Concerted aryl-sulfur reductive elimination from PNP pincer-supported Co(III) and subsequent Co(I)/Co(III) comproportionation†

Bryan J. Foley, a Chandra Mouli Palit, a Nattamai Bhuvanesh, a Jia Zhou a, b and Oleg V. Ozerov a, c

This report discloses a combined experimental and computational study aimed at understanding C–S reductive elimination from Co(III) supported by a diarylamido/bis(phosphine) PNP pincer ligand. Divalent (PNP)Co-aryl complexes could be easily oxidized to five-coordinate Co(III) derivatives, and anion metathesis provided five-coordinate (PNP)Co(Ar)(SAr) complexes of Co(III). In contrast to their previously described (POCOP)Co(Ar)(SAr) analogs, but similarly to the (PNP)Rh(Ar)(SAr) and (POCOP)Rh(Ar)(SAr) analogs, (PNP)Co(Ar)(SAr) undergo C–S reductive elimination with the formation of the desired diarylsulfide product ArSAr. DFT studies and experimental observations are consistent with a concerted process. However, in contrast to the Rh analogs, the immediate product of such reductive elimination, the unobserved Co(I) complex (PNP)Co, undergoes rapid comproportionation with the (PNP)Co(Ar)(SAr) starting material to give Co(II) compounds (PNP)Co–Ar and (PNP)Co–SAr.

Introduction

Carbon-heteroatom cross coupling has become an immensely powerful synthetic tool in recent years. The existing art on cross-coupling reactions is historically dominated by palladium, with additional prominence by another group 10 metal Ni, as well as a group 11 metal Cu. There has recently been a renewed push to find alternatives to homogeneous precious metal catalysts from among cheaper, more Earth-abundant metals.

Cross-coupling reactions of aryl (pseudo)halides with nucleophiles typically rely on the oxidative addition (OA) – transmetallation (TM) – reductive elimination (RE) cycles such as depicted in Fig. 1. The OA and RE steps are two-electron processes that are well established for Pd. Our group has been interested in the potential of the analogous OA–TM–RE cycle to enable cross-coupling catalysis by group 9 metals. Pd (and Ni) go through the Pd0/PdII oxidation states corresponding to the d5/6 configurations. For group 9 metals, we have targeted the M1/MIII oxidation states (d0). In particular, we were able to establish that a T-shaped Rh3 center supported by an anionic pincer ligand possesses a rather striking similarity in its reactivity to the LPd0 fragment. This approach with Rh proved especially fruitful in catalytic C–S coupling. Catalytic C–S coupling with Pd has received a considerable amount of attention.

It is easy to envisage the steps of the analogous pincer-supported CoIII cycle (Fig. 1). However, in the chemistry of 3d metals, competition from one-electron pathways to the desired two-electron steps is something that must be closely considered. In principle, there is a substantial body of literature describing Co-based cross-coupling catalysis, and CoI/CoIII cycles are often proposed. However, firm mechanistic information remains rather limited. Fout and coworkers analyzed a Co-catalyzed aryl halide amination system in 2014 (ref. 29) where the CoI/CoIII cycle was strongly implicated but...
the individual steps of OA and RE were not observed. Chirik et al. reported on the C–C coupling of aryl triﬂates in 2016, where it appears that the CoI/CoIII cycle should operate but the details were not uncovered.30 Bernskoetter’s group reported a well-deﬁned example of C–C RE from CoIII in 2011,31 but this involved coupling of two CH3 groups, only indirectly related to aryl halide reactions. However, outside of aryl halide coupling reactions, there have in recent years appeared examples of homogeneous catalysis by pincer-supported Co complexes where two-electron OA/RE steps are either well understood or strongly suggested.32–42

In 2018, we reported on the reactivity of (POCOP)Rh(Ph)(SPh).43 In contrast to (PNP)Rh(Ph)(SPh)18 or (POCOP)Rh(Ph)(SPh),19 it did not undergo C–S RE but instead a RE of the phenyl with the pincer aryl (Scheme 1). Because of this, the POCOP system did not allow for the investigation of the C–S RE. We surmised that the analogous RE with the amido of a PNP pincer should be less likely and set oﬀ to examine the reactivity of (PNP)CoII(Ar)(SAr) complexes. The present report details our eﬀorts in the synthesis of 5-coordinate CoIII-aryl/thiolate complexes supported by the PNP ligand, their propensity to undergo concerted C–S RE, and the subsequent comproportionation reactivity that again diverges from the Rh system.

Results and discussion

Synthesis and characterization of (PNP)CoII complexes

Treatment of the previously reported square planar, low spin, S = 1/2 (PNP)CoCl44 (1) with selected aryl nucleophiles resulted in the formation of the corresponding CoII aryl complexes 2a-c (Scheme 2). Clean transmetallation of 1 was also accomplished using sodium thiophenolate reagents to give CoII thiolate complexes 3a-c (Scheme 2). Complexes 2a-c and 3a-c were green to dark teal in color. They exhibited paramagnetically shifted 1H NMR resonances contained in the +40 to ~30 ppm range, except for the resonances at around ~90 ppm in complexes 2a–2c which we tentatively assign as ortho-hydrogens of the Co-bound aryl rings. No 31P NMR resonances were detected for these complexes.

Examination of the literature shows that four-coordinate Co(ii) complexes of anionic pincer ligands are known with both a low-spin S = 1/2 conﬁguration (square-planar geometry) and a high-spin S = 3/2 conﬁguration (pseudotetrahedral geometry).43–52 Low-spin, square-planar Co(ii) complexes give rise to paramagnetically shifted 1H NMR resonances that are broad compared to diamagnetic compounds, but are typically interpretable in terms of their relative integration and chemical
(in)equivalence. High-spin Co(II) compounds tend to produce "H NMR spectra that are broadened beyond useful interpretation. Complexes 2a–c and 3a–c in the present work and the (POCOP)CoX complexes (Fig. 2) recently reported by us and Heinekey et al. are all low-spin compounds. The same is true for the (PNP1)CoX complexes of the pyrrolyl-based PNP ligand.

Fig. 3 POVRay renditions of ORTEP drawings (50% probability ellipsoids) of (PNP)Co(Tol), (PNP)Co(Ph)(OAc), and (PNP)Co(Ph)(SPh). All hydrogen atoms omitted. Selected bond distances (Å) and angles (degrees) for (PNP)Co(Tol) (2b, left): N1–Co1, 1.9262(17); P1–Co1, 1.7256(7); P2–Co1, 2.1789(7); C15–Co1, 1.9392; N1–Co1–C15, 178.99(9); P1–Co1–P2, 172.63(5). Selected bond distances (Å) and angles (degrees) for (PNP)Co(Ph)(OAc) (4a, middle): N1–Co1, 1.9333(12); O1–Co1, 1.9896(12); O2–Co1, 2.1166(11); P1–Co1, 2.2619(7); P2–Co1, 2.2335(6); C29–Co1, 1.9403(15); C29–Co1–N1, 97.59(6); N1–Co1–O1, 165.17(5). Selected bond distances (Å) and angles (degrees) for (PNP)Co(Ph)(SPh) (6a, right): N1–Co1, 1.9497(18); P1–Co1, 2.2597(7); P2–Co1, 2.2313(7); C33–Co1, 1.933(2); S1–Co1, 2.2069(6); N1–Co1–C33, 98.54(8); N1–Co1–S1, 149.60(6).

Synthesis and characterization of (PNP)Co(III)(Ar)(X) complexes

As is the case in our (POCOP)Co system, reacting (PNP)Co(aryl) complexes 2a–b with 0.5 eq. of PhI(OAc)2 led to the clean formation of (PNP)Co(aryl)(OAc) (4a–b), isolated in good yield as tan solids after workup (Scheme 3). Treatment of 4a with Me3SiI furnished dark blue-green (PNP)Co(Ph)(I) (5a). 5a can also be prepared via reaction of 2a with 0.5 equiv. of I2. Transmetallation from 5a using sodium thiophenolate proceeded smoothly providing (PNP)Co(Ph)(SPh) complex 6a as a dark blue solid in good yields after recrystallization (Scheme 3). The analogous synthesis of (PNP)Co(Ar)[SAr′] complexes 6b–c from 4b–c can be achieved without the isolation of the intermediate 5b–c.
The (PNP)Co[Ar][X] compounds (4a–b, 5a, and 6a–c) gave rise to $^1$H, $^13$P, and $^13$C NMR spectra expected for these diamagnetic complexes. The resonances arising from the Co-bound aryl group exhibited inequivalence between the two ortho- and between the two meta-hydrogens, characteristic of restricted rotation of the metal-bound aryl oriented cis to the central donor of a pincer ligand with two side –PPr$_2$ arms. In the cases of the aryl/thiolate complexes 6a–6c, these aromatic resonances were broad humps, whereas in the aryl/halide 5a and aryl-acetato complexes 4a–4b, sharp resonances with well-resolved fine structure were observed.

### Synthesis and characterization of (PNP)Co$^I$ complexes

The dimeric compound [[(PNP)Co]$_2$] (7) (Scheme 4) was previously reported by Mindiola et al. We were also able to observe a Co$^I$ complex [PNP]Co[PPh$_3$]$_2$ (8) by treatment of (Ph$_3$P)$_2$Co[N(SiMe$_3$)$_2$]$_2$ with (PNP)H (10). This reaction liberated triphenyl phosphine and HN(SiMe$_3$)$_2$ (Scheme 4). A wide $^1$H NMR spectral window revealed a new set of paramagnetically shifted $^1$H NMR resonances which we have assigned to 8. Compound 8 was not isolated as it appears to be in equilibrium with diamagnetic 7 on the timescale of experimental handling. For example, freshly made 8 was observed to produce 7 when left overnight in a −35 °C freezer, while addition of 12 equiv. of PPh$_3$ to 7 led to the observation of 8 (Scheme 4). Addition of 12 eq. of tris(4-methoxyphenyl)phosphine to this mixture gave rise to a second set of distinct but very similar paramagnetically shifted $^1$H NMR resonances which we interpret as belonging to 11 (Scheme 4, Fig. S12†). This observation supports the notion that 8 is a PPh$_3$-bound Co complex.

Based on the paramagnetically shifted $^1$H NMR spectra, we assume that both 8 and 11 possess an $S = 1$ ground state. As with four-coordinate Co(ii), there are examples of both high- and low-spin pincer complexes of Co(ii) ($S = 1$ or 0) (Fig. 2, bottom). With the pyridine-centered PN$^+$P ligand, complexes substituted with stronger field Me or Ph are low-spin, while Cl or OAr as the fourth donor are high-spin. With the PNP ligand, CO in place of PPh$_3$ in 8 was reported to give a low-spin carbonyl complex (PNP)Co(CO). Thus, it appears that the presence of at least one strong-field ligand (CO, or hydride/alkyl/aryl) is needed to ensure an $S = 0$ ground state.

### X-ray structural studies

Single crystals of 2b, 4a, and 6a suitable for X-ray diffraction were grown from hydrocarbon solvents at −35 °C (Fig. 3). The geometry about the cobalt center in the solid-state structure of 2b is slightly distorted square planar. The Co-bound tosyl ring in 2b is approximately perpendicular to the Co/P/N/P plane.

The structure of 4a is pseudo-octahedral about the metal center, with a $\kappa^2$ acetate coordination. The two oxygens of the acetate are bound trans to two donors of markedly different trans-influence (amido N vs. phenyl C), which is reflected in the large difference between the two Co–O bond distances (ca. 0.13 Å). The geometry about Co in 6a is intermediate between square-pyramidal with the phenyl trans to the empty site and Y-shaped (with the thiolate at the base of the Y). The preference of low-spin five-coordinate d$^6$ complexes for square-pyramidal and Y-shaped geometries have been discussed elsewhere. The angles, bond lengths, and orientation of the thioaryl ligand about the cobalt center for 6a are similar to those that we reported for [POCOP]Co[Ph][SPh].

### Thermolysis of (PNP)Co$^{III}$[Ar][SAr] complexes

Thermolysis of 6a in benzene led to the formation of 2a, 3a, and A in a 1 : 1 : 1 ratio (Scheme 5, top). Further investigation showed that this process is first order in 6a (Fig. S1†). Thermolysis of this complex in the presence of 1 eq. of 2,6-di-tert-butyl-4-methylphenol (BHT) resulted in the same distribution of products in the same time period, providing evidence against generation of free aryl radicals. Similarly, thermolysis of 6b in benzene resulted in the formation of 2b, 3b, and C in a 1 : 1 : 1 ratio (Scheme 5, bottom; Fig. S3 and S4†).

Attempting to determine whether the C–S bond formation step happened at a single Co center, thermolysis of 6a in a 1 : 1 ratio with 6b was carried out. In principle, strict unimolecular C–S reductive elimination should lead to only two diarylsulfide products as a result of this thermolysis. In the event, formation of four diarylsulfides was instead observed, along with the four expected Co$^{II}$ products: 2a, 2b, 3a, and 3b (Scheme 6). $^{19}$F NMR analysis during the course of the reaction at 80 °C revealed the formation of the Co(ii) crossover product 6c (Fig. S5†). This suggested that during the thermolysis, thiolate ligands can exchange between the Co(ii) centers prior to RE. This exchange would then lead to the formation of crossover diarylsulfides,
even if RE happens unimolecularly, and thus prevent us from firmly excluding crossover via other pathways. Performing this reaction at double the initial concentration of Co(II) complexes still showed 6c during thermolysis and a very similar distribution of Co(II) products and diaryl sulfides after the reaction had completed.

The thiolate exchange between Co(III) complexes could occur in at least two non-exclusive ways: (1) direct thiolate exchange between two Co(III) complexes, (2) via exchange between Co(II) and Co(III) thiolate complexes. To probe the ability of Co(II) to exchange thiolate ligands with Co(III), 6a was thermolysed in the presence of 1 eq. 3b. In situ $^{19}$F NMR observation at 80 °C revealed the formation 6c during the reaction (Scheme 7, top). After the thermolysis was complete, 6% of the total starting fluorinated thiolate was found as (PNP)Co(Ph)(SPh) (6b) during the reaction (Scheme 7, bottom). By way of a control experiment, thermolysis of 6b with 2-isopropylphenyl-4-$\text{CF}_3$SPh (2a) at 80 °C for 7 d resulted in no detectable change, establishing that Co(II) compounds do not react with diarylsulfides.

Comproportionation hypothesis and reactions with Co(I) compounds

By analogy with our work on pincer rhodium complexes, we envisioned that after the concerted C–S reductive elimination from 6a, an unsaturated (PNP)Co fragment (12) would be generated. We further hypothesized that this unsaturated (PNP)Co species 12 undergoes rapid comproportionation with the remaining 6a to generate the observed Co(II) products. To test this hypothesis, 7 was combined with 6a in benzene at ambient temperature. An immediate color change to green was observed upon mixing, indicating the formation of (PNP)Co(II) complexes (Scheme 8). $^1$H NMR spectroscopic observation confirmed the formation of 2a and 3a in a 1 : 1 ratio. Similarly, mixing freshly made 8 with 6a resulted in an immediate comproportionation producing 2a and 3a in a 1 : 1 ratio by $^1$H NMR spectroscopy (Scheme 8). In this case, free triphenylphosphine was also observed by $^1$H and $^{31}$P($^1$H) NMR spectroscopy.

Reversibility of C–S RE?

Treatment of 7 with diphenyl sulfide (A) and heating overnight in a 55 °C oil bath resulted in the formation of 2a and 3a in a 1 : 1 ratio (Scheme 8). This experiment shows that Co(i) here can cleave a C–S bond in a diarylsulfide, suggesting that C–S RE might be reversible. A related observation is that thermolysis of 6b in the presence of A resulted in the formation of a small amount of C in addition to D (Scheme 7, bottom); which can be interpreted as occasional trapping of a Co(i) species formed in the RE of D by Ph$_2$S(E) as opposed to by the Co(III) starting material 6b. By way of a control experiment, thermolysis of 2b and 3b with A at 80 °C for 7 d resulted in no detectable change, establishing that Co(II) compounds do not react with a diarylsulfide.

In order to gain some insight into whether this C–S cleavage by Co(i) occurs via concerted OA, we subjected 7 to thermolysis with 2-isopropylphenyl-4-$\text{F}$-fluorophenyl sulfide (E). Based on

![Scheme 8](image-url)
what we learned of the preferences of the (pincer)Rh systems in OA with aryl halides, it seemed reasonable to assume that the concerted OA mechanism with (PNP)Co should favor the C–S bond unencumbered by the ortho-isopropyl substituent (C\textsuperscript{\text{F}}–S, Scheme 9). DFT calculations (see ESI†) predicted that homolytic cleavage of the C\textsuperscript{\text{F}}–S bond is 1.6 kcal mol\textsuperscript{−1} less thermodynamically favorable than the cleavage of the C–S bond connecting to the 2-isopropylphenyl substituent (C\textsuperscript{\text{R}}–S, Scheme 9). Thus, a radical abstraction mechanism for the C–S cleavage might be expected to favor the cleavage of C\textsuperscript{\text{R}}–S.

Heating the mixture of 7 with E in at 80 °C for three days resulted in the complete consumption of 7 with the formation of a 1 : 1 mixture of 2c and 3e (Scheme 9). Compound 3b was not observed by either \textsuperscript{1}H or \textsuperscript{19}F NMR spectroscopy. Treatment of this solution with anhydrous HCl resulted in the formation of 1 along with 2c with presumed liberation of 2-isopropylthiophenol. GC-MS and APCI-MS analysis of this solution revealed the formation of 2-isopropylthiophenol and E as the only two volatile components; p-FC\textsubscript{6}H\textsubscript{4}SH was not detected. We did not detect any biaryl or bisulfide products by GC-MS. These observations show that only the C\textsuperscript{\text{F}}–S bond was cleaved, consistent with a concerted OA C–S activation pathway.\textsuperscript{44}

DFT calculations

In order to gain better understanding of the system, DFT calculations were carried out with the Gaussian 09 (ref. 65) program to address a few salient points (Scheme 10). The calculations were carried out with the Gaussian 09 (ref. 65) program to address a few salient points (Scheme 10). The geometries were optimized using [B3LYP/LANL2DZ/6-31G(d)] level of theory\textsuperscript{66} in the gas phase and the energies for these geometries were then determined with the [M06/SDD/6-311+G(d,p)] method\textsuperscript{67} incorporating the benzene solvent effect via the SMD model.\textsuperscript{68} Further details are given in the ESL† We first evaluated the thermodynamics of the overall observed reaction. Conversion of 1 equiv. of 6a into a 0.5 : 0.5 : 0.5 mixture of 2a : 3a : A was calculated to be favorable by −22.1 kcal mol\textsuperscript{−1} in free energy. The geometries of 2a and 3a in the doublet ground state were approximately square-planar geometry and consistent with the X-ray structure of 2b. The calculated structure of 6a reproduced the overall geometry determined in the XRD study, as well. Fig. 4 shows the calculated SOMO’s and spin density profiles for 2a and 3a. Interestingly, the nature of the SOMO’s in these two compounds differs. In 2a, it is essentially a pure d\textsubscript{xy} whereas in 3a it is primarily d\textsubscript{xz} (x axis along Co–S) with small contributions from the amido and thiolate ligands. This disparity reflects the fact that a stronger σ-donor Ph elevates the energy of d\textsubscript{xy} in 2a relative to d\textsubscript{xz}. In either case, the SOMO is firmly metal-based.

We then considered the monomeric Co(\textit{i}) intermediates in the reaction. Both the “naked” (PNP)Co fragment 12 and its SPh\textsubscript{3} adduct 13 were calculated to favor a triplet ground state (by 15.5 kcal mol\textsuperscript{−1} and 9.9 kcal mol\textsuperscript{−1} in free energy, respectively). The geometry of the triplet (PNP)Co(SPh\textsubscript{3}) (13t) about Co is decidedly not planar, and can be described as attempting to approach tetrahedral within the constraint of the pincer. The array of donor atoms in 13t is the same as in the low-spin doublet 3a, but all the calculated bond distances to Co are considerably longer, especially that for the C–S bond (2.538 Å in 13t vs. 2.264 Å in 3a).

The reductive C–S coupling in 6a to give singlet (PNP) Co(SPh\textsubscript{3}) (13s) is nearly ergoneutral, but the conversion of 6a to 13t is favorable on the enthalpy (by 4.5 kcal mol\textsuperscript{−1}) and on the free energy (by 9.5 kcal mol\textsuperscript{−1}) surfaces. The dissociation of
SPh₂ from 13t to give triplet 12t and free SPh₂ is endothermic, but is of course favored entropically, resulting in a favorable free energy of dissociation. Thus the complete RE from 6a to give 12t and A is exoergic by 13.6 kcal mol⁻¹, but that is less favorable than the formation of a mixture of 2a : 3a : A.

The dimerization of 12t to form 7 was calculated to be enthalpically favorable, but disfavored entropically and overall slightly exoergic (by 2.8 kcal mol⁻¹ per Co). This is consistent with the experimental observation of the dimer 7 as the ground state.

The thermodynamics of the standalone Co(i)/Co(III) comproportionation reactions were calculated to be consistent with our hypothesis outlined above. The reaction of 12t with 6a to give 2a and 3a was found to be exotherosmic and exoergic (by −14.6 and −15.3 kcal mol⁻¹, respectively). A similar comproportionation starting from 7 instead of 12t was also found to be favorable (by −13.9 kcal mol⁻¹ per mole of Co).

The substantial (ca. 15 kcal mol⁻¹) calculated preference for the triplet state of (PNP)Co(12t) is at odds with the recent report by Lee and coworkers, which presented three-coordinate (PNP5)Co as a singlet species (Fig. 5). This interpretation by Lee et al. is also at odds with the unambiguously established triplet ground states for the (PNP3)Co and (PNP4)Co by the Caulton™ and Gade groups, respectively (Fig. 5). Both (PNP3)Co and (PNP4)Co were isolated and fully characterized, including by X-ray crystallography, magnetic moment measurement, as well as by elemental analysis for (PNP4)Co. (PNP5)Co was purported to be isolated, but no structural determination or magnetic moment was reported, and satisfactory elemental analysis was not obtained. (PNP5)Co was analyzed by DFT calculations as a singlet, but the calculations examining the viability of the triplet state were not carried out. Given these facts and the very close similarity of the PNP and PNP4 ligands, it would be very surprising indeed if they led to different spin state preferences in 12 vs. (PNP5)Co. Although we do not observe free 12, it is also worth pointing out that even its adduct with Ph₃P (8) does not present as a low-spin complex based on the appearance of its NMR spectra. It is possible that the (PNP5)Co system needs to be reexamined more closely.

For the C–S reductive coupling en route to 13 from 6a, a transition state was found, lying 24.8 kcal mol⁻¹ above 6a in free energy (TS, Fig. 6). This transformation requires spin crossover in the process, which we propose happens after the singlet TS on the reaction coordinate. A singlet state of the reductive coupling product (PNP)Co(SPh₂) (13s) is only 0.4 kcal mol⁻¹ endoergic relative to 6a. However, 13t is lower in energy still. The activation barrier magnitude calculated by DFT agrees reasonably well with the experimental observations. The observed half-life of 0.6 h at 80 °C for 6a corresponds to ca. 26 kcal mol⁻¹ in free energy barrier (ΔG°₂₉₈).

Examination of the geometry of TS (Fig. 7) shows that it can be thought of as reflecting the migration of the Co-bound Ph group onto the S atom, which in turn is brought more closely into the plane defined by P/N/P/Co. The Co–S distance in TS is actually slightly shorter than in 6a, and much shorter than calculated in 13t. The Co–C₆ distance elongates by ca. 0.13 Å in TS (2.055 Å) vs. 6a (1.929 Å), while the newly forming C–S distance (2.085 Å) is about 0.29 Å longer than the expected C–S distances of ca. 1.80 Å in Ph₃S or its complexes. The other geometric feature of TS that needs to be emphasized is the necessary rotation of the Co-bound phenyl ring from edge-on relative to S in 6a to side-on in TS. The hindrance of this rotation by the Pr groups is a major contributor to the magnitude of the activation barrier. This is a rather general observation for the reductive elimination of R-X from five-coordinate d⁶ complexes [pincer]M(R)(X) where R = aryl or alkenyl, first articulated by Goldman and Krogh-Jespersen for the (PCP)Ir system. We previously discussed this issue for the closely related RE reactions from [pincer]Rh(Ar)(X) complexes.

Lastly, we considered the experimental observations of the apparent reversibility of C–S RE in reactions of A with Co(III) complexes. Thermodynamically, the experimentally observed reaction of [(PNP)Co]₂ with Ph₃S to give 2a and 3a was indeed calculated to be favorable (Scheme 10). At first glance, the microscopic reverse C–S OA might appear kinetically feasible as the energy of 13s is similar to that of 6a. However, given that (1) 13t, (2) 12t + free SPh₂, and (3) 7 + free SPh₂ are all considerably lower in energy than 13s, the barriers for the microscopic reverse C–S OA starting from these states are prohibitively high.

In rationalization, two possibilities might be considered. First, it is possible that our DFT calculations do not accurately describe the relative energies of compounds in...
The second option is that the reaction of \( A \) with 7 proceeds as an C–S OA within the dimer, without the formation of monomeric intermediates. The putative single C–S OA dicobalt product may then comproportionate intramolecularly to give 2a and 3a without the intermediacy of free 6a. This reaction pathway would thus not be a microscopic reverse of the monomolecular C–S RE. The complexity of the many potential pathways that would need to be considered to properly analyze the reaction of \( ([PNP]Co)_2 \) with \( A \) has deterred us from pursuing this problem computationally within the scope of this report.

**Conclusion**

In summary, \([PNP]Co\) complexes in the +1, +2, and +3 oxidations states relevant to potential cross-coupling reactions were prepared and fully characterized. A switch to a PNP ligand prevented intramolecular reductive elimination of the Co–Ar unit with the central donor of the pincer and permitted observation of concerted C–S reductive elimination. However, it appears that the PNP supporting ligand does not have a strong enough ligand field strength to prevent promotion of an electron from the \( (PNP)Co \) fragment to a triplet ground state. This fundamental realization is probably related to the swift \( Co(i)/Co(ii) \) comproportionation investigated in this work, which removes potentially catalytically competent odd-oxidation state cobalt complexes from the reaction.

Interestingly, the \( Co(i)/Co(ii) \) comproportionation observed here directly mimics the Ni(0)/Ni(II) comproportionation observed and studied by the Hazari group.72 The similarity further underscores the close parallels in reactivity that exist between group 9 metals in the \( d^{10}/d^8 \) manifold and the group 10 metals in the \( d^{10}/d^8 \) manifold, as well as the contrast between the 3d metals (Co or Ni comproportionate) and the 4d metals (Rh or Pd do not comproportionate) within the same group.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

We are grateful to the Welch Foundation (grant A-1717 to O. V. O.) for support of this research. This work was also supported by the startup of Harbin Institute of Technology (Shenzhen) through the Talent Development Starting Fund from Shenzhen Government. Computer time made available by the National Supercomputing Center of China in Shenzhen (Shenzhen Cloud Computing Center) is gratefully acknowledged. We thank Samuel R. Lee for assistance with the composition of the manuscript.

**Notes and references**

53 Steric bulk of the side donors in the pincer ligand may also be a factor that influences the spin state of the Co complex, see: S. P. Semproni, C. Milsmann and P. J. Chirik, J. Am. Chem. Soc., 2014, 136, 9211–9224.
55 Compounds 5b and 6e were not isolated.
59 It also cannot be excluded that undetectable traces of NaSAr or HSAr may be catalyzing the thiolate exchange.
63 No observable change was noted within 10 min after mixing the reagents at RT.
65 M. J. Frisch, et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.


