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Revisiting Claims of the Iron-, Cobalt-, Nickel-, and Copper-Catalyzed Suzuki Biaryl Cross-Coupling of Aryl Halides with Aryl Boronic Acids

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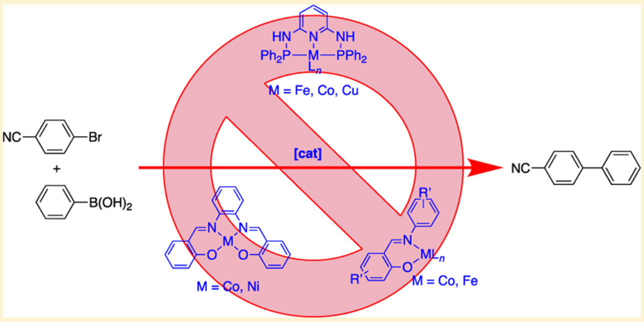
Supporting Information

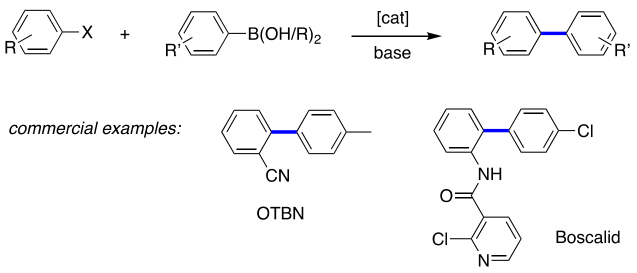
ABSTRACT: Intrigued by recent reports on the surprisingly excellent activity of a range of cobalt-, iron-, copper-, and nickel-based catalysts in the Suzuki biaryl cross-coupling of simple aryl boronic acids with aryl halides, we undertook a reexamination of the syntheses of representative examples of the reported precatalysts and their application to the catalytic reaction. A reported PNP−Fe pincer complex proved to be a mixture of starting materials; a mono-Schiff base cobalt complex in fact the bis-ligated adduct and a monomeric copper(II) PNP−pincer complex a di- or oligomeric copper(I) species. In our hands, neither these complexes nor any other of the selected precatalysts investigated showed any activity in a Suzuki cross-coupling reaction of an electronically activated aryl bromide with phenyl boronic acid. Meanwhile, switching the nucleophile to the BuLi-activated phenyl boronic pinacol ester gave some promising activity with cobalt precatalysts.



INTRODUCTION

The Suzuki biaryl cross-coupling reaction[1] (Scheme 1) is a robust and widely used method for the formation of aryl−aryl bonds. Commercial applications that have exploited Suzuki biaryl bond formation include the synthesis of 2-cyano-4′-methyl biphenyl, an intermediate in the production of a range of the sartan class of drugs for the treatment of hypertension, and boscalid, a broad-spectrum fungicide used in crop protection.[2]

Scheme 1. Suzuki Biaryl Cross-Coupling and Selected Commercial Applications



A vast majority of Suzuki biaryl cross-coupling reactions rely on palladium-based catalysts. However, the high cost of this metal, combined with the need to remove it to the low ppm level from active pharmaceutical intermediates,[3] has inspired the hunt for more sustainable catalysts for Suzuki cross-coupling based on cheap, readily available first-row transition metals. Of these, nickel-[4−6] and copper-catalyzed[7,8] Suzuki cross-coupling reactions are arguably the most well developed. Of particular note is the coupling of aryl halides with aryl boronic acids, as this represents the simplest, yet perhaps most synthetically valuable, variant of the cross-coupling reaction.[4,5,6a,7]

Cobalt-catalyzed Suzuki biaryl cross-coupling is rapidly developing[9] but is currently largely limited to the coupling of aryl boronic esters, activated with either an organolithium reagent or an alkoxide base, rather than free aryl boronic acids. Meanwhile, despite growing success in iron-catalyzed Suzuki couplings,[10] simple biaryl cross-coupling under mild conditions[11] remains limited to either highly activated 2-pyridyl or 2-pyrimidyl halide substrates,[10a] or aryl halide substrates that can engender directed aryl halide activation.[12] Again, in all of these cases, the free boronic acid cannot be exploited, rather a tetraorganoborate or an activated aryl boronic ester is required.

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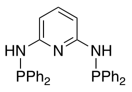
A series of apparent exceptions to the failure to exploit simple aryl boronic acids using Fe and Co (as well as Cu and Ni) precatalysts have recently been published across five papers by Bhat and co-workers.[13] The authors reported that attractively simple precatalysts based on the easily produced ligands **1**−**3** and closely related ligands all show good to excellent activity in the highly desirable Suzuki coupling of aryl halides with aryl boronic acids. Intrigued as to why these classes of ligands should confer such exceptional activity in a profoundly important, yet previously elusive, process, we undertook a reexamination of the authors' reported syntheses of representative examples of precatalysts based on these ligands, as well as structurally well-defined or previously reported analogues, and their application in Fe-, Co-, Ni- and Cu-catalyzed Suzuki biaryl cross-coupling, and the results from this study are summarized below.[14]



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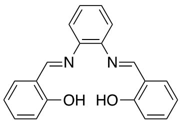

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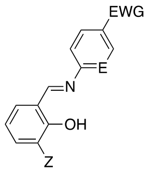


3a: E = CH; Z = OMe; EWG = C(O)Me
b: E = N; Z = OMe; EWG = Br
c: E = CH; Z = H; EWG = C(O)Me

■ RESULTS AND DISCUSSION

Attempted Syntheses of the Precatalysts. The Co and Ni complexes of ligand **2** (salophen), complexes **4** and **5**, respectively, have been reported many times; indeed, they are commercially available and were readily prepared by Bhat's procedures.[13d] The IR data we obtained for the complexes were in agreement with the data reported in the literature,[15] while the NMR spectroscopic data of the diamagnetic Ni(II) complex **5** were in accord with literature values.[15b] Bhat reported a value of 1.23 μ_B for the solid-state magnetic moment of complex **4**,[13d] which we note is far too low for a pure sample; low-spin square-planar cobalt(II) complexes typically show "normal" room-temperature magnetic moments in the range 2.1−2.9 μ_B,[16] while the room-temperature magnetic moment of closely related cobalt(II) salen has variously been reported in the range 2.2−2.7 μ_B.[17] We obtained a room-temperature magnetic moment for **4** of 3.02 μ_B, essentially identical to a previously reported value.[15d]

The synthesis of the bis-Schiff base iron complex **6a** was attempted according to Bhat's method from hydrated iron(III) chloride and ligand **3a** in aqueous ethanol at reflux temperature.[13c] As reported by Bhat, we obtained a purple solid and the IR and UV spectroscopic data (see the Supporting Information) were in broad agreement with the reported data. Bhat reported a magnetic moment of 1.8 μ_B for complex **6a**,[13c] which is a little surprising given that iron(III) chloride bis-Schiff base adducts are reported to be high-spin (S = 5/2).[18] Indeed, a density functional theory (DFT) computational analysis of the ground-state structure of **6a** (B3LYP-D3BJ/cc-pVTZ//cc-pVDZ) showed the S = 5/2 configuration to be preferred over the S = 1/2 configuration by around 23 kcal/mol.

Perhaps, the most important data in support of the proposed formulation is the ESI mass spectrum of **6a** presented by Bhat,[13c] which shows a single mass peak at m/z = 568.10, as well as single mass peaks consistent with the loss of chloride and the appearance of free Schiff base ligand. While this mass is consistent with $[MH]^+$, the complete absence of any isotopic pattern is highly surprising, if not incredible, not least due to the large contribution to the pattern expected for the ^{37}Cl isotope, which is entirely absent.[19] It is also worth noting that while the peak in the mass spectrum is labeled as appearing at m/z = 568.10, the x-axis on the spectrum would seem to put the peak nearer to m/z = 584, clearly inconsistent with the formulation.[13c] The nanospray-MS spectrum we recorded for the purple compound does not show this unusual peak but instead, among others, significant peaks at m/z = 506.5, 1012.0, and 1518.5. The observed masses and isotope patterns are consistent with either the iron-containing species, being a monomer, dimer, and trimer of an as yet undetermined composition, or fragmentation of the trimeric species.

Taken together, the data are inconsistent with the formulation of **6a**. Structurally characterized examples of bis-Schiff base Fe(III) chloride complexes of the general type **6** are surprisingly rare with, to the best of our knowledge, only two reported in the literature,[20] while the products of reactions of $FeCl_3$ with Schiff base ligands are highly dependent on the presence or absence of water (note here water is used as a cosolvent in ethanol at reflux temperature) and the presence or absence of base.[18] Nevertheless, the purple solid "**6a***" was used, as is, in subsequent Suzuki cross-coupling reactions (vide infra). Meanwhile, we prepared the previously reported, closely related complex **6b**[20b] and used the same synthetic approach to prepare what we believe is a genuine sample of **6a**. The HR-electrospray ionisation-mass spectrometry (HR-ESI-MS) of **6a** prepared this way showed a peak at m/z = 568.0820 corresponding to $[MH]^+$ (calculated m/z = 568.0847), with the expected isotope distribution pattern (see Figure S4, Supporting Information). Both of the complexes **6a** and **6b** were investigated in the Suzuki reaction (vide infra).

From the outset, the reported formulation of the cobalt complex **7**[13e] appeared extremely unlikely to us, first, because the proposed κ^3-N,O,O-chelation appeared impossibly strained, as is clearly apparent from the distorted tetrahedral and square-planar geometries obtained from DFT calculations (B3LYP-D3BJ/cc-pVDZ) of both the high- and low-spin ground-state configurations, respectively (Figure 1). Second, while many structurally characterized cobalt bis-Schiff base complexes are known, monoadducts of simple aryl Schiff bases are rare.[21] Furthermore, Bhat reported that complex **7** has a low-spin (S = 1/2) ground-state electronic configuration,[13e] based on a (presumably ambient temperature) solid-state magnetic moment measurement of 1.26 μ_B,[13e] a value far too low for a typical Co(II) low-spin complex. In addition, the low-spin assignment is perhaps unexpected for a five-coordinate Co(II) with only a single Schiff base ligand and moderate to weak-field

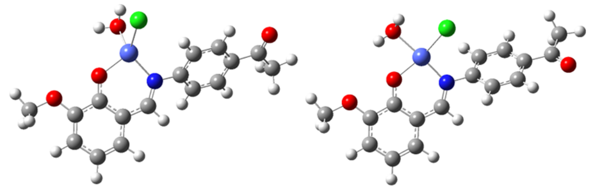


Figure 1. DFT (B3LYP-D3BJ/cc-pVDZ)-calculated high-spin (left) and low-spin ground-state geometries for the putative complex **7**. Single point energy calculations at the B3LYP-D3BJ/cc-pVTZ//cc-pVDZ level of theory indicate that the high-spin structure is preferred by around 12.2 kcal/mol.

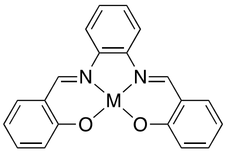
coligands. Indeed, DFT calculations (B3LYP-D3BJ/cc-pVTZ//cc-pVDZ) of the putative complex **7** revealed a significant preference for a high-spin ground-state configuration at room temperature of around 12.2 kcal/mol, suggesting that the reported low-spin configuration for this mononuclear complex is unlikely, at least at room temperature.[22]

Following the synthetic procedure reported by Bhat for complex **7**,[13e] namely, heating 1 equivalent of ligand **3a** with hydrated cobalt(II) chloride in ethanol gave a red-brown solid, the same solid was produced on reaction of cobalt chloride with 2 equivalents of **3a** (see Figure S10, Supporting Information for UV−vis spectroscopic data). The IR spectroscopic data for the sample produced from a 2:1 ratio of **3a**/$CoCl_2 \cdot 6H_2O$ matched the data reported by Bhat.[13e] Taken together, the data do not support the reported formulation of **7** but indicate that the reaction instead yields a bis-Schiff base adduct, **8a**, irrespective of the ratio of ligand to metal used. The high-resolution spectrum supported the formulation of **8a**, with a peak at m/z = 596.1338 corresponding to the $[MH]^+$ ion (calculated m/z = 596.1358), with the anticipated isotope distribution pattern (Figure S11, Supporting Information).[23] The room-temperature magnetic moment recorded of 4.02 μ_B is consistent with a tetrahedral $S = 3/2$ Co(II) complex. Finally, it should be noted that Bhat reported separately that, in sharp contrast, the equivalent reaction with the analogous Schiff base derived from salicylaldehyde gives the bis-Schiff base complex **8b**,[13c] a finding with which we concur.

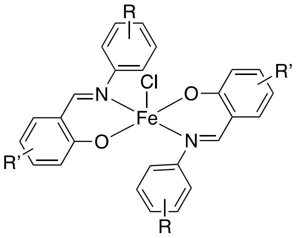
We next reexamined the reported syntheses of iron, cobalt, and copper complexes of the PNP−pincer ligand **1**. The synthesis of the iron-containing complex **9** was attempted following Bhat's reported procedure,[13b] which consisted of heating ligand **1** with $[Fe(OH_2)_6]SO_4 \cdot H_2O$ in tetrahydrofuran (THF) at reflux temperature for 4 h. In our hands, this gave a pale brown precipitate that proved insoluble in THF, dichloromethane, acetonitrile, and acetone. An IR spectrum of the precipitate was essentially identical to that of the starting material, hydrated iron(II) sulfate (see Figure S15), dominated by a large, broad peak at 1081 cm^{-1} corresponding to the sulfate ion. Removal of the solvent from the supernatant from the synthetic reaction gave a pale brown residue, which proved to be predominantly the free ligand **1**, as determined by ^1H and ^{31}P NMR spectroscopy. In summary, in our hands at least, no reaction was obtained between ligand **1** and hydrated ferrous sulfate. The same results were obtained on repeated attempts.

The reaction of ligand **1** with cobalt(II) acetate, employing the method of Bhat,[13a] gave a brown solid whose IR spectrum (Figure S19) had some similar peaks to those reported for complex **10**, most notably those associated with the acetate ligands. The ESI-MS spectrum of a methanol solution (Figure S20) showed, along with higher mass peaks, a peak of m/z = 627.1 consistent with loss of an acetate ligand from **10** and coordination of a solvent molecule. Attempts to produce crystals of **10** suitable for X-ray analysis were unsuccessful, and at this stage, we remain hesitant about the assignment of the structure.

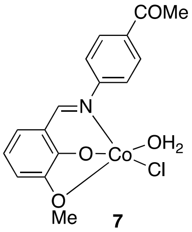
Our attempts to produce the reported copper complex **11** by the method described by Bhat from $Cu(OAc)_2 \cdot H_2O$ proved fruitless.[13b] The NMR spectroscopic data obtained (see Figures S21−S24, Supporting Information) for the product mixture was entirely inconsistent with a monometallic Cu(II)



4: M = Co
5: M = Ni



6a: R = 4-COMe; R' = H
b: R = 2,6-$^iPr_2$, R' = H



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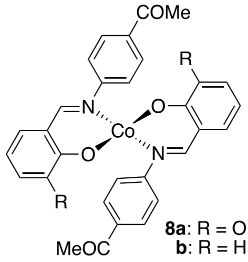
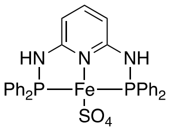


8a: R = OMe
b: R = H



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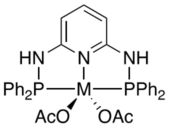
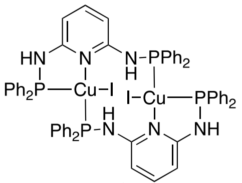


10: M = Co
11: M = Cu

species of the formulation **11**. First, the ^1H NMR spectrum showed peaks in the standard range for a diamagnetic complex, whereas, as formulated, the monomeric complex **11** should be paramagnetic, with $S = 1/2$. Second, the ^{31}P spectrum showed, in addition to some free ligand **1**, an AB system with broad doublets observed at δ 24.1 and 20.3 ppm with a mutual coupling of around 166 Hz and a very broad, featureless peak centered at around ∼17 ppm. Interestingly, the same AB pattern was observed when the reaction was repeated with copper(I) acetate as the precursor, along with other peaks indicative of di- or polymetallic products. In addition, the ESI-MS of the product mixture indicated some oxidation of the ligand **1** to a diphosphine oxide, which in turn coordinated to a copper center.[24] Taken together, the data indicate that if the mononuclear copper(II) complex **11** is indeed produced at any stage, it undergoes very facile reduction to copper(I) with concomitant oxidation of the phosphine residues.[25] This is perhaps not surprising in view of the well-known instability of Cu(II)−phosphine adducts with respect to facile reduction to Cu(I), especially in the presence of even trace amounts of adventitious water,[26] such as the water of crystallization in the copper(II) acetate used in the reported synthesis of **11**.[13b] Furthermore, reported copper(I) often consists of dimetallic or higher-order copper clusters rather than monometallic complexes; indeed, dinuclear Cu(I) complex formation has been demonstrated previously for ligand **1**.[27]

In view of the facile reduction of the putative intermediate **11** to a mixture of dimeric (or higher nuclearity) Cu(I) species and in light of the proven catalytic activity of copper(I) complexes in the Suzuki coupling of aryl iodides with aryl boronic esters,[8f] we decided instead to focus our efforts on a well-defined Cu(I) complex of ligand **1**, the previously reported dimeric copper(I) iodide species, complex **12**, which could be readily prepared and isolated according to a literature method.[27a]



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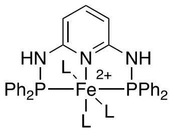
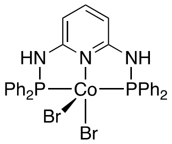


13: L = NCMe



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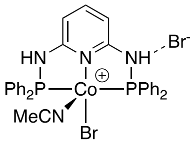

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Similarly, our lack of success in preparing complex **9** as reported, or indeed any tractable material other than starting materials, led us to investigate another closely related iron-based analogue containing ligand **1**. The best catalytic activity reported for the material described as complex **9** was obtained in acetonitrile.[13] Therefore, we reasoned that if **9** were indeed accessible, when dissolved in acetonitrile, as per the reported catalytic conditions, it would be highly likely to form the adduct $[\mathrm{Fe}(\mathbf{1})(\mathrm{NCMe})_3]^{2+}$, **13**, which has previously been reported and structurally characterized as the tetrafluoroborate, $[\mathbf{13}][\mathrm{BF}_4]$, by Kirchner and co-workers.[28] This complex was therefore synthesized and examined as a well-defined precatalyst (vide infra).

While the data we obtained for complex **10** were not entirely inconsistent with those reported by Bhat,[13a] in the absence of definitive structural characterization, we were keen to also target a well-defined cobalt precatalyst. During catalysis, it is highly likely that bromide ligands from the aryl bromide substrates will coordinate to the metal center, suggesting that the bromide-containing adducts of the PNP-Co motif should be catalytically competent. Indeed, Bhat proposed that the acetate ligands in **10** are lost during precatalyst activation to be replaced by a halide on oxidative addition.[13a] Accordingly, we synthesized the cobalt dibromide adduct of ligand **1**, complex **14**. The single-crystal X-ray structure of **14** is shown in Figure 2a, and the structure is broadly similar to that for the previously reported chloride analogue.[29] Recrystallization of **14** from acetonitrile/acetone gave the cationic complex **15**, the crystal structure of which is shown in Figure 2b, supporting the assertion made above that acetonitrile is likely to replace halide ligands during catalysis. In both cases, the distorted square-based pyramidal structures obtained are consistent with low-spin ($S = 1/2$) five-coordinate Co(II) complexes. This ground state is further supported by a value of 2.22 μ_B for the effective magnetic moment of **14** recorded in solution (Evans' method) at room temperature, a value which is in line with the data published for a range of Co(II)−PNP complexes, including the dichloride analogue of **14**.[29]

Summarizing our synthetic efforts, we were able to reproduce Bhat's syntheses of the previously very well known Co- and Ni-salophen complexes **4** and **5**, although we note that Bhat's reported value for the magnetic susceptibility of **4** is far too low for a pure sample, but were unable to conclusively reproduce most of the otherwise previously unreported claims. The reaction of ligand **3c** under the conditions described yields a purple complex with the same IR and UV−vis spectroscopic data as that reported by Bhat, but in toto the data obtained by Bhat and us do not support the formulation of **6a**. Of particular note is the fact that the MS data presented by Bhat are remarkably devoid of any isotope patterns and the $[\mathrm{MH}]^+$ peak appears to be in the wrong place in the spectrum shown in their supplementary material. The complex **6a** could, however, be isolated by an alternative synthetic procedure. Similarly, ligand **3a** does not, in our hands, give a monoligated Co(II) complex **7** but rather the bis-ligated adduct **8a**, the structural analogue of **8b**, a complex also reported by Bhat, irrespective of the ligand-to-metal ratio used in the synthesis. Furthermore, the magnetic data for "**7**" presented by Bhat and co-workers does not support their formulation, and the proposed chelating tridentate nature of the Schiff base ligand is highly improbable; indeed, a search of the CCDC database revealed no such motif in any crystallographically characterized complex.[30] Turning to the PNP ligand **1**, this may possibly give the cobalt(II) acetate adduct **10** as reported (we believe, there is insufficient data across Bhat's and our work to state this definitively), but no reaction was obtained between **1** and ferric sulfate, while the reaction with copper(II) acetate led to the formation of di- or oligomeric copper(I) species, rather than the monomeric copper(II) adduct claimed. Accordingly, we also synthesized well-defined Co(II), Fe(II), and Cu(I) adducts of the ligand **1** for the catalytic testing described in the following section.

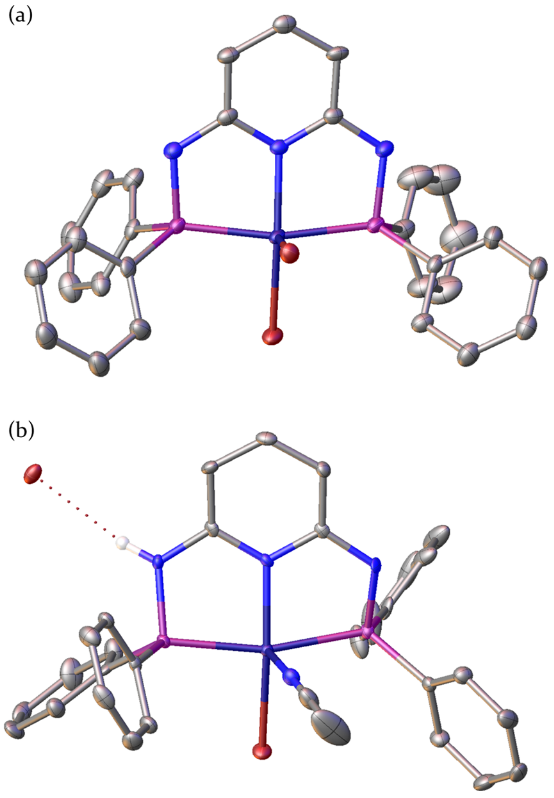

Figure 2. Single-crystal X-ray structures of (a) complex **14** and (b) complex **15**. Hydrogen atoms (except for H-bond in **15**) and solvent molecules are omitted for clarity, with thermal ellipsoids set at 50% probability.

Suzuki Biaryl Cross-Coupling Reactions. Across the papers reported by Bhat and co-workers,[13] particularly good results were claimed in the coupling of the electronically activated aryl bromide substrate, 4-bromocyanobenzene, **16**, with phenyl boronic acid, **17**, to give 4-cyanobiphenyl **18**, using a variety of bases and solvents (Scheme 2a). Indeed, replotting the catalytic data obtained by Bhat in this reaction,

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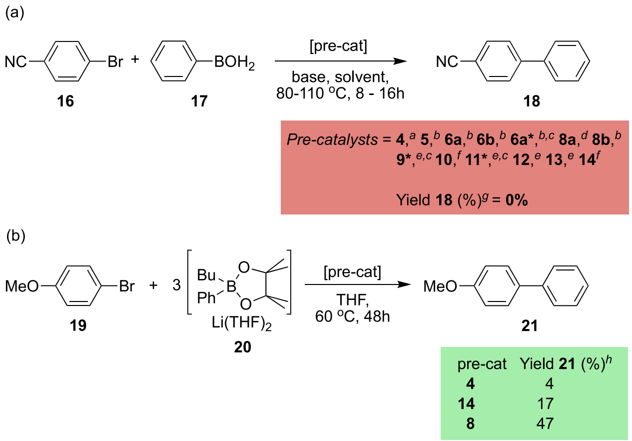
Scheme 2. (a) Unsuccessful and (b) Successful Suzuki Biaryl Cross-Coupling Reactions[a,b,c,d,e,f,g,h,i]



[a] Full conditions for the reactions are given in the Supporting Information. All attempted couplings of **16** with **17** were repeated independently by (at least) two separate authors. [b] 1,4-Dioxane, K_2CO_3, 110 °C. [c] MeCN, NEt_3, 80 °C. [d] **6a***, **9***, and **11*** refer to the solids obtained according to Bhat's synthetic procedures, incorrectly formulated by Bhat as **6a**, **9**, and **11**, respectively. [e] Toluene, K_2CO_3, 110 °C. [f] MeCN, CS_2CO_3, 80 °C. [g] MeCN, K_2CO_3, 80 °C. [h] Lack of conversion to product demonstrated by GC-MS (see Figure S33). [i] Spectroscopic yield, determined by ^1H NMR spectroscopy (1,3,5-$(MeO)_3C_6H_3$, internal standard).

using acetonitrile as the solvent at 80 °C and a selection of precatalyst types[13a−c] (Figure 3), shows a remarkable insensitivity of catalyst performance to variations in either the metal (Co, Fe or Cu) or the ligand (PNP−pincer or Schiff base).[31] Unfortunately, under these conditions, we were unable to produce any of the desired biaryl **18** using the salophen or Schiff base Co-, Ni-, or Fe-based precatalysts **4**, **5**, and **6a*** (the purple solid incorrectly formulated as **6a**), a genuine sample of **6a** prepared by an alternative method, or the closely related analogue **6b**, **8a** (the actual formulation for the reported precatalyst **7**), or **8b**.[32]

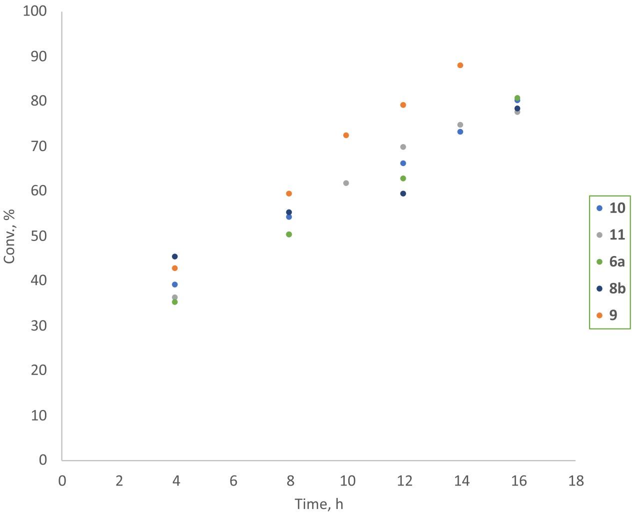


Figure 3. Replotting of Bhat's reported data[13a−c] for the claimed coupling of **16** with **17** in acetonitrile at 80 °C, catalyzed by the PNP−Fe, −Co, and −Cu complexes (**9**−**11**) and the Fe(II) and Co(II) bis-Schiff base complexes **6a** and **8b**.

Iron−salen-type complexes have been successfully exploited in both the coupling of secondary alkyl Grignard reagents with activated aryl chlorides[33] and the coupling of aryl Grignard reagents with primary and secondary alkyl halides,[34] while the latter reactions can also be catalyzed by an iron Schiff base complex;[35,36] however, it appears that here the use of phenyl boronic acid and an aryl bromide as substrates is beyond the scope of these catalyst types. The lack of activity with the cobalt and nickel complexes **4**, **5**, and **8a** is in accord with the previous observation that salen complexes of Co(II) and Ni(II), in contrast with the Fe(III) analogue, give only traces of cross-coupled product in the coupling of alkyl halides with aryl Grignards.[34]

Similarly, no cross-coupled product **18** was obtained using the cobalt PNP−pincer complex tentatively ascribed as **10**, nor with the structurally authenticated analogue, complex **14**. Neither was any catalytic activity observed with the preformed iron complex of ligand **1**, complex **13**, nor with the intractable residue "**9***" obtained under Bhat's synthetic conditions (most likely the starting material, $[Fe(OH_2)_6]SO_4$, vide supra). Likewise, neither the ill-defined solid "**11***", obtained under Bhat's conditions, nor the well-defined copper(I) adduct of **1**, complex **12**, showed any activity. Instead, in all cases, we observed peaks in the GC-MS corresponding with unreacted **16** and the trimeric cyclic ester of phenyl boronic acid, $(PhBO)_3$ (see Figure S33, Supporting Information for a representative example).

Following our complete failure to reproduce any of the catalysis reported by Bhat using a simple aryl boronic acid substrate with an electronically activated aryl bromide, we decided to briefly investigate the application of selected cobalt precatalysts in the coupling of the electronically deactivated aryl bromide **19** with the activated nucleophilic substrate, **20**, under conditions that we have previously reported (Scheme 2b).[9b] While the salophen complex **4** and the PNP−pincer complex **14** gave only low spectroscopic yields of the desired cross-coupled product **21**, a modest spectroscopic yield (47%) was obtained when the bis-Schiff base complex **8a** was employed as a precatalyst.

■ CONCLUSIONS

In conclusion, while we were able to substantiate some of Bhat's simpler synthetic claims, notably of complexes that have previously been reported multiple times, the majority of the complexes reported for the first time by Bhat proved to be either starting materials or to have structures very different from those claimed. An examination of some of the reported mass spectra pivotal to Bhat's reported formulations raise intriguing questions regarding lack of observable isotope patterns and positions of peaks. Contrary to Bhat's findings, none of the Fe, Co, Cu, or Ni complexes, nor structurally closely related examples, proved, in our hands at least, to be viable catalysts in the Suzuki biaryl cross-coupling of a simple aryl boronic acid with an electronically activated aryl bromide.

While we did not screen all of the reported complexes, we believe that the examples chosen reflect the wider set of catalysts reported and we are confident that the selected examples represent a fair cross section. Interestingly, while we observed no reaction with phenyl boronic acid, some activity was observed with cobalt catalysts when a BuLi-activated aryl pinacol boronic ester was employed under our previously reported conditions;[9b] we are currently examining this promising lead further and these results will be published in due course.

The coupling of simple aryl boronic acids with aryl halides catalyzed by cobalt or, ideally, iron, remains, in our opinion, a highly desirable, yet unmet, goal.[37]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00083.

> *xyz* coordinate file of the DFT-calculated structures (XYZ)
>
> Synthesis of complexes and catalytic reactions; spectroscopic data including UV−vis absorption spectra, FT-IR spectra, mass spectra, HRMS, ^{1}H NMR spectra, UV−vis absorption spectra, ^{31}P NMR spectra, and GC trace of the organic extracts; reexamination of (lack of) solvent influence including replotting of Bhat's claimed catalytic data; crystallographic data; computational methods; and DFT calculations (PDF)

Accession Codes

CCDC 1885663−1885664 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(31) An examination of Bhat's papers (ref 13) shows that this remarkable insensitivity extends to variations in other parameters as well. For instance, replotting the results from the variation in solvents in the same reaction, catalysed by **9** or **11** (ref 13b) shows that while

there is a difference claimed between the performance of the two catalysts, the slope of the linear trend line applied to the five data points in each solvent is constant (4.7(1) with **9**, 3.89(4) with **11**) across toluene, ethanol, 1,4-dioxane and acetonitrile, which suggests a notable insensitivity to the rate across a wide range of solvent types. See Figure S34, Supporting Information for details.

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