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Synthesis of (POCOP)Co(Ph)(X) Pincer Complexes and Observation of Aryl−Aryl Reductive Elimination Involving the Pincer Aryl

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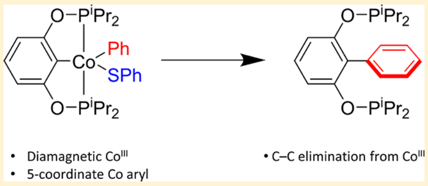
Supporting Information



ABSTRACT: A series of square-planar, low-spin Co(II) and Co(III) complexes supported by the POCOP pincer ligand have been prepared for the purpose of exploring the reactions potentially involved in aryl halide coupling catalysis (POCOP = 2,6-diisopropylphosphinoxyphenyl). The investigations determined that the Co(III)−aryl intermediates of the envisioned catalytic cycle are accessible, but the desired catalysis is derailed by a C−C reductive elimination reaction that involves the POCOP ligand. Metalation of the parent (POCOP)H ligand with $CoCl_2$ and DMAP led to the formation of (POCOP)CoCl (**A-1**). Metathesis of **A-1** with Me_3SiX reagents allowed isolation of (POCOP)CoBr (**A-2**), (POCOP)CoI (**A-3**), and (POCOP)CoOTf (**A-4**). Reactions of **A-1** with NaO^{t}Bu, MeLi, and PhLi led to (POCOP)CoO^{t}Bu (**A-5**), (POCOP)CoMe (**A-6**), and (POCOP)CoPh (**A-7**). Treatment of **A-1** with PhSH surprisingly led to (POCOP)CoSPh (**A-8**) without the need for added base. **A-7** could be oxidized to (POCOP)Co(Ph)(Cl) (**B-1**) using *N*-chlorosuccinimide; however, samples of **B-1** produced in this fashion were unstable with respect to decomposition to **A-1**. Oxidation of **A-7** to (POCOP)Co(Ph)(OAc) (**B-2**) was accomplished with $PhI(OAc)_2$, and metathesis of **B-2** with Me_3SiX produced clean samples of **B-1** and (POCOP)Co(Ph)(I) (**B-3**) that were thermally stable. Treatment of **B-1** or **B-3** with NaSPh resulted in the formation of (POCOP)Co(Ph)(SPh) (**B-4**). Complexes **B-1**−**B-4** are low-spin Co(III) complexes. Thermolysis of **B-4**, instead of the expected C−S reductive elimination, resulted in the C−C elimination with the POCOP aryl, producing (POCOP)-Ph (**D-1**). Hydrolysis of **D-1** yielded the known 2-phenylresorcinol (**D-2**). The solid-state structures of **A-8**, **B-3**, and **B-4** were determined by X-ray crystallography.

INTRODUCTION

Transition metal-mediated coupling reactions of aryl halides have become an irreplaceable part of a chemist's repertoire because of their ever increasing scope and applicability. The majority of these coupling reactions use palladium[1−3] in chemistry that was honored by the 2010 Nobel Prize.[4,5] Expansion of this chemistry to include other metals, especially the cheaper and more abundant 3d elements such as Ni,[6−8] Cu,[9,10] and Fe,[11,12] has been receiving an increased amount of attention.[13−15] Classical aryl halide coupling reactions rely on two-electron, concerted processes taking place at a single metal center: oxidative addition (OA) to break the Ar−Hal bond and reductive elimination (RE) to make the Ar−Z bond in the product (Figure 1).[16] Two-electron processes such as these present a well-known challenge in the chemistry of 3d metals.[17,18]

We have reported on the ability of (POCOP)Rh complexes and other pincer complexes of Rh to catalyze coupling reactions of aryl halides.[19−21] In addition, we extensively documented the elementary reactions of OA and RE taking place at pincer-supported Rh.[22−25] In these reactions, the three-coordinate, monovalent (pincer)Rh fragment acts as a functional mimic of an LPd^0 species in the Pd-catalyzed cycles (Figure 1). The Rh reactions thus involve cycling between Rh(I) and Rh(III) oxidation states (d^8/d^6) in contrast to Pd(0) and Pd(II) (d^{10}/d^8). An analogous cycle can also be imagined for cobalt in which it cycles between Co(I) and Co(III) through OA and RE steps. We became interested in examining whether the requisite OA and RE reactions might indeed be feasible for the (pincer)Co system.

Examples of aryl halide coupling[26] catalysis with simple cobalt(II) halide precursors have been reported.[27] Oshima et al. disclosed alkylation of aryl bromides with primary alkyl Grignard reagents catalyzed by $CoCl_2$ with NHC supporting ligands.[28] Cheng et al. described arylation of thiols using CoI_2/DPPE with a stoichiometric Zn additive.[29] Amatore and Gosmini reported reductive cross-coupling of two aryl halides using $CoBr_2/PPh_3$ with added stoichiometric Mn.[30] The latter two groups proposed a Co(I)/Co(III) catalytic cycle; however, mechanistic details were not investigated, and direct evidence that favored this pathway was not reported. Duan et al. described coupling of aryl fluorides with aryl Grignards catalyzed by $CoCl_2$ in the presence of near stoichiometric $Ti(OEt)_4$, proposing a Ti-assisted C−F OA to Co in an undefined oxidation state.[31]

In 2014, Fout and co-workers published a study of Co-catalyzed amination of aryl halides with $LiN(SiMe_3)_2$ and, less successfully, with other amine derivatives.[32] In this case, the key intermediate $(Ph_3P)_2CoN(SiMe_3)_2$ was isolated and identified. It was shown to effect catalysis and to react with iodobenzene in a stoichiometric reaction to produce Ph-

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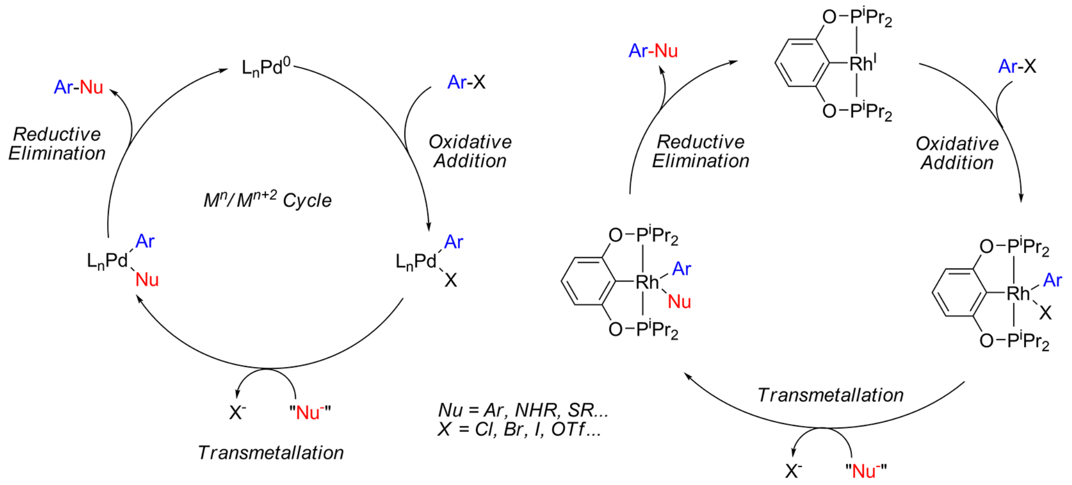

Figure 1. Generic mechanism (left) for Pd-catalyzed coupling of aryl halides with nucleophiles. Previously proposed mechanism (right) for coupling of aryl halides with nucleophiles using (POCOP)Rh.

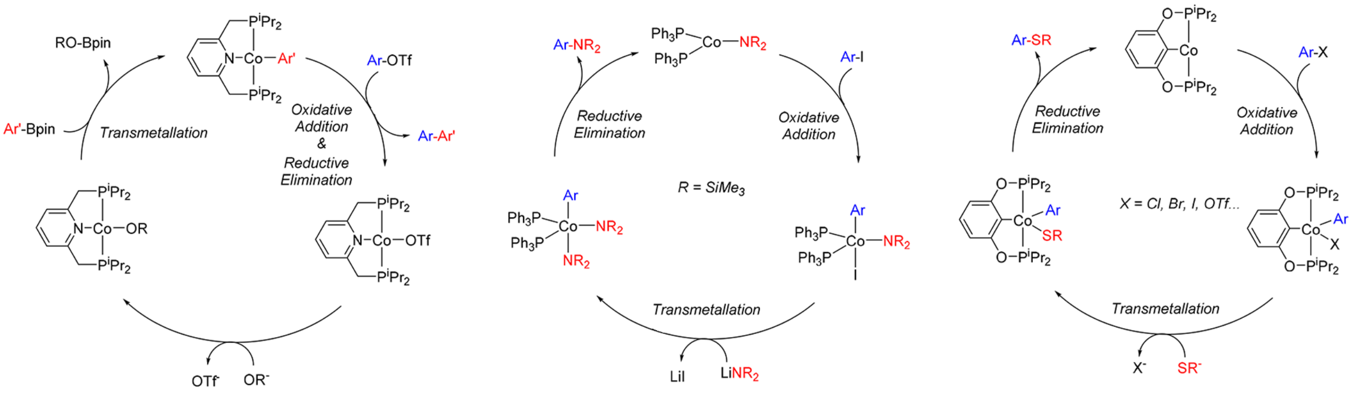

Figure 2. Proposed mechanisms for Co-catalyzed coupling reactions. Suzuki−Miyaura coupling (left) of aryl triflates from ref 37, aryl iodide amination (center) from ref 32, and arylation of thiols (right) envisaged in this work.

$N(SiMe_3)_2$. This provided some experimental support for the Co(I)/Co(III) mechanism proposed by Fout and co-workers (Figure 2). Nonetheless, the Co(III) intermediates were not observed, and consequently, the RE from Co(III) was not directly documented. A rare example of well-defined C−C RE from Co(III) involving two sp^3-hybridized carbons was reported by Xu and Bernskoetter in 2011, who demonstrated that elimination of ethane from $(Me_3P)_3CoMe_2I$ required initial dissociation of a PMe_3 ligand.[33] The results of Fout and Bernskoetter dovetail our findings with Rh in the sense that concerted RE from a d^6 Co(III) or Rh(III) center requires a five- and not six-coordinate complex, while OA to the d^8 Co(I) or Rh(I) requires a three-coordinate complex. This dynamic is also well understood for a number of d^6/d^8 systems in general.[34] With Co, however, there is also the likelihood of the involvement of different spin states ($S = 0$ or $S = 1$) for the Co(I) and Co(III) complexes. For example, Fout's $(Ph_3P)_2CoN(SiMe_3)_2$ possesses a triplet configuration as does the analogous T-shaped (^{Si}PNP)Co complex {where ^{Si}PNP is $[(^tBu_2PSCH_2Me_2Si)_2N]$, Fryzuk's[35] pincer} investigated by Caulton et al.[36] Five-coordinate Co(III) complexes relevant as products of OA of aryl halides to Co(I) and their derivatives meant to undergo aryl−X RE have not been closely studied, to the best of our knowledge. However, Li et al. described *o*-imine-directed OA of aryl−fluoride bonds to Co(I) to give six-coordinate Co(III)−aryls, which subsequently underwent apparent C−C reductive elimination upon carbonylation.[37]

In 2016, the Chirik group reported catalysis of a version of a Suzuki−Miyaura cross-coupling between aryl triflates and arylboronates.[38] This reaction was catalyzed by a Co complex supported by a neutral pyridine/bis(phosphine) PN*P pincer ligand. What appeared to be unusual about this system is that it ostensibly required OA of aryl triflate to a four-coordinate, square planar (PN*P)Co−aryl complex (Figure 2). The stoichiometric reaction between PhOTf and (PN*P)Co−Ar was indeed observed, but curiously, the analogous reactions with PhCl, PhBr, and PhI did not proceed similarly, yielding only partial conversion to the expected C−C coupling product. It is possible that the modest and varied catalytic success in this work (0−20 TON spread with a series of substrates) is reflective of the fact that OA to four-coordinate Co is accessible only with the most favorable substitution patterns, although it is also possible the behavior of Co in this system differs from what would be expected from its heavier, precious metal brethren. The Chirik group also disclosed a series of studies of the various borylations of C−H bonds catalyzed by similar PN*P-supported Co catalysts.[39−42] In those reports, OA to four-coordinate Co intermediates also appears to be necessary; however, OA of C−H, B−H, or B−B bonds can in general be viewed as kinetically more facile than OA of aryl halides. Fout et al. have described catalytic hydrogenation,

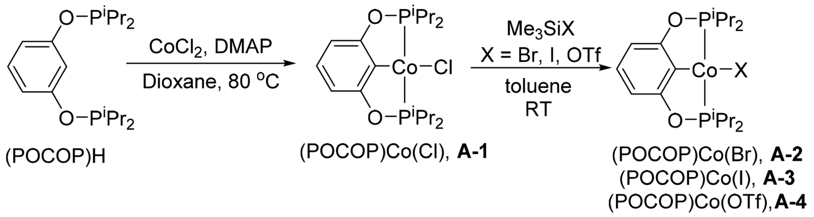

Figure 3. Synthesis of (POCOP)Co^{II}−Hal complexes.

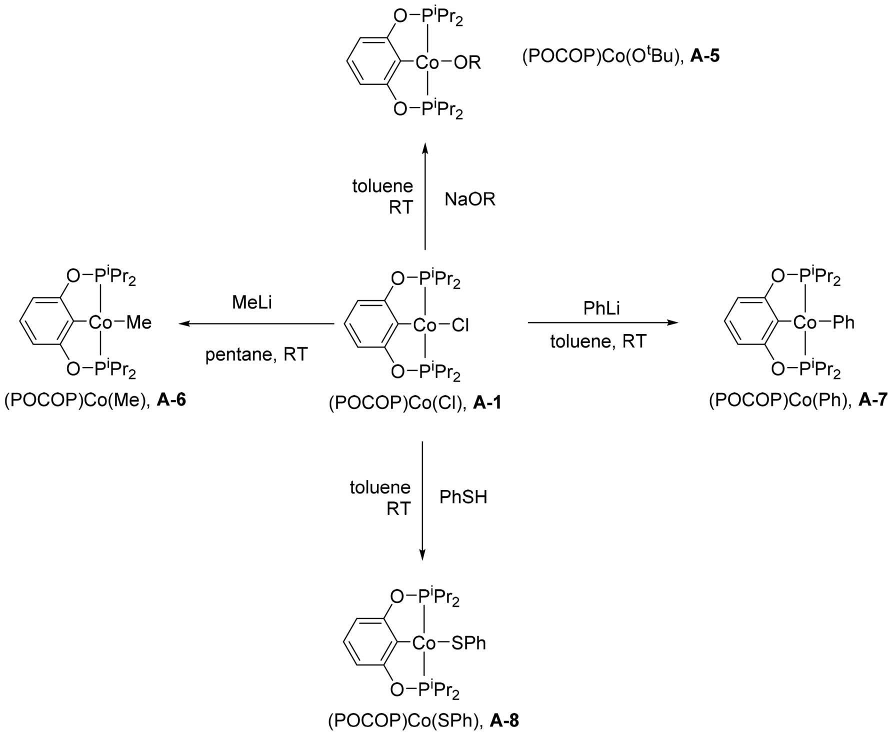

Figure 4. Synthesis of (POCOP)Co^{II}-X compounds.

hydroboration, and hydrosilylation using Co catalysts supported by an anionic CCC pincer and ostensibly operating via Co^{I}/Co^{III} cycles.[43−47]

With this background in mind, we envisaged that an anionic pincer support such as POCOP would provide access to three-coordinate Co(I) and five-coordinate Co(III) complexes (Figure 2), as it did in the case of Rh. In this report, we focused on accessing the Co(III) intermediates in the expected catalytic cycle and on evaluating the potential for RE. In particular, we chose to pursue C−S RE, based on the recent success in catalyzing such coupling with Rh and on the general grounds of the C−S reaction being one of the easier aryl−heteroarom RE reactions.[48]

■ RESULTS AND DISCUSSION

Synthesis of Co^{II} Complexes. The introduction of the POCOP ligand into the coordination sphere of Co was accomplished by reaction of (POCOP)H with anhydrous $CoCl_2$ in the presence of dimethylaminopyridine (DMAP), producing (POCOP)Co(Cl) (**A-1**) as a bright yellow solid in a 29% yield upon workup (Figure 3). This reaction produced a large amount of a blue byproduct. This solid was collected, and single crystals suitable for X-ray diffraction were grown from a concentrated acetonitrile solution. The structure was determined to be [(DMAP)H][(DMAP)$CoCl_3$] with a unit cell matching that previously reported.[49] **A-1** is most closely related to (POCOP^{tBu})CoI reported by Goldberg, Heinekey, and co-workers.[50] A few differently substituted (POCOP)Co$(CO)_n$ (n = 1 or 2) complexes were very recently disclosed by Guan et al.[51]

The ^{1}H nuclear magnetic resonance (NMR) spectrum of **A-1** displayed four broad, strongly contact-shifted signals with integral ratios of 24:4:2:1, consistent with formation of a paramagnetic Co^{II} complex. The signals with relative intensities of 24 (two overlapping resonances of 12 H each) and 4 correspond to the methyl and methine protons of the isopropyl groups, respectively; the resonances with intensities of 2 and 1 correspond to the aromatic protons of the aryl backbone. An Evans method measurement of the magnetic moment in solution yielded 2.2(1) μB, consistent with a single unpaired electron, as would be expected for an approximately square-planar, low-spin Co(II) complex. Strongly contact-shifted but resolved ^{1}H NMR resonances are consistent with a low-spin, square-planar complex of Co(II), in contrast to the (pseudo)tetrahedral Co(II) complexes with the $S = {}^3/_2$ ground state. It appears that the preference for low spin versus high spin for four-coordinate Co(II) pincer complexes may vary depending on the strength of field of the substituents about the Co center. For example, Fryzuk reported that (^{Si}PNP^{Ph})CoCl was pseudotetrahedral, possessed an $S = {}^3/_2$ ground state, and

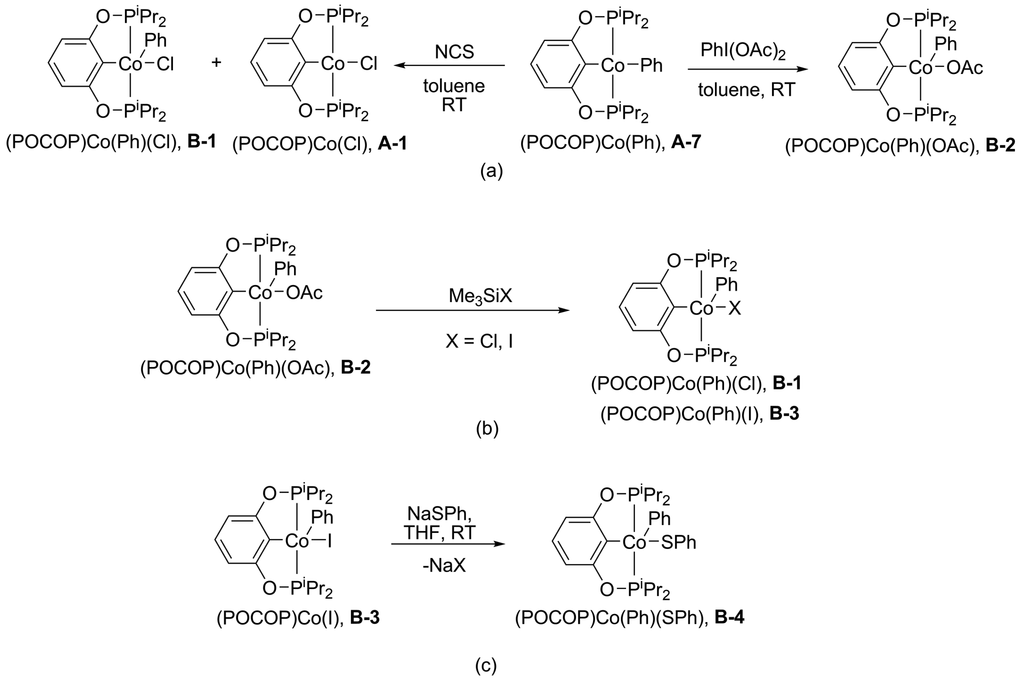

Figure 5. Synthesis of (POCOP)Co^{III} compounds **B-1**–**B-4**.

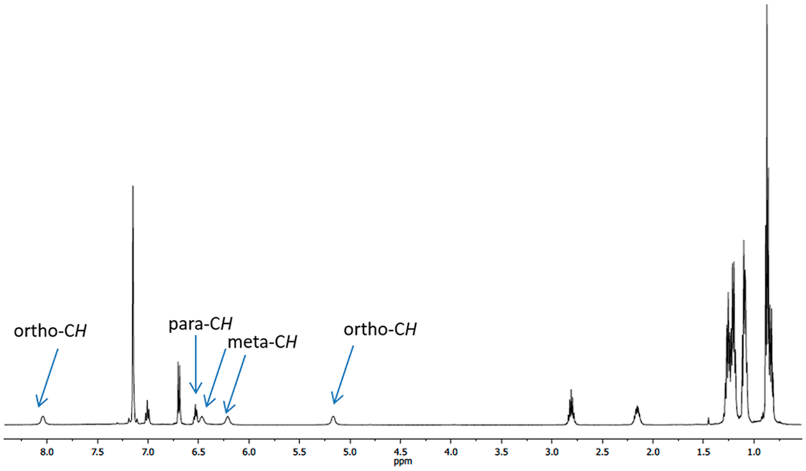

Figure 6. ^{1}H NMR spectrum of (POCOP)Co(Ph)(Cl) (**B-1**) showing the inequivalence of the five hydrogens of the Co-bound C_6H_5 group.

was NMR-silent, but replacement of the chloride with a more donating, stronger-field methyl resulted in a low-spin, square-planar (^{Si}PNP^{Ph})CoMe, for which ^{1}H NMR spectra could be observed, integrated, and interepreted.[52] The presence of a central aryl donor along with two phosphinites in the POCOP ligand appears to be enough to ensure a low-spin configuration. In addition, the stronger preference of POCOP for a square-planar over tetrahedral geometry should further stabilize the low-spin geometry. Indeed, Co(II) complexes of similar aryl/bis(phosphine) type 5,5-pincers[53] have also been reported to be low-spin, square-planar compounds.[49,54]

A-1 readily served as a starting material for the synthesis of derivative (POCOP)CoX complexes. Treatment of solutions of **A-1** with Me$_3$Si-X (X = Br, I, or OTf) resulted in rapid and clean formation of (POCOP)Co(Br) (**A-2**), (POCOP)Co(I) (**A-3**), and (POCOP)Co(OTf) (**A-4**) (Figure 3).

Reaction of **A-1** with NaO^{t}Bu, MeLi, and PhLi resulted in the formation of (POCOP)Co(O^{t}Bu) (**A-5**), (POCOP)Co(Me) (**A-6**), and (POCOP)Co(Ph) (**A-7**), respectively. The synthesis of (POCOP)Co-SPh (**A-8**) was readily accomplished in 77% isolated yield by treatment of **A-1** with thiophenol, surprisingly not requiring addition of a base (Figure 4). All of the Co^{II} complexes (**A-1**–**A-8**) displayed clearly analogous patterns in their ^{1}H NMR spectra, corresponding to the same 12:12:4:2:1 set of resonances noted for **A-1**. These data are indicative of all these compounds being low-spin Co(II) complexes possessing C_{2v} symmetry on the NMR time scale in solution.

Synthesis of Co^{III} Complexes. Oxidation of (POCOP)-CoPh (**A-7**) with NCS at room temperature (RT) for 12 h in pentane resulted in a mixture of (POCOP)CoCl (**A-1**) and a new compound identified as (POCOP)Co(Ph)(Cl) (**B-1**), along with some biphenyl (Figure 5). Compound **B-1** in these mixtures decayed over time into biphenyl and **A-1**. Pure samples of **B-1** could be isolated in minute yields by recrystallization from these reaction mixtures; however,

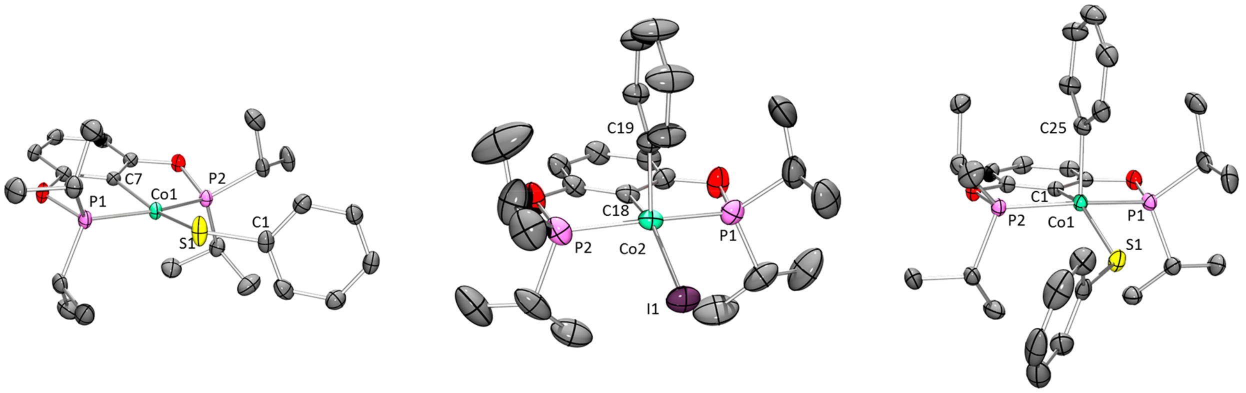

Figure 7. ORTEP drawings (50% probability ellipsoids) of (POCOP)Co(SPh) (**A-8**, left), (POCOP)Co(Ph)(I) (**B-3**, center), and (POCOP)Co(Ph)(SPh) (**B-4**, right). Hydrogen atoms have been omitted for the sake of clarity. Selected bond distances (angstroms) and angles (degrees) for **A-8**: Co1−P1, 2.1816(8); Co1−P2, 2.1719(9); Co1−S1, 2.1706(8); S1−C1, 1.773(2); P1−Co1−P2, 161.86(2); C7−Co1−S1, 163.15(6); Co1−S1−C1, 119.89(7). Selected bond distances (angstroms) and angles (degrees) for **B-3**: Co2−P1, 2.210(2); Co2−P2, 2.204(2); Co2−I1, 2.601(2); Co2−C18, 1.907(3); Co2−C19, 1.940(3); P1−Co2−P2, 161.83(4); C18−Co2−I1, 155.19(9); C19−Co2−I1, 115.86(9); C18−Co2−C19, 88.9(1). Selected bond distances (angstroms) and angles (degrees) for **B-4**: Co1−C25, 1.947(2); Co1−P3, 2.222(1); Co1−P1, 2.223(1); Co1−S1, 2.215(1); Co1−C1, 1.933(2); C1−Co1−C25, 89.54(8); C1−Co1−P3, 81.80(5); C1−Co1−P1, 80.24(5); C1−Co1−S1, 148.98(6); C25−Co1−S1, 119.96(6).

solutions of **B-1** obtained in this fashion inevitably degraded into (POCOP)CoCl (**A-1**) and biphenyl, as well. In contrast, oxidation of (POCOP)Co-Ph (**A-7**) with 0.55 equiv of $PhI(OAc)_2$ overnight in toluene led to clean isolation of (POCOP)Co(Ph)(OAc) (**B-2**) in 80% yield without any detectable amounts of paramagnetic impurities or biphenyl. **B-2** was found to be stable at RT in a solution in C_6D_6, and no detectable decomposition was observed after heating the same solution at 80 °C for 90 min. **B-2** offered an alternative synthetic route to Co^{III} aryl halide complexes. Metathetic reactions of **B-2** with Me_3SiCl and Me_3SiI in C_6D_6 cleanly yielded (POCOP)Co(Ph)(Cl) (**B-1**) and (POCOP)Co(Ph)(I) (**B-3**), after 18 h and 10 min, respectively (Figure 5). **B-3** readily reacted with sodium thiophenolate to furnish (POCOP)Co(Ph)(SPh) (**B-4**). Interestingly, **B-1** synthesized by this route was much less prone to decomposition (<5% after 2 days at RT in C_6D_6) than the material obtained from **A-7** and NCS. No decomposition was evident by NMR upon aging solutions of **B-3** for 5 days at RT. It is possible that decomposition of **B-1** is catalyzed by traces of NCS or some other NCS-derived impurities, possibly in combination with residual Co(II) complexes.

Spectroscopic Characterization of Co^{III} Complexes. Co^{III} complexes of the type (POCOP)Co(Ph)(X) [where X = Cl, OAc, I, and SPh (**B1−B4**, respectively)] all show well-resolved NMR spectra with resonances in the diamagnetic region. One interesting feature shared by the ^1H NMR spectra of **B1−B4** is the observation of five separate resonances for the protons on the phenyl ligand spread between ~5 and ~8 ppm in chemical shift (Figure 6). The *ortho* and *meta* protons of the C_6H_5 group appear as broad humps, whereas the proton of the *para* position appears as a sharp triplet. These features indicate restricted rotation of the Ph ligand about the Co−Ph bond. Such restricted rotation was also observed for analogous (POCOP)Rh systems in our previous reports for Rh-catalyzed C−S and C−N coupling,[19−21] as well as other complexes of the type (pincer)Rh(Ar)(X) where the aryl group is *cis* to the central pincer donor.[22,23,55] We previously discussed how this orientation of the metal−aryl group (edge-on toward the X) and its restricted rotation are a detriment to the reductive elimination reactions with Rh[21] and, presumably, Co, as well.

The low-spin nature of these Co(III) complexes is ostensibly due to the presence of strong-field aryl ligands in the coordination sphere of Co. A comparison can be drawn with the report of Lippard et al. on five-coordinate Co(III) complexes of the type (NNNN)CoX, where NNNN is a dianionic, tetradentate tropocoronand ligand.[56] In their case, X = Cl corresponded to a paramagnetic Co(III) center whereas X = alkyl corresponded to a diamagnetic Co(III). Five-coordinate, low-spin Co(III) compounds with acyl and alkenyl donors were also reported by Klein et al.[57]

X-ray Structural Studies. The solid-state structures of **A-8**, **B-3**, and **B-4** complexes were determined via X-ray diffraction studies of crystals grown from pentane solutions at −35 °C. (POCOP)Co(SPh) (**A-8**) was observed to crystallize in the monoclinic system in the $P2_1/c$ space group, yielding yellow crystals. The ligands attain a slightly distorted square-planar geometry around the Co center, with the P1−Co1−P2 and C7−Co1−S1 angles being <180° at 161.86(2)° and 163.15(6)°, respectively (Figure 7). (POCOP)Co^{III} compounds **B-3** and **B-4** crystallized attaining the $P2_1/n$ and $P2_1/c$ space groups, respectively. The geometry around the Co centers is distorted square pyramidal with the Ph ligand occupying the apical position placing the strongly *trans* influence ligands (Ph and central C_{aryl} of POCOP) *cis* to each other with the I and S atoms distorted slightly out of plane from their ideal positions in a square pyramidal structure.[58] Comparison of the structures of **B-3** and **B-4** with the analogous Rh structures published previously by our group[19,20] reveals very similar geometrical arrangements of donor atoms about Co^{III} and about Rh^{III}, only with shorter Co−ligand distances.

Thermolysis and Observation of C_{ligand}−C_{Ph} Reductive Elimination from B-4. In the analogous (POCOP)Rh system,[19] thermolysis of (POCOP)Rh(Ph)(SPh) (**C-1**) at 65 °C for 32 h yielded a 48:1 mixture of (POCOP)Rh(SPh_2) (**C-2**) and (POCOP)Rh(Ph)(SPh) (**C-1**) (Figure 8). Thermolysis of (POCOP)Co(Ph)(SPh) (**B-4**) in C_6D_6 at 80 °C however, proceeded to give **D-1** in 1 h (Figure 8) as the predominant

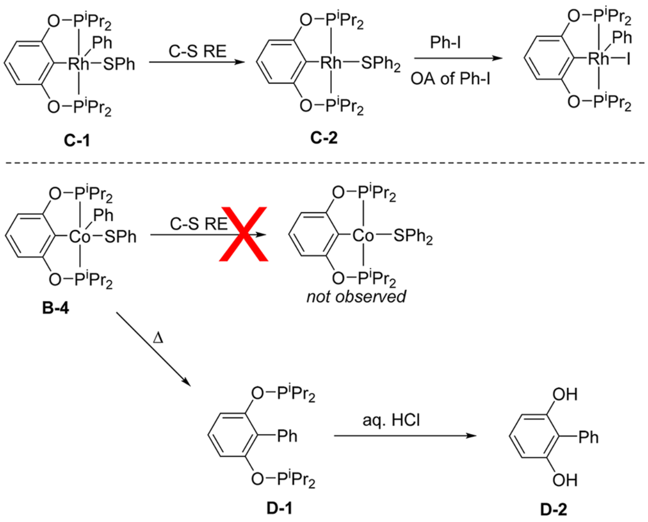

Figure 8. Previously reported (ref 19) observations (top) upon thermolysis of (POCOP)Rh(Ph)(SPh). Observations for thermolysis (bottom) of (POCOP)Co(Ph)(SPh).

product that could be observed by NMR spectroscopy (80% conversion with respect to an internal standard, ^{31}P NMR δ 148.7). The rest of the NMR-observable species is a mixture of (POCOP)Co(Ph) (10%) and other unidentified paramagnetic products. Formation of free **D-1** implies ejection of the "CoSPh" fragment, but we were not able to determine the fate of Co in this transformation.

D-1 was identified on the basis of comparison of its ^{1}H, ^{13}C, and ^{31}P spectra with those of the free (POCOP)H ligand and the various (POCOP)Co compounds. The ^{1}H NMR spectra of **D-1** are clearly those of a diamagnetic compound and do not show virtual coupling features that are present in diamagnetic transition metal POCOP complexes with *trans*-disposed phosphines. The ^{31}P NMR chemical shift of the **D-1** resonance is quite close that of that (POCOP)H. Hydrolysis of **D-1** with aqueous HCl followed by extraction with dichloromethane and filtration through silica gave the known 2-phenylresorcinol[59] (**D-2**) in near-quantitative yield, confirming the proposed nature of **D-1**.

CONCLUSION

The POCOP supporting ligand allowed preparation of a series of Co(II) and Co(III) complexes. In particular, we were successful in preparing five-coordinate Co(III) complexes envisioned as intermediates in the catalytic cycle for catalytic coupling of aryl halides with thiols. They were found to be structurally similar to the catalytically competent Rh analogues. In contrast to the Rh behavior,[19] thermolysis of Co(III) aryl/thiolato complex (POCOP)Co(Ph)(SPh) (**B-4**) did not result in the desired carbon−sulfur reductive elimination. Instead, **B-4** underwent an apparent intramolecular carbon−carbon RE, coupling the aryl of the POCOP pincer with the Ph group on Co. Such intramolecular C−C RE was not observed in the analogous Rh system. However, calculations on the related (POCOP)Rh(Ar)(NHR) complexes previously showed[21] that the intramolecular C−C RE is kinetically easily accessible yet does not lead to a favorable product in the case of a unimolecular Rh system. On the other hand, we did previously observe intramolecular C−C RE from (POCOP)Rh(CH=CH$_2$)(I) with the formation of a dimeric Rh^{I} product.[60] It appears likely that C−C RE in the present Co system is likewise kinetically accessible, and ostensibly, ejection of Co from the pincer framework happens more readily than with Rh. All in all, our observations suggest that the POCOP ligand is not well suited for supporting catalysis of aryl halide coupling in the Co(I)/Co(III) cycle because of preferential intramolecular C−C RE from Co(III) aryl complexes. This may well be a detriment to the use of carbon-centered pincers in general for this purpose, and our further explorations will focus on pincer ligands with different central donor atoms.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise specified, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ether, tetrahydrofuran (THF), pentane, and isooctane were dried and deoxygenated (by purging) using an Innovative Technologies MD-5 solvent purification system and stored over molecular sieves in an Ar-filled glovebox. C_6D_6 and hexanes were dried over and distilled from a NaK/Ph$_2$CO/18-crown-6 mixture and stored over molecular sieves in an Ar-filled glovebox. (POCOP)H[61] was synthesized according to published procedures. NaSPh was prepared by reacting PhSH with 1 equiv of NaH in THF followed by removal of volatiles and washing of the residue with Et$_2$O. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian NMRS 500 spectrometer (^{1}H NMR, 499.686 MHz; ^{13}C NMR, 125.659 MHz; ^{31}P NMR, 202.298 MHz; ^{19}F NMR, 470.111 MHz) and a Varian Inova 300 spectrometer (^{1}H NMR, 299.951 MHz; ^{13}C NMR, 75.413 MHz; ^{31}P NMR, 121.425 MHz). All ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent signal (C_6D_6 at δ 7.16 for ^{1}H NMR and δ 128.06 for ^{13}C NMR). ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0. ^{19}F NMR spectra were referenced externally using neat CF_3CO_2H at δ −78.55. Elemental analyses were performed by CALI Laboratories, Inc. (Parsippany, NJ).

*Synthesis of (POCOP)CoCl (**A-1**).* (POCOP)H (2.054 g, 5.99 mmol) was combined with CoCl$_2$ (1.68 g, 12.9 mmol) and DMAP (1.54 g, 12.6 mmol) in a Teflon-capped flask and partially dissolved in dioxane. The flask was heated at 90 °C for 20 h, producing a green solution. The solution was passed through a pad of Celite, and volatiles were removed by vacuum. The product was extracted with pentane, passed through a pad of Celite, and dried under vacuum to give a bright yellow-green solid. The product was recrystallized from pentane at −35 °C to give a yellow crystalline solid (750 mg, 29%). The compound displayed broad signals outside of the standard diamagnetic range in its ^{1}H NMR spectrum, indicative of a paramagnetic complex: ^{1}H NMR (500 MHz, C_6D_6) δ 43.72 (bs, 4H), 12.11 (bs, 24H), −14.71 (bs, 2H), −53.02 (bs, 1H). Anal. Calcd for $C_{18}H_{31}ClCoO_2P_2$: C, 49.61; H, 7.17. Found: C, 49.54; H, 7.08. The magnetic moment for **A-1** was determined to be 2.2(1) μ_B by the Evans method.

*Synthesis of (POCOP)CoBr (**A-2**).* (POCOP)CoCl (**A-1**) (28 mg, 0.064 mmol) was added to a J. Young tube and dissolved in C_6D_6. Me$_3$SiBr (10 μL, 0.076 mmol) was added to the sample, resulting in a color change to slightly yellow-green. The reaction was complete after 10 min at RT as indicated by complete conversion to a new paramagnetic product and the presence of Me$_3$SiCl in the ^{1}H NMR spectrum. The volatiles were removed by vacuum to give a yellow powder. The product was recrystallized from a saturated pentane solution at −35 °C to give an orange crystalline solid (22 mg, 72%): ^{1}H NMR (500 MHz, C_6D_6) δ 45.16 (bs, 4H), 12.75 (bs, 12H), 12.00 (bs, 12H), −17.91 (bs, 2H), −41.58 (bs, 1H). Anal. Calcd for $C_{18}H_{31}BrCoO_2P_2$: C, 45.02; H, 6.51. Found: C, 44.95; H, 6.63.

*Synthesis of (POCOP)CoI (**A-3**).* (POCOP)CoCl (**A-1**) (30 mg, 0.069 mmol) was added to a J. Young tube and dissolved in C_6D_6. Me$_3$SiI (11 μL, 0.078 mmol) was added to the sample, resulting in a color change to yellow-green. The color was slightly darker than that observed with (POCOP)CoBr. The reaction was complete after 10 min at RT as indicated by complete conversion to a new paramagnetic product and the presence of Me$_3$SiCl in the ^{1}H NMR spectrum. The volatiles were removed by vacuum to give a yellow powder. The product was recrystallized from a saturated pentane solution at −35 °C to give a dark orange crystalline solid (15 mg, 43%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 40.35 (bs, 4H), 12.81 (bs, 12H), 12.01 (bs, 12H), −20.18 (bs, 2H), −27.73 (bs, 1H).

*Synthesis of (POCOP)CoOTf (**A-4**).* (POCOP)CoCl (**A-1**) (712 mg, 1.64 mmol) was added to a Schlenk flask and dissolved in C$_6$D$_6$. The solution was treated with Me$_3$SiOTf (592 μL, 3.27 mmol). This led to no noticeable color change; however, the ^{1}H NMR spectrum of this reaction showed conversion to a new product along with the signal for Me$_3$SiCl. The volatiles were removed from the reaction mixture by vacuum to give a yellow-orange solid (850 mg, 94%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 39.06 (bs, 4H, C*H*Me$_2$), 11.26 (bs, 12H, CH*Me*$_2$), 9.99 (bs, 12H, CH*Me*$_2$), −24.72 (bs, 1H, Ar-*H*), −26.33 (bs, 2H, Ar-*H*); ^{19}F NMR (470 MHz, C$_6$D$_6$) δ −92.6. Anal. Calcd for C$_{19}$H$_{31}$CoF$_3$O$_5$P$_2$S: C, 41.54; H, 5.69. Found: C, 41.37; H, 5.58.

*Synthesis of (POCOP)CoO^{t}Bu (**A-5**).* (POCOP)CoCl (**A-1**) (185 mg, 0.42 mmol) was added to a Schlenk flask and dissolved in toluene. NaO^{t}Bu (41 mg, 0.43 mmol) was added to the solution, resulting in an immediate color change to orange. The reaction mixture was stirred at RT for 1 h. The volatiles were removed under vacuum. The product was extracted with pentane, passed through a pad of Celite, and dried under vacuum. The product was recrystallized from a concentrated toluene solution layered with pentane at −35 °C to give a brown solid (127 mg, 63%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 14.98 (bs, 4H), 4.34 (bs, 26H), −9.93 (bs, 9H), −80.23 (bs, 1H). Anal. Calcd for C$_{22}$H$_{40}$CoO$_3$P$_2$: C, 55.81; H, 8.52. Found: C, 55.71; H, 8.36.

*Synthesis of (POCOP)Co(Me) (**A-6**).* (POCOP)Co(Cl) (**A-1**) (170 mg, 0.391 mmol) was added to a Schlenk flask and dissolved in pentane. The solution was treated with MeLi (293 μL, 1.6 M in OEt$_2$, 0.25 mmol), leading to an immediate color change from light yellow to dark green. After being stirred for 30 min at RT, the solution was passed through a pad of Celite, and the volatiles were removed by vacuum to give a green solid. The solid was recrystallized from toluene layered with pentane at −35 °C to give a dark green crystalline solid (120 mg, 74%). The compound displayed broad signals outside of the standard diamagnetic range in the ^{1}H NMR spectrum, indicative of a paramagnetic complex: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 53.26 (bs, 4H), 13.14 (bs, 12H), 11.71 (bs, 12H), −9.08 (bs, 5H), −45.83 (bs, 1H). Anal. Calcd for C$_{19}$H$_{34}$CoO$_2$P$_2$: C, 54.94; H, 8.25. Found: C, 54.85; H, 8.50.

*Synthesis of (POCOP)Co(Ph) (**A-7**).* (POCOP)CoCl (**A-1**) (91 mg, 0.21 mmol) was added to a Schlenk flask and dissolved in pentane. The solution was treated with PhLi (140 μL, 1.8 M in ^{n}Bu$_2$O, 0.25 mmol), leading to an immediate color change from light yellow to dark green. After being stirred for 30 min at RT, the solution was passed through a pad of Celite, and the volatiles were removed by vacuum to give a green solid. The solid was recrystallized from toluene layered with pentane at −35 °C to give a dark green crystalline solid (81 mg, 81%). The compound displayed broad signals outside of the standard diamagnetic range in the ^{1}H NMR spectrum, indicative of a paramagnetic complex: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 36.21 (bs, 4H), 13.87 (bs, 1H), 12.04 (bs, 12H), 7.54 (bs, 12H), −7.38 (bs, 1H), −15.84 (bs, 2H), −20.15 (bs, 2H), −40.56 (bs, 2H). Anal. Calcd for C$_{24}$H$_{36}$CoO$_2$P$_2$: C, 60.38; H, 7.60. Found: C, 60.22; H, 7.69.

*Synthesis of (POCOP)Co(SPh) (**A-8**).* (POCOP)CoCl (**A-1**) (100 mg, 0.229 mmol) was added to a Schlenk flask and dissolved in ~10 mL of toluene. To this was added PhSH (24.6 μL, 26.5 mg, 0.240 mmol) using a syringe. The reaction mixture was stirred at RT for 4 h. The volatiles were removed under vacuum. The product was extracted with pentane, passed through a pad of Celite, and dried under vacuum. The product was recrystallized from a concentrated pentane solution at −35 °C to give yellow crystals (90 mg, 77%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 35.78 (br, 4H), 8.58 (br, 24H), 6.20 (br, 2H), 4.08 (br, 1H), −2.84 (br, 2H), −20.89 (br, 2H), −67.93 (br, 1H). Anal. Calcd for C$_{24}$H$_{36}$CoO$_2$P$_2$S: C, 56.58; H, 7.12. Found: C, 56.48; H, 7.04.

*Synthesis of (POCOP)Co(Ph)(Cl) (**B-1**).* Method 1. (POCOP)Co(Ph) (**A-7**) (194 mg, 0.41 mmol) was added to a Schlenk flask and dissolved in pentane. The solution was treated with NCS (58 mg, 0.44 mmol) and stirred at RT for 12 h, producing a green-yellow solution. A blue insoluble solid crashed out of the pentane solution and was removed by filtration. The volatiles were removed under vacuum to give a green-yellow solid. The ^{1}H NMR spectrum of this solid shows paramagnetic signals corresponding to (POCOP)CoCl (**A-1**) as well as diamagnetic signals corresponding to (POCOP)Co(Ph)(Cl) (**B-1**). The solid was dissolved in pentane and crystallized at −35 °C. The recrystallization produced a green crystalline solid and yellow crystalline solid. The yellow solid was determined to be (POCOP)CoCl (**A-1**), and the green solid was determined to be (POCOP)Co(Ph)(Cl) (**B-1**). Dissolution of the green solid in C$_6$D$_6$ showed clean **B-1** in the ^{1}H NMR spectrum. After several hours at RT, the same sample showed formation of (POCOP)Co(Cl) (**A-1**) and biphenyl in addition to (POCOP)Co(Ph)(Cl) (**B-1**) in the ^{1}H NMR spectrum.

Method 2. (POCOP)Co(Ph)(OAc) (**B-2**) (12 mg, 0.022 mmol) was dissolved in ~800 μL of C$_6$D$_6$ in a J. Young NMR tube with a PTFE screw cap. To this was added Me$_3$SiCl (3.40 μL, 2.91 mg, 0.27 mmol) using a syringe. The mixed solution was left to stir at RT for 18 h, and complete conversion to (POCOP)Co(Ph)(Cl) (**B-1**) was observed using NMR spectroscopy. The volatiles were removed, and pure (POCOP)Co(Ph)(Cl) (**B-1**) was observed as a green solid. The green solid was dissolved in a minimal amount of pentane and placed in the freezer at −35 °C overnight, after which dark green crystals were obtained: ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 8.04 (bs, 1H, Ph-*H*), 7.01 (t, *J* = 8.5 Hz, 1H, Ar-*H*), 6.69 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.53 (t, *J* = 7.0 Hz, 1H, Ph-*H*), 6.47 (bs, 1H, Ph-*H*), 6.21 (bs, 1H, Ph-*H*), 5.17 (bs, 1H, Ph-*H*), 2.81 (m, 2H, C*H*Me$_2$), 2.16 (m, 2H, C*H*Me$_2$), 1.21 (dvt, *J* = 7.7 Hz, *J* = 7.1 Hz, 6H, CH*Me*$_2$), 1.09 (overlapping dvt, 12H, CH*Me*$_2$), 0.83 (dvt, *J* = 8.1 Hz, *J* = 7.5 Hz, 6H, CH*Me*$_2$); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$) δ 171.0 (t, *J* = 8 Hz, *C*-Co), 140.9 (br), 137.5 (br), 128.9 (br), 127.6 (br), 125.0 (br), 123.7 (s), 106.8 (t, *J* = 5.4 Hz, *C*-O), 29.9 (t, *J* = 9.2 Hz, *C*HMe$_2$), 27.9 (t, *J* = 11.7 Hz, *C*HMe$_2$), 18.6 (s, CH*Me*$_2$), 17.5 (s, CH*Me*$_2$), 16.0 (s, CH*Me*$_2$), 15.7 (s, CH*Me*$_2$); ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$) δ 176.7 (bs).

*Synthesis of (POCOP)Co(Ph)(OAc) (**B-2**).* (POCOP)Co(Ph) (**A-7**) (300 mg, 0.629 mmol) was added to Schlenk flask and dissolved in toluene to give a dark green solution. PhI(OAc)$_2$ (101 mg, 0.314 mmol) was added to the reaction mixture. The solution quickly became light yellow in color. After being stirred overnight at RT, the solution became red in color. The volatiles were removed *in vacuo*. The product was extracted with pentane and passed through a pad of Celite. The volatiles were removed to give a red-orange solid. The solid was dissolved in a minimum amount of pentane and left overnight at −35 °C to yield a red crystalline solid (270 mg, 80%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 8.07 (d, *J* = 9.5 Hz, 1H, Ph), 6.99 (t, *J* = 6.5 Hz, 1H, Ar), 6.96 (t, *J* = 6.5 Hz, 1H, Ph), 6.81 (t, *J* = 6.5 Hz, 1H, Ph), 6.68 (d, *J* = 6.0 Hz, 2H, Ar), 6.63 (t, *J* = 9.5 Hz, 1H, Ph), 5.79 (d, *J* = 9.5 Hz, 1H, Ph), 2.58 (bm, 2H, C*H*Me$_2$), 1.94 (m, 2H, C*H*Me$_2$), 1.75 (s, 3H, CO$_2$*Me*), 1.29 (dvt, *J* = 6.9 Hz, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 1.17 (dvt, *J* = 7.2 Hz, *J* = 7.1 Hz, 6H, CH*Me*$_2$), 1.02 (dvt, *J* = 6.8 Hz, *J* = 6.5 Hz, 6H, CH*Me*$_2$), 0.88 (dvt, *J* = 8.6 Hz, *J* = 7.6 Hz, 6H, CH*Me*$_2$); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$) δ 182.6 (s, *C*O$_2$Me), 168.5 (t, *J* = 8.4 Hz, C-Co), 141.8 (s), 141.2 (s), 134.9 (s), 129.1 (s), 127.6 (s), 125.4 (s), 123.4(s), 106.3 (t, *J* = 5.0 Hz, C-O), 28.6 (t, *J* = 6.7 Hz, *C*HMe$_2$), 28.2 (t, *J* = 11 Hz, *C*HMe$_2$), 23.7 (s, CO$_2$*Me*), 17.8 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$), 16.4 (s, CH*Me*$_2$), 15.8 (s, CH*Me*$_2$); ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$) δ 179.3 (bs).

*Synthesis of (POCOP)Co(Ph)(I) (**B-3**).* (POCOP)Co(Ph)(OAc) (**B-2**) (54 mg, 0.099 mmol) was dissolved in ~800 μL of C$_6$D$_6$ in a J. Young NMR tube with a PTFE screw cap. To this was added Me$_3$SiI (16 μL, 22 mg, 0.110 mmol) using a syringe. Complete conversion to (POCOP)Co(Ph)(I) was observed using NMR spectroscopy after 10 min. The contents of the NMR tube were transferred to a 25 mL Schlenk flask; the volatiles were removed, and pure (POCOP)Co-

(Ph)(I) was obtained as a green solid (40 mg retrieved from the flask, 67% yield): ^{1}H NMR (300 MHz, C_6D_6) δ 7.43 (bs, 1H, Ph-*H*), 7.05 (t, *J* = 8.5 Hz, 1H, Ar-*H*), 6.67 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.42−6.35 (overlapping m, 2H, Ph-*H*), 6.09 (bs, 1H, Ph-*H*), 5.16 (bs, 1H, Ph-*H*), 3.22 (m, 2H, C*H*Me$_2$), 2.31 (m, 2H, C*H*Me$_2$), 1.34 (dvt, *J* = 8.0 Hz, *J* = 7.4 Hz, 6H, CH*Me*$_2$), 1.13 (dvt, *J* = 6.7 Hz, *J* = 5.7 Hz, 6H, CH*Me*$_2$), 0.91 (dvt, *J* = 8.5 Hz, *J* = 7.3 Hz, 6H, CH*Me*$_2$), 0.83 (dvt, *J* = 8.3 Hz, *J* = 7.4 Hz, 6H CH*Me*$_2$); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 170.2 (t, *J* = 8 Hz, *C*-Co), 140.5 (s), 138.2 (s), 131.1 (br), 129.0 (s), 124.3 (s), 124.0 (s), 106.9 (t, *J* = 5.4 Hz, *C*-O), 31.8 (t, *J* = 9.2 Hz, *C*HMe$_2$), 28.5 (t, *J* = 11.7 Hz, *C*HMe$_2$), 18.8 (s, CH*Me*$_2$), 17.6 (s, CH*Me*$_2$), 17.0 (s, CH*Me*$_2$), 16.6 (s, CH*Me*$_2$); ^{31}P{^{1}H} NMR (120 MHz, C_6D_6) δ 184.5 (bs). Anal. Calcd for $C_{24}H_{36}CoIO_2P_2$: C, 47.70; H, 6.00. Found: C, 47.62; H, 5.81. No significant decomposition of **B-3**, in a solution in ∼800 μL of C_6D_6 in a J. Young NMR tube with a PTFE screw cap, to (POCOP)Co(I) was detected by NMR spectroscopy over a period of 5 days

*Synthesis of (POCOP)Co(Ph)(SPh) (**B-4**).* (POCOP)Co(Ph)(I) (**B-3**) (40 mg, 0.067 mmol) was dissolved in ∼5 mL of THF in a Schlenk flask, and the solution was cooled to −35 °C. To this was added sodium thiophenolate (10 mg, 0.069 mmol) while the mixture was being stirred. The reaction mixture was left to stir at RT for 1 h. The volatiles were pumped off, and the products were extracted by pentane and filtered through a pad of Celite on a glass frit. The volatiles were removed under vacuum, producing a brownish yellow powder. This material was extracted with ∼3 mL of cold Me_3Si_2O, and the resultant solution was placed in the freezer for recrystallization at −35 °C. Overnight recrystallization yielded (POCOP)Co(Ph)(SPh) (**B-4**) as a brown powder (30 mg, 84%): ^{1}H NMR (500 MHz, C_6D_6) δ 8.30 (bs, 1H, Ph-*H*), 7.77−7.72 (m, 2H, Ar-*H*), 7.07−6.91 (overlapping m, 4H, Ar-*H*), 6.74 (d, *J* = 9 Hz, 2H, Ar-*H*), 6.61 (t, *J* = 5.8 Hz, 2H, Ar-*H*), 6.34 (bs, 1H, Ph-*H*), 5.38 (bs, 1H, Ph-*H*), 2.42 (m, 2H, C*H*Me$_2$), 2.32 (m, 2H, C*H*Me$_2$), 1.17−1.02 (overlapping dvt, 18H, CH*Me*$_2$), 0.72 (dvt, *J* = 7.6 Hz, *J* = 7.4 Hz, 6H, CH*Me*$_2$); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 169.0 (t, *J* = 9 Hz, *C*-Co), 141.7 (s), 137.2 (s), 133.5 (s), 124.6 (br), 123.6 (s), 106.2 (t, *J* = 5.5 Hz, *C*-O), 29.8 (t, *J* = 8.5 Hz, *C*HMe$_2$), 29.1 (t, *J* = 11.7 Hz, *C*HMe$_2$), 19.6 (t, *J* = 1.6 Hz, CH*Me*$_2$), 17.1 (t, *J* = 2.2 Hz, CH*Me*$_2$), 16.5 (s, CH*Me*$_2$), 16.2 (s, CH*Me*$_2$); ^{31}P{^{1}H} NMR (120 MHz, C_6D_6) δ 183.3 (bs). Anal. Calcd for $C_{30}H_{41}CoO_2P_2S$: C, 61.43; H, 7.05. Found: C, 61.61; H, 6.91.

*Decomposition of (POCOP)Co(Ph)(Cl) (**B-1**) at RT.* (POCOP)-Co(Ph)(Cl) (**B-1**) (8.1 mg, 0.016 mmol) was dissolved in ∼600 μL of C_6D_6 in a PTFE-capped J. Young NMR tube. 1,4-Dioxane (2 μL, 2 mg, 0.02 mmol) was added using a syringe to serve as an internal standard. The NMR tube was left at RT for several days, and the decomposition of (POCOP)Co(Ph)(Cl) (**B-1**) was monitored by ^{1}H NMR spectroscopy. After 4 days, the composition of the reaction mixture as observed by ^{1}H NMR was (POCOP)Co(Ph)(Cl) (70% of the initial concentration), (POCOP)Co(Cl) [28% of the initial concentration of (POCOP)Co(Ph)(Cl)], and (POCOP)Co(Ph) [<2% of the initial concentration of (POCOP)Co(Ph)(Cl)]. Biphenyl [14% of the initial concentration of (POCOP)Co(Ph)(Cl)] was also observed.

*Decomposition of (POCOP)Co(Ph)(Cl) (**B-1**) at RT with BHT as a Radical Inhibitor.* (POCOP)Co(Ph)(Cl) (**B-1**) (8.1 mg, 0.016 mmol) was dissolved in ∼600 μL of C_6D_6 in a PTFE-capped J. Young NMR tube. 1,4-Dioxane (2 μL, 2 mg, 0.02 mmol) was added using a syringe to serve as an internal standard. Butylated hydroxytoluene (BHT) (3.5 mg, 0.016 mmol) was also added to this mixture. The NMR tube was left at RT for several days, and the decomposition of (POCOP)Co(Ph)(Cl) (**B-1**) was monitored by ^{1}H NMR spectroscopy. After 4 days, the composition of the reaction mixture as observed by ^{1}H NMR was (POCOP)Co(Ph)(Cl) (75% of the initial concentration), (POCOP)Co(Cl) [24% of the initial concentration of (POCOP)Co(Ph)(Cl)], and (POCOP)Co(Ph) [<1% of the initial concentration of (POCOP)Co(Ph)(Cl)]. Biphenyl [12% of the initial concentration of (POCOP)Co(Ph)(Cl)] was also observed.

Thermolysis of (POCOP)Co(Ph)(SPh) with an Internal Standard. (POCOP)Co(Ph)(SPh) (**B-4**) (4 mg, 7 μmol) was dissolved in ∼600 μL of C_6D_6 in a PTFE-capped J. Young NMR tube. 1,4-Dioxane (2 μL, 2 mg, 0.02 mmol) was added using a syringe to serve as an internal standard. The NMR tube was then placed in an oil bath at 80 °C for 30 min. Upon analysis of the sample by ^{1}H and ^{31}P NMR spectroscopy, 80% conversion to **D-1** was observed: ^{1}H NMR (C_6D_6) δ 7.52−7.42 (m, 3H, Ar-*H*), 7.36−7.24 (overlapping m, 5H, Ar-*H*), 7.22−7.05 (m overlapping with solvent, 4H, Ar-*H*), 7.22−7.05 (overlapping m, 2H, Ar-*H*), 1.55 [m, 4 H, C*H*(Me)$_2$], 0.99−0.81 (m, 24H, CH*Me*$_2$); ^{31}P{^{1}H} NMR (C_6D_6) δ 148.7.

Scaled-Up Thermolysis of (POCOP)Co(Ph)(SPh) with an Internal Standard and Subsequent Hydrolysis and Analysis of the Obtained Products. (POCOP)Co(Ph)(SPh) (**B-4**) (34 mg, 58 μmol) was dissolved in ∼600 μL of C_6D_6 in a PTFE-capped J. Young NMR tube. 1,4-Dioxane (2 μL, 2 mg, 0.02 mmol) was added using a syringe to serve as an internal standard. The NMR tube was then placed in an oil bath at 80 °C for 30 min. Upon analysis of the sample by ^{1}H and ^{31}P NMR spectroscopy, 80% conversion to **D-1** was observed, with the rest of the (POCOP)Co(Ph)(SPh) (**B-1**) converting to (POCOP)Co(Ph) (**A-7**) and other unidentified decomposition products. The volatiles were removed *in vacuo*, and the solids were redissolved in ∼2 mL of CH_2Cl_2. The solution was washed with 3 × 5 mL of concentrated HCl followed by 3 × 5 mL of distilled water. The organic layer was extracted and passed through silica, and the volatiles were removed *in vacuo* to yield a pale yellow solid. The solid was washed with 2 × 2 mL of hexanes and dried *in vacuo* to give a solid **D-2** (7 mg, 66%). ^{1}H and ^{13}C NMR data for **D-2** matched those of 2-phenylresorcinol: ^{1}H NMR (C_6D_6, 500 MHz) δ 7.58 (t, *J* = 7.5 Hz, 2H, Ar-*H*), 7.49 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.43 (d, *J* = 7.0 Hz, 2H, Ar-*H*), 7.15 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 6.59 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 4.83 (s, 2H, O-*H*); ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz) δ 153.6 (Ar-*C*), 131.0 (Ar-*C*), 130.8 (Ar-*C*), 130.4 (Ar-*C*), 129.7 (Ar-*C*), 129.4 (Ar-*C*), 115.5 (Ar-*C*), 107.8 (Ar-*C*).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00511.

Graphical depictions of the NMR spectra and descriptions of X-ray diffraction experiments (PDF)

Accession Codes

CCDC 1858833−1858835 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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