffective (entries 5 and 6). Notably, in the absence of an additive, the reaction did not proceed at all (entry 8). However, despite numerous efforts, the yield could not be further improved by the choice of the additive. Moreover, we also encountered reproducibility issues,

---

[a] *RIKEN Center for Sustainable Resource Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. E-mail: yuichiro.mutoh@riken.jp; laurean.ilies@riken.jp*

[b] *Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan*

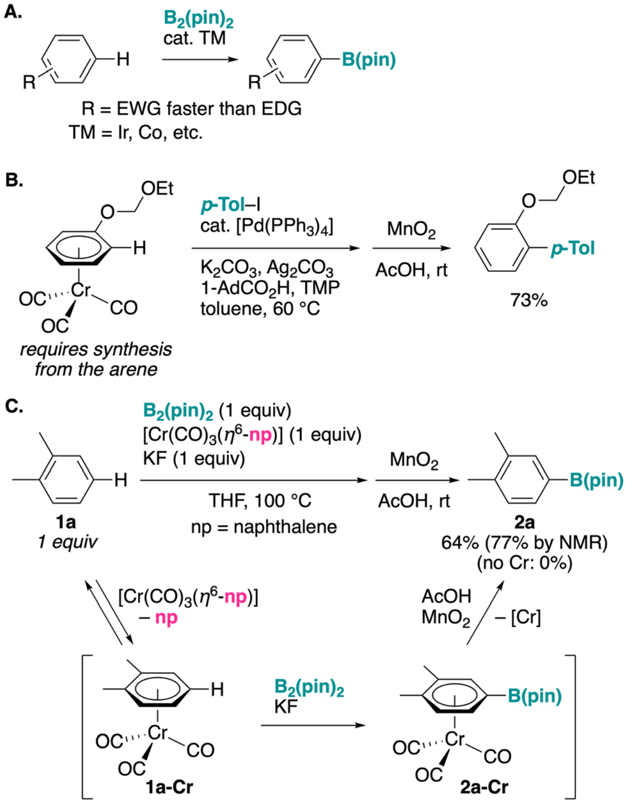
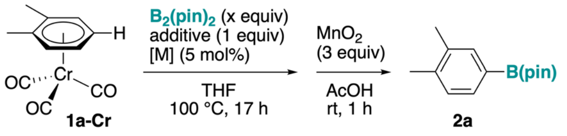


Fig. 1 Strategies for C–H functionalization. (A) Transition-metal-catalyzed borylation of arenes. (B) Palladium-catalyzed arylation of chromium arene complexes prepared from the corresponding arenes prior to use. (C) This work: nucleophilic borylation of electron-rich arenes through transient π-coordination to chromium.

Table 1 Investigation of key parameters for a model reaction, the borylation of **1a-Cr** with $B_2(pin)_2$



Entry	*x*	Additive	[M]	**2a**[a] (%)	**1a**[a] (%)
1	1	K_2CO_3	None	68	28
2	1	Na_2CO_3	None	62	33
3	1	Li_2CO_3	None	38	61
4	1	KF	None	47	49
5	1	CsF	None	5	85
6	1	KO*t*-Bu	None	3	79
7	1	KOMe	None	37	53
8	1	None	None	nd[b]	>99
9	2	K_2CO_3	None	77	27
10	2	K_2CO_3	[Cr(acac)$_3$]	92	8
11	2	None	[Cr(acac)$_3$]	<1	>99
12[c]	2	K_2CO_3	[Cr(acac)$_3$]	nd[b]	>99
13	2	K_2CO_3	[$CrCl_3$]	83	11

[a] The yields were determined using GC in the presence of tridecane as an internal standard. [b] nd = Not detected. [c] **1a** was used instead of **1a-Cr** as the substrate.

with the yields fluctuating in the 40–80% range. We wondered if a small amount of chromium, which may leak from complex **1a-Cr** during the course of the reaction could affect the result, and we added a catalytic amount of [Cr(acac)$_3$] to find that the reaction proceeded reproducibly with a high yield (92% yield as determined by GC, entry 7), when 2 equiv. of borylating reagent was used. The reaction proceeded cleanly, and recovery of the starting material accounted for the rest of the material balance. Product **2a** was obtained after decomplexation using MnO_2/AcOH;[14,15,17,20] for sensitive compounds (**2m** in Fig. 3), we used LED (450 nm) irradiation[42] for decomplexation. Monitoring the reaction mixture before decomplexation by GC and GC/MS confirmed the formation of **2a-Cr** (Fig. S1). The additive is important even in the presence of [Cr(acac)$_3$], and in its absence the reaction did not proceed (entry 11). According to our hypothesis that π-coordination is the key enabler for this reactivity, when we conducted the reaction using **1a** instead of **1a-Cr** as the substrate, the product did not form at all (entry 12). Changing the chromium source to [$CrCl_3$] gave a similarly high yield (entry 13). At the moment, we do not have an explanation for the effect of the added chromium on the reaction of chromium complexes **1-Cr**. The reaction also proceeded well in its absence (entries 1 and 2), but sometimes less reproducibly; as described below (Table 2 and Fig. 2), the *in situ* activation of arenes **1** with a chromium complex precursor does *not* require additional chromium.

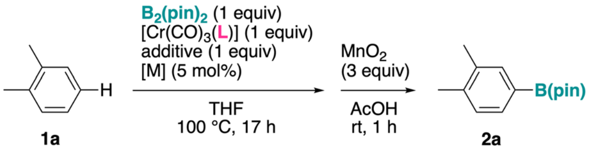
Preliminary scope of the model reaction

Under the optimized conditions (Table 1, entry 10), we briefly investigated the reaction of several arene chromium complexes (Fig. 2). *Ortho*-dialkyl (**1a–1c**) and *ortho*-dialkoxyarenes (**1d**, **1e**) reacted with good yields. Interestingly, the reaction of **1d** and **1e** proceeded with different site selectivity, possibly due to steric control in the reaction of the bulkier **1d**, as opposite to the *ortho*-directing effect in the reaction of the smaller **1e**, as also observed for iridium catalysis.[43] A small amount of diborylated product was also observed in some cases, and its amount increased in the case of **1e**. *Meta*-xylene (**1g**) reacted well, selectively at the least hindered site; however, the borylation proceeded also at the sterically hindered C–H *ortho* to the methyl group (selectivity 14 : 86), whereas iridium-catalyzed borylation is typically sensitive to sterics. Accordingly, sterically demanding *para*-disubstituted alkylbenzenes (**1h** and **1i**) reacted with moderate yields upon prolonged reaction time. Monosubstituted electron-rich arenes such as toluene (**1j**), anisole (**1k**), and phenyltrimethylsilane (**1l**) reacted well, but the product was obtained as a mixture of regioisomers, and diborylation also proceeded. A chromium complex of electron-deficient 1,2-dichlorobenzene (**1f**) reacted poorly, probably because of its lower stability under the reaction conditions.

Activation of an arene through transient π-coordination

Next, we investigated the reaction of a stoichiometric amount of xylene (**1a**) with $B_2(pin)_2$ in the presence of a chromium complex that can undergo arene exchange with **1a** (Table 2). In the presence of a naphthalene (NP) chromium complex, known to

Table 2 Investigation of the key parameters for the borylation of **1a** with $B_2(pin)_2$ in the presence of a chromium complex



Entry	L	Additive	[M]	**2a**[a] (%)	L–B(pin)[a] (%)	**1a**[a] (%)
1	NP[b]	K_2CO_3	None	48	5	50
2	NP	KF	None	67	5	34
3	NP	KF	[Cr(acac)$_3$]	65 (1)[c]	4	28
4[d]	NP	KF	None	44	4	98
5	1,5-DMN[e]	KF	None	58	9	39
6	2,6-DMN[f]	KF	None	63	4	20
7	Pyrene	KF	None	63	3	30
8	TMTACH[g]	KF	None	4	nd[h]	>99
9	3Py[i]	KF	None	nd[h]	10	>99
10[j]	3CO	KF[k]	None	4	nd[h]	98

[a] The yields were determined using GC in the presence of tridecane as an internal standard. [b] NP = naphthalene. [c] Yield of a diborylated product. [d] With 5 equiv. of **1a**. [e] 1,5-DMN = 1,5-dimethylnaphthalene. [f] 2,6-DMN = 2,6-dimethylnaphthalene. [g] TMTACH = 1,3,5-trimethyl-1,3,5-triazacyclohexane. [h] nd = Not detected. [i] Py = pyridine. [j] Under static vacuum. [k] With 2 equiv. of KF.

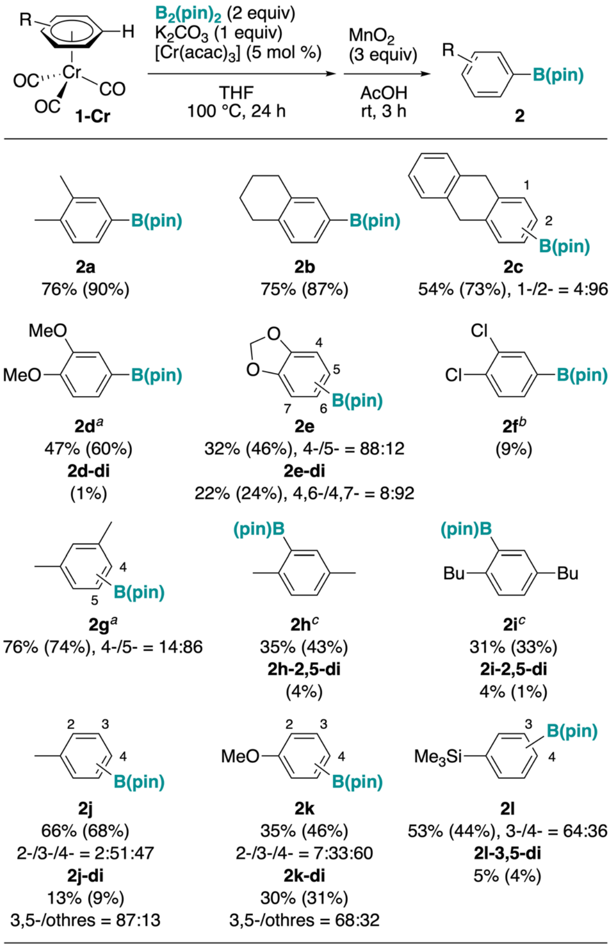


Fig. 2 Preliminary investigation of a model reaction, the borylation of arene chromium complexes **1-Cr**. The yields were determined by isolation; the yields in parentheses were determined by using ^1H NMR or GC in the presence of an internal standard. See the SI for details. [a]Reaction time was 68 h. [b]Reaction time was 17 h. [c]Reaction time was 4 days.

undergo fast arene exchange,[20,44–46] and using K_2CO_3 as an additive, **1a** reacted with $B_2(pin)_2$ in THF at 100 °C to produce **2a** in 48% yield after oxidative demetallation, together with a small amount of borylated naphthalene, and recovery of the substrate in 50% (entry 1). Changing the additive to KF slightly increased the yield (entry 2). In contrast to the reaction of chromium complex **1a-Cr**, a catalytic amount of [Cr(acac)$_3$] did not affect the reaction (entry 3), reinforcing that its presence is not essential for the reaction to proceed. Increasing the amount of substrate did not improve the yield (entry 4). Under the optimal reaction conditions at entry 2, we studied several chromium complex precursors (entries 5–9). To prevent the unproductive borylation of the naphthalene ligand, we used dimethylnaphthalene complexes (entries 5 and 6), but significant improvement was not achieved. A pyrene complex gave a similar result (entry 7). A triamine chromium complex[47] could also be used, albeit with a decreased yield (entry 8). A trispyridine complex did not promote the reaction at all (entry 9). Commercially available [Cr(CO)$_6$] was a less efficient precursor and gave the product in 4% yield, together with recovery of the starting material (entry 10).

Reaction scope for the borylation of arenes (1) *in situ* activated by π-coordination

Under the reaction conditions in Table 2, entry 2, we investigated the reaction of several arene substrates (Fig. 3). To avoid regioselectivity issues and multiborylation, we mainly investigated the reaction of di- and trisubstituted arenes. As expected, the reactivity trend paralleled that of chromium complexes **1-Cr** (Fig. 2), and alkylarenes and electron-rich arenes reacted with moderate yields, slightly lower than those for the corresponding **1-Cr** substrates. In most of the cases, recovery of the starting material accounted for the remaining of the material balance,

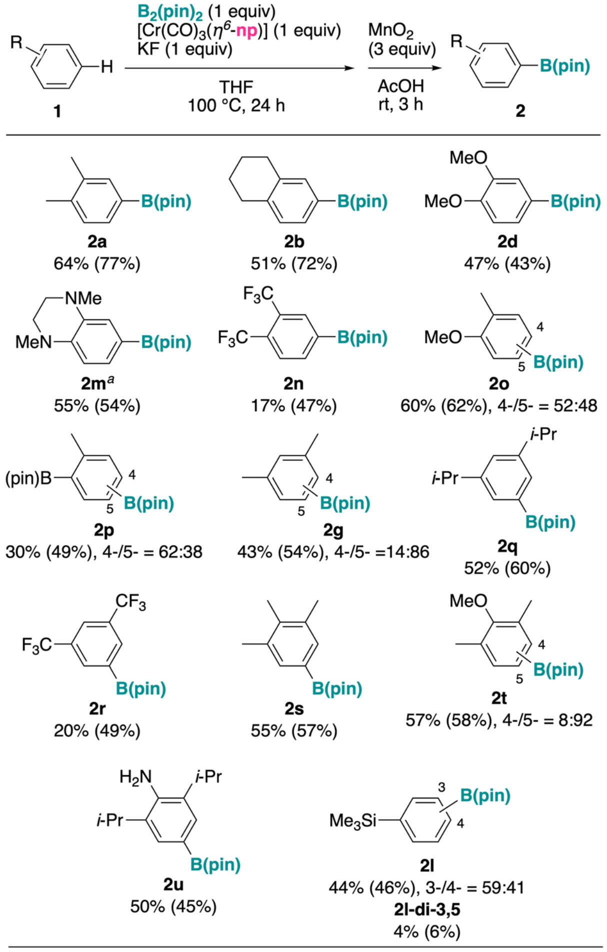


Fig. 3 Borylation of arene **1** in situ-activated by a chromium naphthalene complex. The yields were determined by isolation; the yields in parentheses were determined by using ^{1}H NMR or GC in the presence of an internal standard. See the SI for details. ^{a}LED (450 nm) irradiation for decomplexation.

and a small amount of borylated naphthalene also formed (similarly with the reaction profile of the model substrate **1a** in Table 2, entry 1). *Ortho*-Dialkylbenzenes **1a** and **1b** were borylated at the less sterically hindered position with good yields. Dimethoxybenzene **1d** and diaminobenzene (**1m**), electron-rich substrates challenging for iridium-catalyzed borylation,[48] reacted well. The reaction of an unsymmetric *ortho*-disubstituted arene (**1o**) gave an essentially 1 : 1 mixture of regioisomers. Trisubstituted arenes (**1s–u**) also reacted well. Notably, *ortho*-disustituted aniline (**1u**) reacted without the need of *N*-protection. A monosubstituted arene such as phenyltrimethylsilane (**1l**) reacted well, but a mixture of regioisomers and a small amount of diborylated product was obtained. Using the *in situ* exchange procedure, electron-deficient arenes such as **2n** and **2r** also reacted with moderate yields.

Borylation followed by functionalization

To demonstrate the synthetic utility of π-coordination-enabled borylation, we carried out several representative transformations of boroester **2** (Fig. 4). Suzuki–Miyaura cross coupling of **2a** and **2s** with 4-bromoanisole afforded the corresponding biaryls **1a-Ar** and **1s-Ar**, the latter known to exhibit a relatively large Stokes shift.[49] Iridium-catalyzed deuteration[50,51] of **2s** afforded **1s-*d*$_1$** selectively labeled at C5. Likewise, copper-mediated iodination[52] selectively occurred at the aromatic carbon–boron bond to give the aryl iodide **1b-I**, which is typically obtained *via* a Sandmeyer reaction from the corresponding aniline precursor, method that requires multiple synthetic steps.

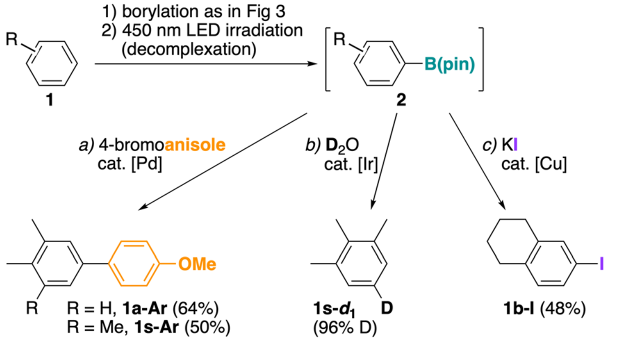


Fig. 4 Borylation of **1**, followed by derivatization of **2**. (a) 4-Bromoanisole (1.2 equiv.), [Pd$_2$(dba)$_3$]·CHCl$_3$ (2.5 mol%), XPhos (5 mol%), K$_3$PO$_4$ (3 equiv.); THF/H$_2$O (10 : 1), 80 °C, 12 h. (b) D$_2$O (10 equiv.), [{Ir(cod)(OMe)}$_2$] (2 mol%); THF, 80 °C, 3 h. (c) KI (3 equiv.), [CuI] (10 mol%), Phen (20 mol%); MeOH/H$_2$O (4 : 1), 80 °C, 12 h.

Preliminary mechanistic studies

As shown in Table 1, entry 1, the borylation of a chromium arene complex proceeds without the need of a transition metal catalyst, even if the influence of trace amounts of chromium leaked into solution cannot be completely ruled out. To get insights into the mechanism of this reaction, we performed experimental and theoretical preliminary studies. Radical intermediates or single-electron transfer steps are likely not involved, because the reaction was not inhibited by scavengers such as 9,10-dihydroanthracene (**1c-Cr**, Fig. 3) or 1,4-bis(trifluoromethyl)benzene (Section 4.1 in SI),[53–55] and 1,5-hydrogen transfer was not observed when a complex of 1,4-dibutylbenzene (**1i-Cr**) was used as the substrate (Fig. 2).

The necessary presence of base (Table 1, entries 8 and 11) suggests the involvement of an anionic species. Activation of B$_2$(pin)$_2$ by a base to generate a nucleophilic borate species is well documented in the literature.[56,57] We could not find examples of the attack of such anionic borate species to simple arenes in the literature, but the nucleophilic addition of strong organometallic compounds to arene chromium complexes is known.[58] Also, recent reports on the attack of an Al(I) anion to simple arenes[59–61] suggest that a similar reactivity of borate species is plausible. We reacted trifluorobenzene **1v** under the optimized reaction conditions, and we obtained a mixture of C–H borylated products **2v** and nucleophilic aromatic substitution products **3v** (Fig. 5A),[62] as was also observed for the alumination reaction.[60] Moreover, we also performed a KIE study for two parallel reactions, to find a primary KIE of 2.4, similar to the value observed for the alumination reaction (1.7).[60]

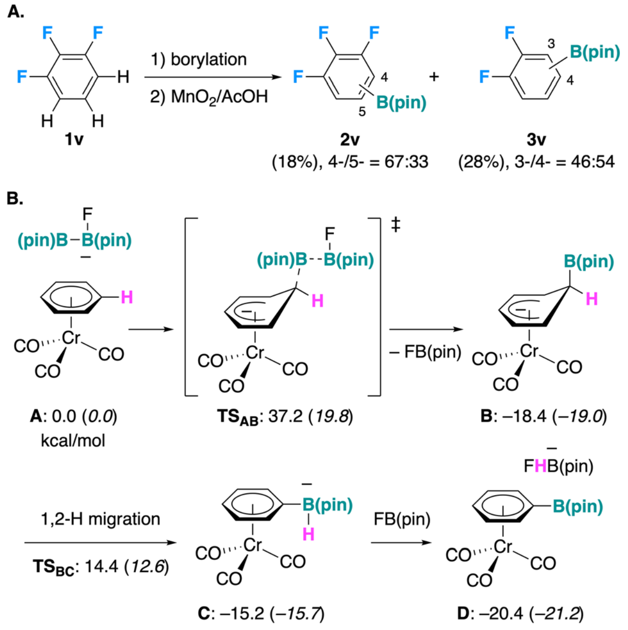


Fig. 5 Mechanistic considerations. (A) Competition between C–H nucleophilic borylation and nucleophilic aromatic substitution. (B) A proposed mechanism. Relative Gibbs energies and enthalpies (italicized) calculated at the M06/SDD:6-31+G(d,p)$_{\text{THF(SMD)}}$//B3LYP-D3/SDD:6-31+G(d,p) level of theory (373.15 K) are shown.

Based on the considerations above, and a very recent example of nucleophilic aromatic substitution of hydrogen in arenes π-coordinated to ruthenium,[63] we propose the mechanism depicted in Fig. 5B, which was also probed by DFT calculations.[64] A base such as fluoride first activates $B_2(pin)_2$ as a borate species, which then attacks the arene coordinated to chromium (**A**) with concomitant C–B bond formation and B–B bond cleavage, releasing F(Bpin). Note that coordination of arene to a $[Cr(CO)_3]$ fragment is well known to enhance the nucleophilic attack of organometallic reagents for example.[58] The resulting intermediate (**B**) then rearomatizes through 1,2-hydride shift from carbon to boron to afford an arylboronate product (**C**, then **D**).

Conclusions

We found that a stoichiometric amount of a simple arene can be transiently activated by π-coordination to chromium *via in situ* ligand exchange with a naphthalene chromium complex, to enable nucleophilic C–H borylation with $B_2(pin)_2$ in the presence of a base such as K_2CO_3 or KF. Electron-rich and sterically biased arenes, challenging substrates for transition-metal-catalyzed borylation, reacted well using the π-coordination strategy.

Author contributions

Y. M.: formal analysis, funding acquisition, investigation, methodology, resources, supervision, validation, visualization, writing – original draft, review and editing. R. K.: formal analysis, investigation, validation. S. A.: formal analysis, methodology, visualization, writing – original draft, review and editing. L. I.: conceptualization, funding acquisition, investigation, project administration, supervision, visualization, writing – original draft, review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data for the manuscript "Transient π-Coordination Enables Nucleophilic Borylation of Simple Arenes" have been included as part of the supplementary information (SI). Supplementary information: experimental procedures, characterization data, compound data, computational data, and copies of NMR charts. See DOI: **https://doi.org/10.1039/d5sc08107f**.

Acknowledgements

This work was supported by JSPS KAKENHI Grant-in-Aid for Scientific Research (B) No. JP25K01777 (L. I.), Grant-in-Aid for Transformative Research Areas No. JP24H01101 (Digi-TOS) (L. I.), JSPS KAKENHI Grant Number JP22K05104 (Y. M.), and RIKEN Incentive Research Project grant (Y. M.). Computational time provided by the Research Center for Computational Science, Okazaki, Japan (Projects: 24-IMS-C061, 25-IMS-C063) and the RIKEN HOKUSAI BigWaterfall are gratefully acknowledged. We thank Dr Zhaomin Hou and Dr Masanori Takimoto (RIKEN) for generously allowing us to use the mass spectrometer.

Notes and references

1 G. Dyker, in *Handbook of C–H Transformations*, ed. G. Dyker, Wiley-VCH, Weinheim, 2005.
2 P. H. Dixneuf and H. Doucet, in *Topics in Organometallic Chemistry: C–H Bond Activation and Catalytic Functionalization*, ed. P. H. Dixneuf and H. Doucet, Springer, Berlin, 2016.
3 J.-Q. Yu, in *Catalytic Transformations via C–H Activation, Science of Synthesis*, ed. J.-Q. Yu, Thieme, Stuttgart, vols 1–2, 2016.
4 S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda and N. Chatani, Efficient Catalytic Addition of Aromatic Carbon-Hydrogen Bonds to Olefins, *Nature*, 1993, **366**, 529–531.
5 S. Rej, A. Das and N. Chatani, Strategic Evolution in Transition Metal-Catalyzed Directed C–H Bond Activation and Future Directions, *Coord. Chem. Rev.*, 2021, **431**, 213683.
6 E. P. Kündig, *Topics in Organometallic Chemistry: Transition Metal Arene π-Complexes in Organic Synthesis and Catalysis*, Springer-Verlag, Berlin Heidelberg, 2004.
7 M. Rosillo, G. Domínguez and J. Pérez-Castells, Chromium Arene Complexes in Organic Synthesis, *Chem. Soc. Rev.*, 2007, **36**, 1589–1604.

8 S. Takemoto and H. Matsuzaka, Recent Topics on Catalytic Transformations of Aromatic Molecules *via* η^6-Arene Transition Metal Complexes, *Tetrahedron Lett.*, 2018, **59**, 697–703.

9 J. W. Walton and L. A. Wilkinson, π-Coordinated Arene Metal Complexes and Catalysis, *Organomet. Chem.*, 2019, **42**, 125–171.

10 L. J. Williams, Y. Bhonoah, L. A. Wilkinson and J. W. Walton, As Nice as π: Aromatic Reactions Activated by π-Coordination to Transition Metals, *Chem.–Eur. J.*, 2020, **27**, 3650–3660.

11 K. Chen and H. Shi, Nucleophilic Aromatic Substitution of Halobenzenes and Phenols with Catalysis by Arenophilic π Acids, *Acc. Chem. Res.*, 2024, **57**, 2194–2206.

12 F. Hu and M. Szostak, Pd-Catalyzed C–H Activation: Expanding the Portfolio of Metal-Catalyzed Functionalization of Unreactive C–H Bonds by Arene–Chromium π-Complexation, *ChemCatChem*, 2015, **7**, 1061–1063.

13 Y. Mutoh and L. Ilies, Activation of Strong Bonds Enabled by Arene π-Coordination, *Synthesis*, 2025, **57**, 2783–2792.

14 P. Ricci, K. Krämer, X. C. Cambeiro and I. Larrosa, Arene–Metal π-Complexation as a Traceless Reactivity Enhancer for C–H Arylation, *J. Am. Chem. Soc.*, 2013, **135**, 13258–13261.

15 P. Ricci, K. Krämer and I. Larrosa, Tuning Reactivity and Site Selectivity of Simple Arenes in C–H Activation: Ortho-Arylation of Anisoles *via* Arene–Metal π-Complexation, *J. Am. Chem. Soc.*, 2014, **136**, 18082–18086.

16 D. Whitaker, J. Burés and I. Larrosa, Ag(I)-Catalyzed C–H Activation: The Role of the Ag(I) Salt in Pd/Ag-Mediated C–H Arylation of Electron-Deficient Arenes, *J. Am. Chem. Soc.*, 2016, **138**, 8384–8387.

17 D. Whitaker, M. Batuecas, P. Ricci and I. Larrosa, A Direct Arylation-Cyclisation Reaction for the Construction of Medium-Sized Rings, *Chem.–Eur. J.*, 2017, **23**, 12763–12766.

18 L. A. Wilkinson, J. A. Pike and J. W. Walton, C–H Activation of π-Arene Ruthenium Complexes, *Organometallics*, 2017, **36**, 4376–4381.

19 M. Batuecas, J. Luo, I. Gergelitsová, K. Krämer, D. Whitaker, I. J. Vitorica-Yrezabal and I. Larrosa, Catalytic Asymmetric C–H Arylation of (η^6-Arene)Chromium Complexes: Facile Access to Planar-Chiral Phosphines, *ACS Catal.*, 2019, **9**, 5268–5278.

20 A. Panigrahi, D. Whitaker, I. J. Vitorica-Yrezabal and I. Larrosa, Ag/Pd Cocatalyzed Direct Arylation of Fluoroarene Derivatives with Aryl Bromides, *ACS Catal.*, 2020, **10**, 2100–2107.

21 M. J. Fuchter, D. K. Judge, M. Weimar and A. J. P. White, Stoichiometric C–H Arylation of Tricarbonyl(Arene) Chromium Complexes Bearing Pyridine Directing Groups, *Dalton Trans.*, 2013, **42**, 5615–5618.

22 E. M. D'Amato, C. N. Neumann and T. Ritter, Selective Aromatic C–H Hydroxylation Enabled by η^6-Coordination to Iridium(III), *Organometallics*, 2015, **34**, 4626–4631.

23 C. Odena, M. Perez-Jimenez, R. Lin and P. J. Chirik, Exploring the Site Selectivity of Arene Oxidation in (η^5-C$_5$Me$_5$)Ir(η^6-arene)$_2$ Complexes, *Organometallics*, 2024, **43**, 3067.

24 W.-Q. Wu, Y. Lin, Y. Li and H. Shi, Catalytic Dehydrogenative (3 + 2) Cycloaddition of Alkylbenzenes *via* π-Coordination, *J. Am. Chem. Soc.*, 2023, **145**, 9464–9470.

25 While this manuscript was in preparation, an example of iridium-catalyzed borylation of chromium arene complexes was reported: A. Mandal, C. Maurer, C. Plett, K. R. K. Chandramohan, R. Fleischer, G. Schnakenburg, S. Grimme and A. Bunescu, Selective C–H Borylation of Polyaromatic Compounds Enabled by Metal-Arene π-Complexation, *J. Am. Chem. Soc.*, 2025, **147**, 15281–15293.

26 I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. B. Murphy and J. F. Hartwig, C–H Activation for the Construction of C–B Bonds, *Chem. Rev.*, 2010, **110**, 890–931.

27 J. F. Hartwig, Borylation and Silylation of C–H Bonds: A Platform for Diverse C–H Bond Functionalizations, *Acc. Chem. Res.*, 2012, **45**, 864–873.

28 L. Xu, G. Wang, S. Zhang, H. Wang, L. Wang, L. Liu, J. Jiao and P. Li, Recent Advances in Catalytic C–H Borylation Reactions, *Tetrahedron*, 2017, **73**, 7123–7157.

29 R. Bisht, C. Haldar, M. M. M. Hassan, M. E. Hoque, J. Chaturvedi and B. Chattopadhyay, Metal-Catalysed C–H Bond Activation and Borylation, *Chem. Soc. Rev.*, 2022, **51**, 5042–5100.

30 D. G. Hall, *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, Wiley-VCH, Weinheim, 2005.

31 T. Ishiyama, J. Takagi, K. Ishida, N. Miyaura, N. R. Anastasi and J. F. Hartwig, Mild Iridium-Catalyzed Borylation of Arenes. High Turnover Numbers, Room Temperature Reactions, and Isolation of a Potential Intermediate, *J. Am. Chem. Soc.*, 2002, **124**, 390–391.

32 T. Ishiyama, J. Takagi, J. F. Hartwig and N. Miyaura, A Stoichiometric Aromatic C–H Borylation Catalyzed by Iridium(I)/2,2′-Bipyridine Complexes at Room Temperature, *Angew. Chem., Int. Ed.*, 2002, **41**, 3056–3058.

33 J. Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka Jr. and M. R. Smith III, Remarkably Selective Iridium Catalysts for the Elaboration of Aromatic C–H Bonds, *Science*, 2002, **295**, 305–308.

34 J. V. Obligacion, P. J. Semproni and P. J. Chirik, Cobalt-Catalyzed C–H Borylation, *J. Am. Chem. Soc.*, 2014, **136**, 4133–4136.

35 N. G. Léonard, M. J. Bezdek and P. J. Chirik, Cobalt-Catalyzed C(sp^2)–H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(acetate) Precatalyst, *Organometallics*, 2017, **36**, 142–150.

36 H. Zhang and L. Wang, Metal-Free Catalytic Aromatic C–H Borylation, *Synlett*, 2020, **31**, 1857–1861.

37 J. Lv, X. Chen, X.-S. Xue, B. Zhao, Y. Liang, M. Wang, L. Jin, Y. Yuan, Y. Han, Y. Zhao, Y. Lu, J. Zhao, W.-Y. Sun, K. N. Houk and Z. Shi, Metal-Free Directed sp^2-C–H Borylation, *Nature*, 2019, **575**, 336–341.

38 L. Britton, A. D. Bage, S. L. McOnie and S. P. Thomas, Multifaceted Hidden Catalysis Revealed by Mechanistic

Analysis of FeBr$_3$-Catalysed Arene Borylation, *Angew. Chem., Int. Ed.*, 2025, **64**, e202423929.

39 M.-A. Légaré, M.-A. Courtemanche, E. Rochette and F.-G. Fontaine, Metal-Free Catalytic C–H Bond Activation and Borylation of Heteroarenes, *Science*, 2015, **349**, 513–516.

40 X. Liu, D. Li, G. Li, M. Wei, S. Yuan, M. Yang, L. He, S. Chen, Z. Li, L. Gao, G. Wang and S. Li, Organometallic-type Reactivity of Stable Organoboronates for Selective (Hetero) arene C−H/C-halogen Borylation and Beyond, *Nat. Commun.*, 2025, **16**, 5458.

41 A. M. Mfuh, V. T. Nguyen, B. Chhetri, J. E. Burch, J. D. Doyle, V. N. Nesterov, H. A. Arman and O. V. Larionov, Additive- and Metal-Free, Predictably 1,2- and 1,3-Regioselective, Photoinduced Dual C−H/C−X Borylation of Haloarenes, *J. Am. Chem. Soc.*, 2016, **138**, 8408–8411.

42 K. Li, W. Wu, Y. Lin and H. Shi, Asymmetric hydrogenation of 1,1-diarylethylenes and benzophenones through a relay strategy, *Nat. Commun.*, 2023, **14**, 2170.

43 B. A. Vanchura II, S. M. Preshlock, P. C. Roosen, V. A. Kallepalli, R. J. Staples, R. E. Maleczka Jr., D. A. Singleton and M. R. Smith III, Electronic Effects in Iridium C–H Borylations: Insights from Unencumbered Substrates and Variation of Boryl Ligand Substituents, *Chem. Commun.*, 2010, **46**, 7724–7726.

44 E. P. Kündig, C. Perret, S. Spichiger and G. Bernardinelli, Naphthalene Complexes V. Arene Exchange Reactions in Naphthalenechromium Complexes, *J. Organomet. Chem.*, 1985, **286**, 183–200.

45 J. A. S. Howell, N. F. Ashford, D. T. Dixon, J. C. Kola, T. A. Albright and S. K. Kang, The Arene-Exchange Reaction in Naphthalene- and Pyrene Chromium Tricarbonyl, *Organometallics*, 1991, **10**, 1852–1864.

46 M. Wang, W. Zeng, L. Chen, Y. Yuan and W. Li, Umpolung-Enabled Divergent Dearomative Carbonylations, *Angew. Chem., Int. Ed.*, 2024, **63**, e202403917.

47 N. L. Armanasco, M. V. Baker, M. R. North, B. W. Skelton and A. H. White, Chromium(0) Tricarbonyl Complexes of 1,3,5-Triazacyclohexanes, *J. Chem. Soc., Dalton Trans.*, 1997, **3**, 1363–1368.

48 Y. Jin, B. Ramadoss, S. Asako and L. Ilies, Noncovalent Interaction with a Spirobipyridine Ligand Enables Efficient Iridium-Catalyzed C–H Activation, *Nat. Commun.*, 2024, **15**, 2886.

49 X. Liu, Y. Zhang, B. Li, L. N. Zakharov, M. Vasiliu, D. A. Dixon and S.-Y. Liu, A Modular Synthetic Approach to Monocyclic 1,4-Azaborines, *Angew. Chem., Int. Ed.*, 2016, **55**, 8333–8337.

50 V. A. Kallepalli, K. A. Gore, F. Shi, L. Sanchez, G. A. Chotana, S. L. Miller, R. E. Maleczka and M. R. Smith, Harnessing C–H Borylation/Deborylation for Selective Deuteration, Synthesis of Boronate Esters, and Late Stage Functionalization, *J. Org. Chem.*, 2015, **80**, 8341–8353.

51 R. Oeschger, B. Su, I. Yu, C. Ehinger, E. Romero, S. He and J. Hartwig, Diverse functionalization of strong alkyl C–H bonds by undirected borylation, *Science*, 2020, **368**, 736–741.

52 B. M. Partridge and J. F. Hartwig, Sterically Controlled Iodination of Arenes *via* Iridium-Catalyzed C–H Borylation, *Org. Lett.*, 2013, **15**, 140–143.

53 T. Niwa, H. Ochiai, Y. Watanabe and T. Hosoya, Ni/Cu-Catalyzed Defluoroborylation of Fluoroarenes for Diverse C–F Bond Functionalizations, *J. Am. Chem. Soc.*, 2015, **137**, 14313–14318.

54 T. Niwa, H. Ochiai and T. Hosoya, Copper-Catalyzed Ipso-Borylation of Fluoroarenes, *ACS Catal.*, 2017, **7**, 4535–4541.

55 Y.-M. Tian, X.-N. Guo, I. Krummenacher, Z. Wu, J. Nitsch, H. Braunschweig, U. Radius and T. B. Marder, Visible-Light-Induced Ni-Catalyzed Radical Borylation of Chloroarenes, *J. Am. Chem. Soc.*, 2020, **142**, 18231–18242.

56 J. J. Carbó and E. Fernández, Alkoxide Activation of tetra-Alkoxy Diboron Reagents in C–B Bond Formation: a Decade of Unpredictable Reactivity, *Chem. Commun.*, 2021, **57**, 11935–11947.

57 Z. Liu, G. K. Kole, Y. P. Budiman, Y. Tian, A. Friedrich, X. Luo, S. A. Westcott, U. Radius and T. B. Marder, Transition Metal Catalyst-Free, Base-Promoted 1,2-Additions of Polyfluorophenylboronates to Aldehydes and Ketones, *Angew. Chem., Int. Ed.*, 2021, **60**, 16529–16538.

58 For example:(*a*) M. F. Semmelhack and G. Clark, Meta-Substituted Aromatics by Carbanion Attack on π-Anisole and π-Toluenechromium Tricarbonyl, *J. Am. Chem. Soc.*, 1977, **99**, 1675–1676; (*b*) R. Bigler and V. K. Aggarwal, *ortho*-Directing Chromium Arene Complexes as Efficient Mediators for Enantiospecific C(sp^2)–C(sp^3) Cross-Coupling Reactions, *Angew. Chem., Int. Ed.*, 2018, **57**, 1082–1086.

59 J. Hicks, P. Vasko, A. Heilmann, J. M. Goicoechea and S. Aldridge, Arene C−H Activation at Aluminium(I): meta Selectivity Driven by the Electronics of S$_N$Ar Chemistry, *Angew. Chem., Int. Ed.*, 2020, **59**, 20376–20380.

60 S. Kurumada, K. Sugita, R. Nakano and M. Yamashita, A Meta-Selective C−H Alumination of Mono-Substituted Benzene by Using An Alkyl-Substituted Al Anion through Hydride-Eliminating S$_N$Ar Reaction, *Angew. Chem., Int. Ed.*, 2020, **59**, 20381–20384.

61 J. J. Cabrera-Trujillo and I. Fernández, Factors Controlling the Aluminum(I)-Meta-Selective C−H Activation in Arenes, *Chem.–Eur. J.*, 2021, **27**, 12422–12429.

62 The formation of **3v-4** having a boryl group at the C4 position can be explained by a second borylation of **2v-5** and **3v-3** followed by protodeborylation. See the SI for details.

63 S. Melnikov, D. Hwang, B. Park, M. Lutz, M.-H. Baik and D. L. J. Broere, Ruthenium-mediated Nucleophilic Aromatic Substitution of Hydrogen in Benzene, *Chem. Sci.*, 2025, **16**, 13422–13434.

64 However, we cannot completely exclude alternative mechanisms such as C–H borylation by a low-valent chromium species at the moment; Y. Mutoh, R. Khalaf, S. Asako and L. Ilies, Transient π-Coordination Enables Nucleophilic Borylation of Simple Arenes, *ChemRxiv*, 2025, preprint, DOI: 10.26434/chemrxiv-2025-bszc1-v3.