C−H Activation

Selective Benzylic CH-Borylations by Tandem Cobalt Catalysis

Pradip Ghosh, Roland Schoch, Matthias Bauer, and Axel Jacobi von Wangelin*

Dedicated to Barry M. Trost on the occasion of his 80th birthday

Abstract: *Metal-catalyzed C−H activations are environmentally and economically attractive synthetic strategies for the construction of functional molecules as they obviate the need for pre-functionalized substrates and minimize waste generation. Great challenges reside in the control of selectivities, the utilization of unbiased hydrocarbons, and the operation of atom-economical dehydrocoupling mechanisms. An especially mild borylation of benzylic CH bonds was developed with the ligand-free pre-catalyst Co[N(SiMe₃)₂]₂ and the bench-stable and inexpensive borylation reagent B₂pin₂ that produces H₂ as the only by-product. A full set of kinetic, spectroscopic, and preparative mechanistic studies are indicative of a tandem catalysis mechanism of CH-borylation and dehydrocoupling via molecular Co^I catalysts.*

Introduction

Catalytic methods of CH-bond functionalization of easily available hydrocarbons constitute key strategic steps in the generation of synthetically valuable molecular building blocks (Scheme 1, top).[1] Among metal-catalyzed C−H functionalizations, borylation protocols are especially attractive by virtue of the availability of various borane reagents and the diverse reactivity of the resultant polarized C−B bond in onward reactions, for example, oxidation, cross-coupling, insertion, metallation, rearrangement.[2,3] Major progress was made in the development of transition metal-catalyzed arene borylations that provide arylboron derivatives (Scheme 1, middle).[2–5] Iridium catalysts have most successfully been employed in these reactions that operate via oxidative addition of the aryl-H substrates with high tolerance of functional groups. Alkyl-H moieties are typically much less reactive under these conditions. CH-borylations of alkyl-H
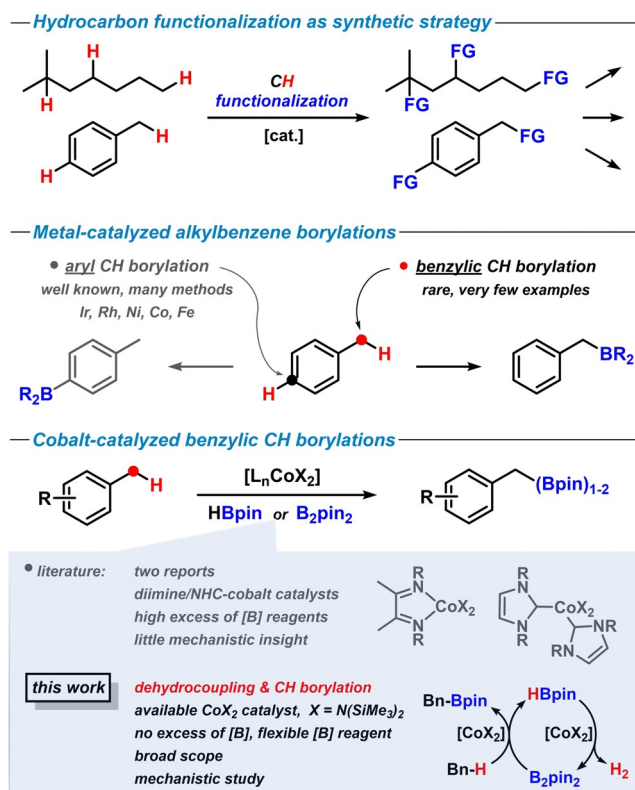
Scheme 1. Catalytic borylations as strategic hydrocarbon functionalization (top). Cobalt-catalyzed benzylic CH borylations (bottom).

moieties are far less advanced and mostly require pre-functionalized substrates, directing groups, and/or forcing conditions.[4b,6] Very few protocols of undirected C_{sp3}−H borylations in benzylic positions have been reported with Ir, Rh, Pd, Co and Ni catalysts.[5c,7–10] Recently, benzylic CH-borylations were observed with two distinct L_2CoX_2 pre-catalysts: An α-diimine cobalt(II) bis(carboxylate) enabled geminal diborylation of alkyl-arenes using combinations of B₂pin₂ and HBpin as borylation reagents in excess (pin = pinacolato).[8] A cobalt(II) *t*-butoxide bearing *N*-heterocyclic carbene ligands afforded mixtures of mono/diboronates in the presence of excess amounts of HBpin.[9] Despite recent progress, the development of efficient methods of selective C_{sp3}−H borylations with first-row transition metals is still in its infancy. Reactions that operate with simple, inexpensive catalysts under mild conditions and display broad substrate scope, high product selectivity, and effective use of the employed borane reagents are being sought. Further, there is very little knowledge of the underlying mechanisms. Here, we report an efficient cobalt-catalyzed CH-borylation protocol with cobalt(II) bis(hexamethyldisilazide), Co(hmds)₂, under

[*] Dr. P. Ghosh, Prof. Dr. A. Jacobi von Wangelin
Dept. of Chemistry, University of Hamburg
Martin Luther King Pl 6, 20146 Hamburg (Germany)
E-mail: axel.jacobi@uni-hamburg.de

Dr. R. Schoch, Prof. Dr. M. Bauer
Dept. of Chemistry, Center for Sustainable Systems Design, CSSD,
University of Paderborn
33098 Paderborn (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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mild conditions. The inexpensive catalyst fulfills dual roles: *i)* catalytic borylation of benzyl C_{sp3}–H positions with B_2pin_2, and *ii)* catalytic dehydrocoupling of HBpin. This tandem cobalt catalysis allows the flexible use of borylation reagents (HBpin or B_2pin_2) and the complete transfer of all boron atoms in the hydrocarbon borylation (Scheme 1, bottom).

Results and Discussion

In continuation of recent studies of catalytic hydrogenations and hydrofunctionalizations with non-rare earth metal catalysts (Li, Mn, Fe) in our laboratories,[11] we have considered the related mechanistic scenarios of the reverse reactions involving metal-catalyzed dehydrocoupling events.[12] The activation of borane reagents R_2B-X by a Lewis basic metal catalyst (such as metal amides) in the presence of activated CH bonds (such as benzyl-H) may serve as an entry into a CH borylation reaction.[2,13] We initiated our investigations with the model reaction between toluene and the inexpensive and crystalline boronate source bis(pinacolato) diboron, B_2pin_2 (Scheme 2, top).[7,8,10] With 5 mol% Co-(hmds)$_2$, excellent conversion and near-perfect chemo-specificity toward benzylic CH-borylation were obtained. The reaction resulted in the clean formation of the double borylation product, benzyl diboronate, at 80 °C in *n*-hexane. Fe(hmds)$_2$ gave moderate yields; cobalt catalysts without the basic, nucleophilic, and lipophilic hmds ligand were not active. No boronate products were detected in the absence of catalyst. Interestingly, the reaction exhibited much higher atom economy than related literature reports[8,9] as only 1 equiv B_2pin_2 sufficed for near-quantitative diboronate formation. With B_2pin_2 as starting material, the cobalt-catalyzed dehydroborylation of toluene is believed to produce low concentrations of HBpin as a primary by-product which itself is most likely engaging in another dehydrocoupling reaction. The latter event can involve toluene or another molecule of HBpin as reaction partner, respectively, to give benzyl boronate or B_2pin_2 upon release of 1 equiv H_2. In full accord with these hypotheses, both dehydrocoupling reactions operated under very similar conditions with the Co-(hmds)$_2$ catalyst (Scheme 2, middle and bottom). The CH-borylation of toluene with B_2pin_2 (1 equiv) is about twice as fast as with HBpin (2 equiv) under identical conditions. Both reactions do not require excess amounts of the borylation reagents and produce H_2 as the only by-product (vide infra). The cobalt-catalyzed toluene borylation protocol appears to be highly selective toward the benzylic C_{sp3}–H position: no reaction of the arene moiety and the solvent *n*-hexane was observed. The choice of B_2pin_2 as the more attractive substrate is governed by its lower price, easier handling, and thermal stability.

The optimized conditions were then applied to a diverse set of substituted alkylarenes (Scheme 3). Substituted toluene derivatives were converted to the benzyl diboronates in moderate to good yields (mostly 50–90 %), while the benzyl monoboronates were only minor products (< 5 % for toluene; 10–20 % for other methylarenes). The benzyl diboronates were separated from the monoboronates by SiO$_2$ column
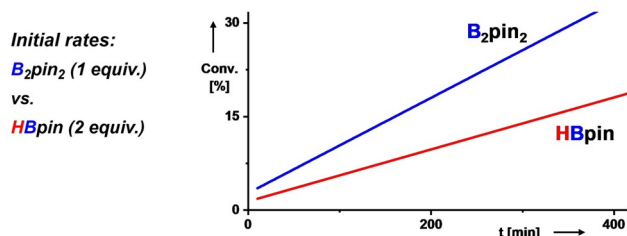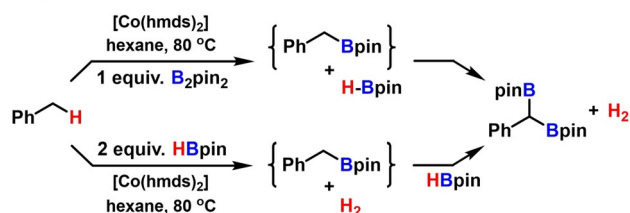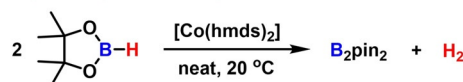
Initial observations:
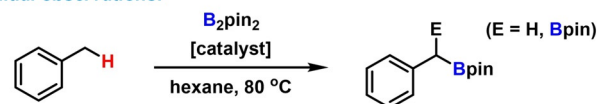
Entry	Catalyst (mol%)	Conversion of B_2Pin_2 (%)[a]
1	-	<5
2	CoBr$_2$ (10)	<5
3	CoBr$_2$ (5) + Lihmds (10)	13
4	**Co(hmds)$_2$ (5)**	**>99 (46)[b]**
5	Co(OAc)$_2$ (5)	12
6	Fe(hmds)$_2$ (5)	73
7	Mn(hmds)$_2$ (5)	23

Conditions: 0.5 mmol toluene, 0.5 mmol B_2pin_2, catalyst, 1 mL *n*-hexane, 80 °C, 20 h. [a] from quantitative GC-FID vs. internal *n*-pentadecane. [b] 20 °C.

Dehydroborylation of toluene:


Dehydroborylation of HBpin:

Borylation reagents:

| HBpin	B_2pin_2
100 g, >100 € (in 2021)	100 g, <50 € (in 2021)
~150 € per mol [B]	~50 € per mol [B]
liquid, (thermo)sensitive	crystalline solid, stable

Scheme 2. Cobalt-catalyzed dehydroborylations: Optimization of toluene borylation (top). Dehydroborylations of toluene and HBpin under similar conditions (middle). Choice of borylation reagents (bottom). hmds = hexa-methyldisilazide, N(SiMe$_3$)$_2$; pin = pinacolato, -OCMe$_2$-CMe$_2$O-.

chromatography (isolated yields are given). Silyl, Bpin, amine, ether, and alkyl substituents were tolerated at the arene. Reaction of 4-methoxytoluene gave minor amounts of C–OMe cleavage product (27 %).[14] Very electron-rich benzyl diboronates were sensitive to protodeborylation and oxidation. The crude mixture of benzyl diboronates and benzyl monoboronates (95/5 to 80/20 ratio) could be converted to the stable benzyl monoboronates in high yields by protolysis with NEt$_3$/SiO$_2$ (isolated yields given). *Ortho-*, *meta-*, and *para-*xylenes gave good yields (65–77 %) of mixtures of α,α-diboronates, α,α'-tri- and tetra-boronates with 2.1 equiv B_2pin_2 (Scheme 3, middle). Geminal α,α-
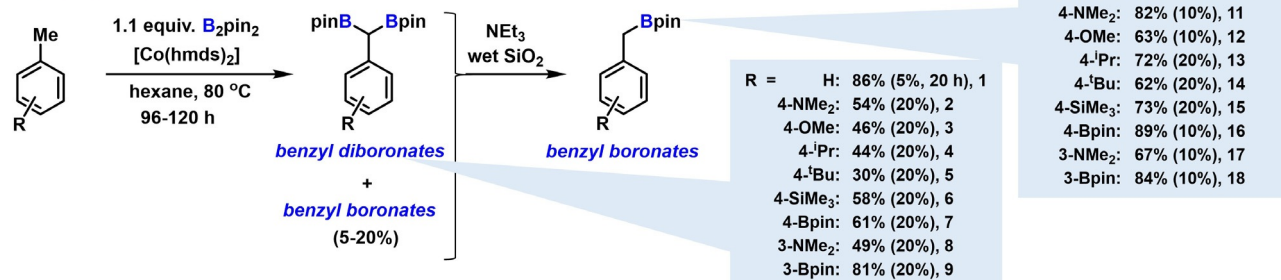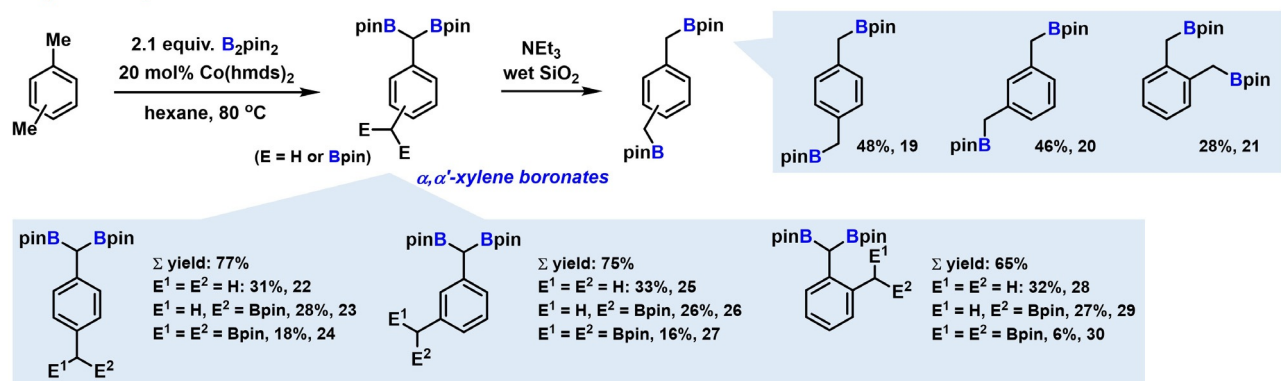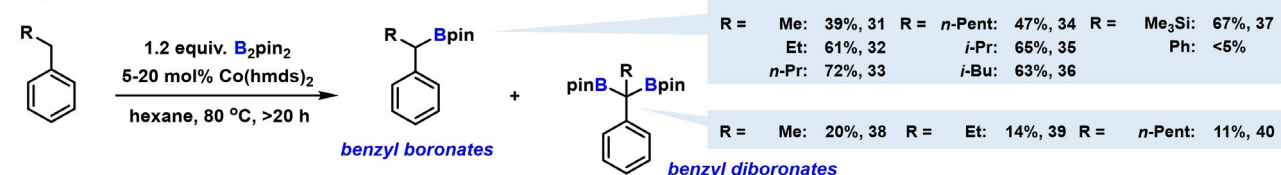
Scheme 3. Borylation of methylarenes (top), xylenes (middle), and alkylarenes (bottom). [a] Isolated yields. Catalyst loading in parentheses. See ESI for details.

diborylation was favoured over α,α′-diborylation. Notably, benzyl diboronates have potential applications in enantioselective reactions[15a] and complex molecule syntheses.[15b] Alkylbenzenes with longer side chains exhibited lower reactivity and afforded the benzyl monoboronates as major products, possibly due to steric repulsion (Scheme 3, bottom). Only 10–20 % of α,α-diborylation were observed for *n*-alkyl benzenes; only traces were formed with the bulkier *i*-butyl and SiMe_3 substituents. Diphenylmethane showed very low reactivity.

Mechanistic studies

We have performed several insightful mechanistic experiments to identify the nature of the operating catalyst which has remained ambiguous in previous reports.[9] Key observations were made in stoichiometric reactions between the precatalyst and reagents, successful trapping reactions of intermediate species, *operando* X-ray absorption spectroscopy, and kinetic studies of reaction progress, reaction orders, and isotope effects.

a) Kinetic studies: The borylation of toluene with 5 mol % Co(hmds)_2 and B_2pin_2 (1.0 equiv) follows a pseudo-1st order rate behaviour. From a van't Hoff plot ln k_{obs} vs. ln[cat] an order in catalyst concentration of ≈1.2 was determined which indicates a monometallic mechanism. The individual order in B_2pin_2 was 0 (zero), that of toluene ≈1 (Table S1). Our studies of a kinetic isotopic effect (KIE)[16] documented identical rates of toluene and d_5-toluene and identical rates of reactions of d_3-toluene and [D_8]toluene, respectively, under identical conditions (Figure S1). The observed k_H/k_D ratio of ≈2.8 suggests a 1° KIE and rate-determining benzylic C−H cleavage by the catalyst, which is in full accord with 1st order rate dependence on toluene concentration.

b) Dehydrocoupling reactions: The borylation of toluene is much slower with HBpin as boronate source than with B_2pin_2 under identical conditions (Scheme 2). In borylations with B_2pin_2, the first CH borylation forms HBpin as by-product which engages subsequently in another CH borylation to give benzyl diboronate. Alternatively, HBpin can undergo acceptorless dehydrocoupling to give B_2pin_2 and H_2 (Scheme 2). The high (primary) KIE makes these reactions very slow for DBpin so that it accumulates as intermediate and can be detected in considerable amounts (Figure S2).

Consistent with these observations, the formation of DBpin and D_2 was observed under catalytic conditions with *[D$_8$]toluene* as substrate (^{1}H, ^{2}H, ^{11}B NMR). The formed D_2 was used in the Pd/C-catalyzed deuterogenation of styrene to give *d$_2$*-ethyl-benzene (Figure S3). The dehydrogenative coupling of HBpin to B_2pin_2 in the presence of Co(hmds)$_2$ gives low yields (< 10%), possibly due to the rapid activation of B_2pin_2 by the catalyst. An indirect proof of this dehydrocoupling is the reaction of the formed B_2pin_2 with 4,4′-bipyridine which is known to react in a formal 1,8-addition.[17] Consistently, we isolated *N,N′*-diboryl-4,4′-bipyridin-ylidene in 73% yield when reacting HBpin (2 equiv) and Co(hmds)$_2$ (5 mol%) in toluene solution in the presence of 4,4′-bipyridine. There is no reaction in the absence of cobalt catalyst.

c) Colours and UV/Vis spectra: All successful methylarene borylation reactions with catalytic Co(hmds)$_2$ displayed characteristic solution colours. Treatment of the pre-catalyst Co(hmds)$_2$ with toluene and B_2pin_2 in hexane resulted in an immediate colour change from green to violet/blue prior to the onset of product formation. Over the course of the reaction, the solution turned rapidly brown. The characteristic blue colour was observed with all arenes including toluene (and the other reactive methylarenes) but also with benzene and naphthalene, so that π-arene coordination to the cobalt complex may be considered. In hexane or methylcyclohexane, the solution colour did not change. UV-vis spectra of mixtures of Co(hmds)$_2$, B_2pin_2 and arenes absorption bands in the 350–370 and 500–650 nm ranges while no absorption bands were visible in alkane solutions (Figure S4).

d) Trapping of reactive intermediates: We performed poisoning experiments of the catalyst under the reaction conditions in an effort to distinguish homotopic and heterotopic mechanisms.[18] Addition of trimethylphosphine (PMe$_3$, 0.1–1 equiv per Co) or dibenzo[*a,e*]cyclooctatetraene (dct, 4 equiv per Co) led to full inhibition of catalyst turnover (Figure S5). From these observations, (equilibrating) homogeneous and hetero-geneous catalyst species may be concluded. Addition of catalytic amounts of the radical scavenger 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO, 1 equiv per Co) completely inhibited the reaction (Figure S6).[19] Organic TEMPO adducts were not observed.

e) Stoichiometric reactions, byproducts, and catalyst derivatives: The operation of acid-base reactivity in the catalytic borylation mechanism was excluded, as treatment of toluene derivatives with equimolar Co(hmds)$_2$ at 80 °C and workup in D_2O did not show any D-incorporation. The equimolar reaction of B_2pin_2 and Co(hmds)$_2$ in hexane exhibited clean formation of pinB-N(SiMe$_3$)$_2$ (^{11}B-NMR: 25 ppm) and another boron-containing compound (^{11}B: 34 ppm), possibly a cobalt boryl complex (Figure S7).[20] From this crude reaction mixture, the literature-known tetrameric cobalt cluster [CoN(SiMe$_3$)$_2$]$_4$ was crystallized (while its characteristic ^{1}H-NMR signals were not observed in the crude reaction).[13] The formation of cobalt amido clusters from reactions containing equimolar amounts of the Lewis acidic component [Bpin] and the Lewis base [N(SiMe$_3$)$_2$] is especially noteworthy and may be indicative of the special role of the amido ligand hmds in the borylation catalysis mechanism.
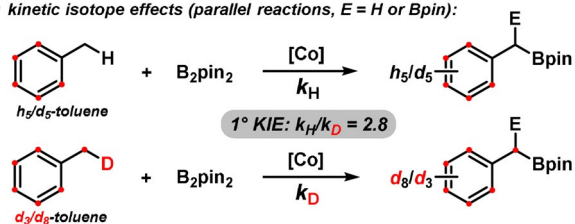
In perfect agreement with this assumption is the isolation of Co(hmds) complexes and the quantification of B_2pin_2 conversion: An equimolar mixture of Co(hmds)$_2$ and B_2pin_2 in C_6D_6 turned immediately blue; ^{1}H NMR spectra showed formation of 1 equiv (Me$_3$Si)$_2$N-Bpin per Co(hmds)$_2$ (Figure S8). The conversion of B_2pin_2 was ≈60% (GC-FID). Addition of phosphine ligands (PPh$_3$, PCy$_3$) to the blue solution of Co(hmds)$_2$ and B_2pin_2 (2:1) in benzene enabled the isolation of cobalt(I) complexes [Co(PR$_3$)$_2$(hmds)] in high yields (e.g. 72% yield, PPh$_3$) (Figure S9).[21] This observation strongly suggests that *i)* the amido ligand hmds may act as a stable spectator ligand under the conditions of the borylation reaction, and *ii)* cobalt(I) catalysts may be operative in the mechanism. The interaction of a postulated cobalt boryl catalyst with π-arenes (such as the substrate toluene) was corroborated by the isolation of the unusual π-cyclohexadienyl boronate cobalt complex (dcpe)Co(η^5-C$_6$H$_6$-Bpin) from the reaction of Co(hmds)$_2$ and B_2pin_2 in benzene followed by addition of 1,2-bis(dicyclohexyl-phosphino)-ethane (dcpe) (Figure S10).[22]

f) X-ray absorption (XAS) spectroscopy provides insight into the nature of metal complexes under reaction conditions. Oxidation states, the number and type of coordinating atoms, and the nucleation of metallic species and coordination compounds can be derived from XAS experiments.[23] The XANES (X-ray absorption near edge structure) spectra of the pre-catalyst Co(hmds)$_2$ in hexane and the reaction mixture of Co(hmds)$_2$, B_2pin_2, and toluene showed distinct features that may be indicative of the coordination of both reactants to the cobalt center (see Figure S11). This is in perfect agreement with the formation of 1 equiv pinB-N(SiMe$_3$)$_2$ and a blue Co complex from equimolar reactions of Co(hmds)$_2$ and B_2pin_2 in toluene (Scheme 4, center). Time-resolved XANES spectra also showed a continuous change of the spectral signatures over the reaction time and the formation of Co nanoparticles (NP) at the end of the reaction (Figures S11–S15). The spectral signatures of the XANES region were translated into structural parameters by analysis of the EXAFS (extended X-ray absorption fine structure) spectra (Figure 1). Monomer and dimer species of Co(hmds)$_2$ were observed (0.3 Co-Co back-scatterers at 2.61 Å distance).[24] This equilibrium shifts completely to dimeric species upon addition of B_2pin_2 (1.0 back-scattering Co). The changes in the XANES spectra can be interpreted by Bpin-coordination to cobalt. (Optimized data fits were obtained from an additional carbon coordination sphere at 2.40 Å which may result from weak interactions with the solvent; see Scheme 6 for CH-borylation of hexane and Figure S16.) After addition of toluene to the reaction, a dimeric catalyst species with additional carbon back-scattering contributions at (the typical π-arene-metal bond distance of) 2.10 Å was observed.[25] At the end of the reaction, EXAFS data documented nanoparticle formation (Co−Co coordination numbers, distances) which appear to contain (surface) light atoms from Bpin or hmds coordination (see ESI for details).
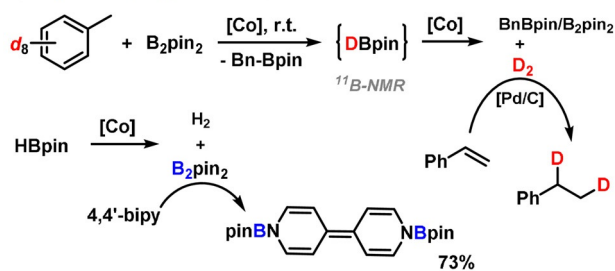
Based on the collected data from preparative, kinetic, isotope labelling, NMR, and X-ray spectroscopy studies, we postulate a reaction mechanism involving Co^I catalysts that may form through bimetallic reductive elimination of 1 equiv
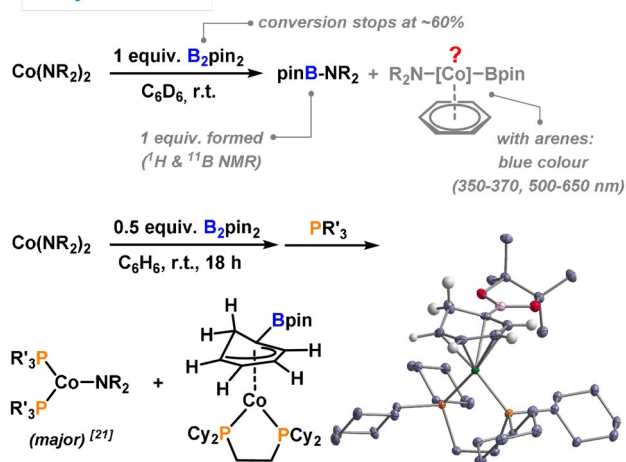
Scheme 4. Key mechanistic experiments: Reaction orders, kinetic isotope effects (top). Products of the dehydrocoupling reactions of toluene and HBpin (center). Stoichiometric reactions toward Co^I catalyst derivatives (bottom); molecular structure of (dcpe)Co(η^5-C$_6$H$_6$-Bpin).
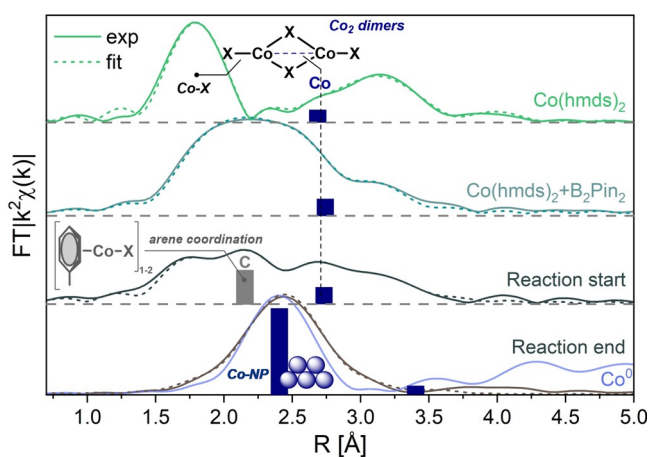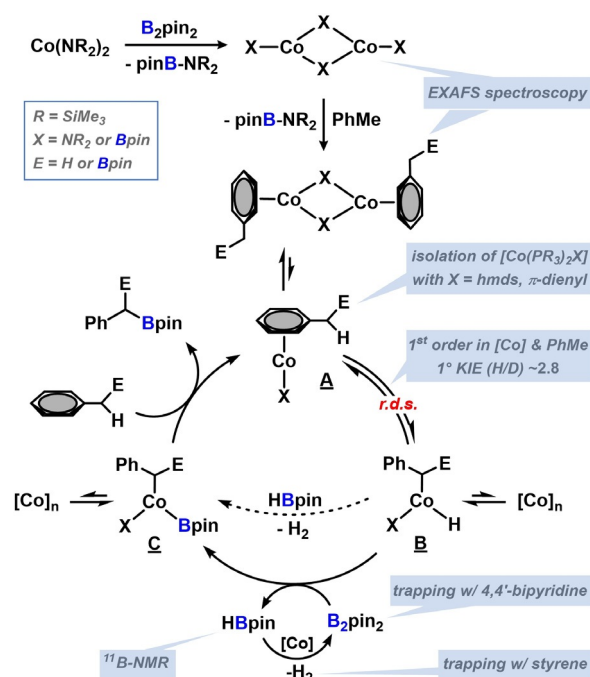

Figure 1. EXAFS spectra with atomic distances, selected back-scattering atoms (Co–Co, grey bars; Co–C(toluene), blue bars), and postulated catalyst species.


Scheme 5. Postulated mechanism of the benzylic CH borylation involving pre-catalyst reduction to a Co^I catalyst (top), toluene borylation (center), and dehydrocoupling of HBpin to B$_2$pin$_2$ and H$_2$ (bottom).

(Me$_3$Si)$_2$N-Bpin from dimeric CoX$_2$ pre-catalysts (Scheme 5, top).[26] The π-coordination of arenes to Co^I complexes (**A**) sets the stage for benzylic CH activation that is most likely facilitated by concomitant B-B cleavage (σ-bond metathesis).[27] Elimination of the benzyl boronate regenerates an active Co^I catalyst. The produced HBpin undergoes another benzylic CH borylation (slower than benzylation of B$_2$pin$_2$) or cobalt-catalyzed dehydrocoupling to give B$_2$pin$_2$ and H$_2$. It is important to note that the chemoselectivity of CH-borylation was very high (Scheme 6). At room temperature, rapid H/D exchange of benzene (after 1 h: 9% deuteration) and toluene (66% deuteration, Figure S17) with HBpin was observed, whereas borylation was the major pathway at >60°C (and with B$_2$pin$_2$ as borylation reagent). Aryl-H borylation only occurred at elevated temperatures and neat conditions (PhH,

full conversion at 80°C, 72 h, by ^{11}B-NMR). Minor amounts of alkyl-H activation of the solvent *n*-hexane were observed in some cases. Traces of alkane borylation were detected from the reaction of cyclooctane with 20 mol% catalyst at 100°C under neat conditions (Scheme 6, bottom).

Conclusion

A new cobalt-catalyzed benzylic CH borylation is reported that produces H$_2$ a byproduct in an overall acceptorless dehydro-coupling reaction. This reaction operates with Co-(hmds)$_2$ as pre-catalyst and the bench-stable and inexpensive
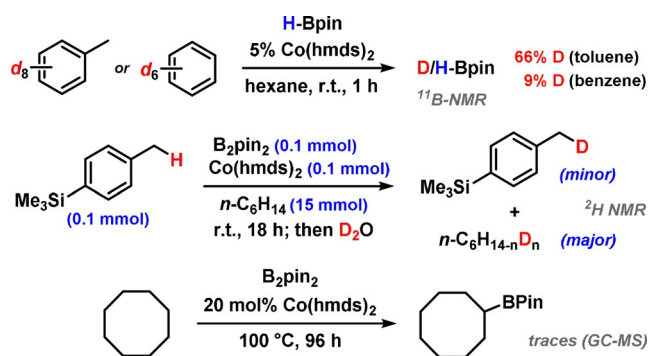
Scheme 6. Competing pathways of aryl, benzyl, and alkyl C—H activations.

B₂pin₂ under mild conditions to give benzyl diboronates and, after protolytic workup, benzyl boronate derivatives. No excess of borylation reagents is required. A full set of mechanistic studies was performed that support the notion of a tandem cobalt catalysis that involves benzylic borylation and borane dehydrocoupling events under identical reaction conditions with H_2 being the only byproduct. Kinetic, spectroscopic, and preparative experiments were indicative of rate-limiting CH activation, the conservation of the amido ligand during catalysis, the presence of dimeric Co^I catalyst species, and π-arene coordination motifs. The borylation reaction is highly chemospecific for benzyl-CH bonds; the activation of aryl-H and alkyl-H positions were not competing under the reaction conditions. The compatibility with different borane sources and the zero-order rate behavior in borane strongly indicate that this method can serve as a template for related CH functionalizations.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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