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Oxidative Addition of Dihydrogen, Boron Compounds, and Aryl Halides to a Cobalt(I) Cation Supported by a Strong-Field Pincer Ligand

Stephan M. Rummelt, Hongyu Zhong, Nadia G. Léonard, Scott P. Semproni, and Paul J. Chirik*

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Abstract

Cationic cobalt(I) dinitrogen complexes with a strong-field tridentate pincer ligand were prepared and the oxidative addition of polar and non-polar bonds was studied. Addition of H₂ to [(iPrPNP)Co(N₂)]⁺ (iPrPNP = 2,6-bis((diisopropylphosphanyl)methyl)pyridine) in THF-*d*8 resulted in rapid oxidative addition and formation of the *cis*-Co(III) dihydride complex, *cis*-[(iPrPNP)Co(H)₂L]⁺ where L = THF or N₂. The addition of H₂ was reversible as evidenced by the dynamics observed by variable temperature ¹H NMR spectroscopy and the regeneration of [(iPrPNP)Co(N₂)]⁺ upon exposure to dinitrogen. In contrast, addition of HBPIn, (Pin = pinacolato) B₂Pin₂ and aryl halides resulted in the formation of net one-electron oxidation products: cationic Co(II)–boryl and Co(II)–halide/aryl complexes, respectively. All products were structurally characterized by X-ray crystallography and the electronic structures were determined by a combination of magnetic moment measurements, EPR spectroscopy and DFT calculations. Monitoring the addition of HBPIn to [(iPrPNP)Co(N₂)]⁺ provided evidence for a transient Co(III) oxidative addition product that likely undergoes comproportionation with the cobalt(I) starting material to generate the observed Co(II) products.

Graphical Abstract

*Corresponding Author: pchirik@princeton.edu.

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR Spectra, additional solid-state molecular structure, input file for DFT calculation (PDF)

Computed coordinates of [(iPrPNP)Co(BPin)]⁺ (xyz)

Accession Codes

CCDC 1879909, 1879910, 1879911, 1879912, 1879913, and 1879930 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: + 441223 336033.

INTRODUCTION

The oxidative addition of polar and non-polar bonds to reduced transition metal complexes is a fundamental organometallic transformation and a key substrate activation step in numerous catalytic cycles.¹ Although in certain instances, one electron chemistry has proven beneficial and enabled unique reactivity with first row transition metal catalysts,² enabling two-electron chemistry over kinetically and thermodynamically accessible one-electron alternatives is an ongoing challenge for realizing catalysis with Earth abundant first row transition metals such as iron and cobalt.³

Introduction of strong field ligands such as phosphines or carbon monoxide to first row metals is an established strategy for increasing *d*-orbital splitting, favoring low spin complexes and in turn increasing the propensity for two-electron, precious metal-like reactivity.³ In contemporary catalysis, tridentate pincers, particularly those containing phosphine or N-heterocyclic carbene donors, have emerged as a privileged class of ligands for enabling oxidative addition to iron⁴ and cobalt.^{5,6} Of particular note, bis(arylimidazol(in)-2-ylidene)pyridine iron bis(dinitrogen) complexes, (CNC)Fe(N₂)₂, originally synthesized by Danopoulos,⁷ support oxidative addition of C-H,^{4a} Si-H,^{4b} and H-H bonds.^{4c} This fundamental organometallic reactivity was leveraged to synthesize new catalysts for hydrogen isotope exchange in pharmaceuticals with site selectivity driven by steric accessibility and orthogonal to that observed with state-of-the-art iridium catalysts.⁸

Milstein's laboratory and our group have independently explored the coordination chemistry of ^RPNP chelates (^RPNP = 2,6-bis((dialkylphosphanyl)methyl)pyridine) with cobalt.^{5,9,10} Neutral cobalt(I) alkyl complexes, (ⁱPrPNP)CoR, exhibit a rich oxidative addition chemistry with non-polar H-H, C-H, B-H and Si-H bonds and form octahedral Co(III) products (Scheme 1a).^{5,11c,d} With these insights, highly active and selective (ⁱPrPNP)Co catalysts were discovered for the C(sp²)-H borylation of arenes and heteroarenes.¹¹ In each case, mechanistic^{11a,c} and computational studies¹² support a Co(I)-Co(III) cycle where oxidative addition of a C(sp²)-H bond to a cobalt(I)-boryl is a key substrate activation step. Strong field all-carbon pincers have been used by Fout and coworkers in cobalt-catalyzed alkene and nitrile hydrogenation reactions and spectroscopic and mechanistic studies support a Co(I)-Co(III) oxidative addition-reductive elimination cycle.^{6a-c}

Attempts to promote the oxidative addition of polar bonds with reduced cobalt complexes have been dominated by one-electron chemistry. Addition of CH₃I to (ⁱPrPNP)CoCH₃ yields

a mixture of cobalt(II) and cobalt(III) products^{5a} while oxidative addition of aryl-halides/triflates to (ⁱPrPNP)Co(aryl) derivatives are proposed in Suzuki-Miyaura cross coupling reactions but are not well understood.¹³ One-electron reactivity was also observed by Budzelaar and coworkers while studying addition of aryl halides to Co(I) complexes ligated to a redox-active weak field pincer ligand, resulting in atom abstraction of the halide.¹⁴ Likewise, Tonzetich and coworkers isolated a 1:1 mixture of Co(II)-phenyl and Co(II)-bromide complexes following addition of bromobenzene to a Co(I)-dinitrogen complex supported by an anionic PNP pincer-ligand.¹⁵

Because of the rich catalytic chemistry associated with cationic rhodium and iridium complexes such as olefin hydrogenation and hydroacylation that involve oxidative addition as a fundamental step,^{16–18} cationic variants of [(ⁱPrPNP)Co] were targeted. Despite an early example of isolated and structurally characterized cationic Co(I) complexes,¹⁹ studies on their reactivity and catalytic activity remain scarce.^{6a,19b} Here we describe the synthesis and characterization of cationic pincer-ligated cobalt dinitrogen complex, [(ⁱPrPNP)Co(N₂)]⁺ and its reactivity with polar and non-polar bonds (Scheme 1b).

RESULTS AND DISCUSSION

Our studies commenced with exploration of the synthesis of a cationic square planar [(ⁱPrPNP)Co(I)] complex with a neutral ligand occupying the fourth coordination site. Addition of Na[BArF²⁴] (BArF²⁴ = B[C₆H₃-3,5-(CF₃)₂]₄) to a fluorobenzene solution of (ⁱPrPNP)CoCl (**1-Cl**)^{5a} resulted in a rapid color change from violet to violet-red (Scheme 2). Filtration of the reaction mixture and recrystallization of the residue from a fluorobenzenepentane mixture at –35 °C yielded [(ⁱPrPNP)Co(N₂)] [BArF²⁴] (**[1-N₂]⁺**) as dark violet crystals in 88% yield. The *tert*-butyl variant, [(^tBuPNP)Co(N₂)] [BArF²⁴] (**[2-N₂]⁺**) was prepared in a similar manner from (^tBuPNP)CoCl (**2-Cl**)¹⁰ in 85% yield.

The solid-state structure of **[1-N₂]⁺** was determined by single crystal X-ray diffraction and established an idealized square planar geometry around the Co(I) center with the N₂ ligand *trans* to the pyridine of the PNP chelate (Figure 1). The geometry contrasts the distorted, near tetrahedral environment observed with **1-Cl**.^{5a} Coordination of dinitrogen in the solid state was also confirmed by IR spectroscopy (ν_{N_2} (KBr) = 2081 cm^{–1}). To accommodate the sp³ hybridized methylene groups of the PNP chelate the pyridine ring is slightly tilted out of the PNP-plane around cobalt, placing one methylene group above and the other below the idealized plane (*Cipso-Npyr-Co-P* dihedral angles = 17.6°, 10.2°), a feature that is present in all cationic (ⁱPrPNP)Co complexes described in this study. Additionally, there are no close contacts between the cation and anion. The solid-state structure of **[2-N₂]⁺** was also determined by single crystal X-ray diffraction and exhibits comparable features to **[1-N₂]⁺** (see Supporting Information for a graphical representation).

The poor solubility of **[1-N₂]⁺** and **[2-N₂]⁺** in hydrocarbon solvents such as pentane, benzene and toluene complicated analysis by NMR spectroscopy. In THF-*d*₈, only signals for the BArF²⁴ anion and two broad features at 3.55 and 1.93 ppm were observed in the ¹H NMR spectrum of **[1-N₂]⁺**, likely because of a fast equilibrium arising from reversible displacement of N₂ by the THF-*d*₈ solvent. Analysis of the solution by ³¹P NMR

spectroscopy did not produce an observable signal at ambient temperature. Cooling the THF-*d*₈ solution to –60 °C resulted in observation of a broad signal at 67.1 ppm. At this temperature, the ¹H NMR spectrum remained broadened demonstrating that the dynamic process is still operative on this timescale.

With the targeted cationic cobalt complexes in hand, oxidative addition of various representative substrates was studied. [1-N₂]⁺ was chosen for this study, because the lower steric profile of ⁱPrPNP in comparison to ^tBuPNP appears to allow for a higher propensity to form 5- and 6-coordinate cobalt products.^{5,9,10} Exposure of a THF-*d*₈ solution of [1-N₂]⁺ to 4 atm of H₂ resulted in an immediate color change from red-violet to yellow and full conversion of the starting material as judged by ¹H NMR spectroscopy (Scheme 3). The ¹H NMR spectrum of the resulting solution at ambient temperature exhibits mostly broad and featureless peaks with observable methyl groups of the ⁱPrPNP ligand located at 1.15 and 1.29 ppm and a broad signal at –26.75 ppm, consistent with a cobalt hydride. No signals were observed by ³¹P NMR spectroscopy under these conditions.

To improve the quality of the spectroscopic data and slow any potential dynamic processes, low temperature ¹H NMR measurements of a THF-*d*₈ solution of [1-N₂]⁺ under 4 atm of H₂ were conducted (Figure 2). At –60 °C, the ¹H NMR spectrum exhibited the number of peaks consistent with a C_s symmetric molecule as evidenced by four well resolved signals for the methyl groups of the ⁱPrPNP chelate. In addition, two triplets of doublets were located at –22.10 and –31.32 ppm (²J_{H-H} = 41.9 Hz), consistent with inequivalent cobalt hydrides coupling to each other and the two spin-active ³¹P atoms (–22.10 ppm: ²J_{P-H} = 56.6 and –31.32 ppm: 63.1 Hz respectively). The low temperature NMR data is consistent with *cis*-[(ⁱPrPNP)Co(H)₂L][BArF²⁴] ([1-(H)₂L]⁺), an octahedral Co(III) product with a meridional coordinated PNP-pincer and *cis* metal hydrides. The sixth coordination site is likely occupied by a molecule of THF-*d*₈ solvent. Notably, a second, minor (~2%) set of hydride signals was detected at –21.74 and –30.29 ppm and may be attributed to N₂ coordination in place of THF. At –20 °C, the coupling of the hydride signals is lost and two broad peaks are observed. At 0 °C the hydride signals coalesced as evidenced by complete disappearance of these signals. The ³¹P NMR spectrum recorded at –60 °C in THF-*d*₈ exhibits a broad signal at 76.1 ppm, significantly shifted upfield by ~30 ppm from neutral (ⁱPrPNP)Co(III) hydride complexes.^{5,11c,d}

The observation of a broad and nearly featureless ¹H NMR spectrum for [1-(H)₂L]⁺ at ambient temperature in THF may be a result of rapid and reversible reductive elimination and oxidative addition of H₂. Consistent with this hypothesis, exposure of a THF-*d*₈ solution of [1-(H)₂L]⁺ to an N₂ atmosphere produced a color change to violet-red within seconds at 23 °C, signaling regeneration of [1-N₂]⁺. The broad ¹H NMR spectrum observed for [1-(H)₂L]⁺ may also be a result of rapid exchange of the L-type ligand, giving rise to a five-coordinate intermediate subject to Berry pseudo rotation.²⁰ With the coalescence temperature of 0 °C and the peak separation of the two hydride signals at –60 °C the barrier for this process at 0 °C was estimated as 11 kcal/mol.²¹ Attempts to grow single crystals suitable for X-ray diffraction under an H₂-atmosphere have been unsuccessful.

It should be noted that $[\mathbf{1-(H)_2L}]^+$ exhibits behavior very similar to *cis*-[(^tBuPNP)Ir(H)₂L]⁺ complexes reported by Milstein and coworkers.²⁰ The corresponding Rh-analogue is unknown because H₂ does not reportedly undergo oxidative addition to the metal center and a dihydrogen complex was isolated instead.²² Nevertheless, $[\mathbf{1-(H)_2L}]^+$ has a similar coordination environment to cationic rhodium dihydride complexes such as [(MeCN)₂*trans*-(PPh₃)₂Rh*cis*-(H)₂]⁺.²³

The oxidative addition of B–B and B–H bonds was also targeted to explore both fundamental reactivity and possible isolation of a cationic Co(III) product. Addition of B₂Pin₂ to a fluorobenzene solution of $[\mathbf{1-N_2}]^+$ followed by removal of the volatiles and washing with pentane yielded a paramagnetic orange solid identified as [(ⁱPrPNP)Co(BPin)] [BArF²⁴] ($[\mathbf{1-BPin}]^+$) in 98% yield (Scheme 4).

Single crystals suitable for X-ray diffraction were grown from a fluorobenzene solution of $[\mathbf{1-BPin}]^+$ at –35 °C and a representation of the solid-state structure is presented in Figure 3. The coordination environment around the Co(II) center is best described as square planar with the pinacolato group almost perpendicular (O1–B–Co–P2 dihedral angle = 83.6°) to the idealized metal-chelate plane. This geometry contrasts related (ⁱPrPNP)Co(BPin)(L) derivatives that coordinate an additional neutral ligand (L = N₂, CO) upon crystallization. In these complexes, the pinacolato group lies essentially parallel to the Co-PNP plane, a structural feature also observed in the neutral Co(III) boryl, *trans*-(ⁱPrPNP)Co(H)₂(BPin).^{11b,c} Despite these geometric differences, the Co–B bond has a bond length of 1.983(8) Å comparable to Co–B bond lengths of other structurally characterized cobalt–boryl complexes across the +1 to +3 oxidation states.^{11c,d,24}

The ¹H NMR spectrum of paramagnetic $[\mathbf{1-BPin}]^+$ in THF-*d*₈ exhibits broad signals with chemical shifts ranging from 15 to –5 ppm. The X-band EPR spectrum of $[\mathbf{1-BPin}]^+$ recorded at 10 K in fluorobenzene exhibits a rhombic signal with a relatively large g-anisotropy, characteristic for low spin Co^{II}-complexes in a planar ligand field (Figure 4a).^{10,19b} The large ⁵⁹Co (I = 7/2, 100% natural abundance) hyperfine coupling interaction on two g values additionally supports a cobalt centered radical. In agreement with the EPR data, the density functional theory (DFT, B3LYP) computed Mulliken spin density plot supports the unpaired electron mainly localized in a dz² orbital of the cobalt(II) center with minor contributions from boron (Figure 4b). The combination of structural, EPR and DFT data and a solution state magnetic moment of 2.2(1) μ_B (Evans' method, 25 °C, THF-*d*₈) establishes $[\mathbf{1-BPin}]^+$ as a low spin S = ½ Co(II) complex with a cobalt centered SOMO (SOMO = singly occupied molecular orbital).

The same cobalt product, $[\mathbf{1-BPin}]^+$, was obtained in 95% yield from addition of HBPIn to $[\mathbf{1-N_2}]^+$ in fluorobenzene (Scheme 4). $[\mathbf{1-BPin}]^+$ was also formed when the reaction was conducted in THF but significant formation of poly-THF accompanied the desired reaction. To investigate the fate of the hydrogen atom of HBPIn, a mixture containing $[\mathbf{1-N_2}]^+$ and HBPIn (1.5 equiv) in THF-*d*₈ was monitored by ¹H NMR spectroscopy in a sealed tube. H₂ was not detected but hydride signals corresponding to $[\mathbf{1-(H)_2L}]^+$ were observed. As the oxidative addition of H₂ to $[\mathbf{1-N_2}]^+$ is reversible (*vide supra*), H₂ is eventually eliminated from $[\mathbf{1-(H)_2L}]^+$ in the preparative experiment and therefore explains the quantitative

formation of **[1-BPin]⁺** upon treatment of **[1-N₂]⁺** with HBPIn (Scheme 4). Notably, the major diamagnetic species observed at –60 °C gives rise to a well resolved triplet at –17.08 ppm (²J_{P-H} = 55.1 Hz) indicative of a Co–hydride and a set of PNP chelate signals corresponding to a molecule of C_s symmetry. The absence of coupling or significant broadening of the hydride signal due to the spin active boron nucleus argues against the formation of a Co(I) σ-borane complex.²⁶ This new product was tentatively assigned as the Co(III) hydride, [(ⁱPrPNP)Co(H)(BPin)L][BARF²⁴],^{11c,d} an intermediate in the formation of **[1-BPin]⁺**. The ¹H NMR spectrum at –60 °C after 60 min did not exhibit the same signals observed for **[1-BPin]⁺** at RT, presumably due to coordination of an L type ligand at low temperature. Instead paramagnetically low field shifted signals were present in the spectrum.

The isolation and structural characterization of **[1-BPin]⁺** completes a series of cobalt-boryl complexes supported by the same pincer ligands across three oxidation states: Co(I), Co(II) and Co(III),^{11c,d} highlighting the redox versatility of a first row transition metal. Because of the well-established intermediacy of cobalt(I) and cobalt(III) boryl complexes in the catalytic C(sp²)–H borylation of arenes and heteroarenes,¹¹ related studies with cationic Co(II)-boryl **[1-BPin]⁺** were conducted. In contrast to the neutral compound, **[1-BPin]⁺** does not borylate activated arenes, such as fluorobenzene or the heteroarene, benzofuran, under the examined reaction conditions. Heating a solution of **[1-BPin]⁺** in THF-*d*₈ in the presence of two equiv of benzofuran to 80 °C for 4 days yielded **[1-N₂]⁺** as judged by ¹H NMR spectroscopy. No borylated benzofuran was detected by ¹H NMR spectroscopy but generation of a BPin radical might explain the formation of poly-THF, which was observed during the preparation of **[1-BPin]⁺**. Reactions under catalytic conditions with **[1-N₂]⁺** as pre-catalyst and B₂Pin₂ or HBPIn as the potential borylating reagents in neat fluorobenzene or benzofuran in fluorobenzene (2 equiv vs. borylating reagent) yielded no borylated arene after 24 h at 80 °C.

The oxidative addition of aryl–halides to transition metal complexes is a ubiquitous substrate activation pathway in the catalytic formation of C–C bonds, principally in cross-coupling reactions.²⁶ Substrates of this type were therefore selected as representative to examine the oxidative addition reactivity of polar bonds with **[1-N₂]⁺**. Addition of 2 equiv of bromobenzene to a fluorobenzene solution of **[1-N₂]⁺** resulted in a rapid color change to orange and formation of a mixture of two cobalt complexes as judged by ¹H NMR and EPR spectroscopies (Scheme 5). After removal of the volatiles and washing with pentane, a paramagnetic orange solid was obtained. Recrystallization of this mixture from fluorobenzene at –35 °C furnished orange crystals identified as [(ⁱPrPNP)CoBr][BARF²⁴] (**[1-Br]⁺**). Addition of pentane to the mother liquor and recrystallization at –35 °C yielded yellow crystals identified as [(ⁱPrPNP)Co(Ph)][BARF²⁴] (**[1-Ph]⁺**). Repeating the experimental procedure with “inverse addition” – adding a fluorobenzene solution of **[1-N₂]⁺** to a solution of bromobenzene – produced an identical product distribution.

The solid-state structure of complex **[1-Ph]⁺** was determined by single crystal X-ray crystallography and is depicted in Figure 5. An idealized square planar geometry was observed around the cobalt(II) center. As with the boryl ligand in **[1-BPin]⁺**, the phenyl group in **[1-Ph]⁺** lies nearly perpendicular to the idealized metalchelate plane, as exemplified by the C12–C11–Co–P2 dihedral angle of 75.6°.

The ^1H NMR spectrum of $[\mathbf{1-Ph}]^+$ in $\text{THF-}d_8$ exhibits broad peaks that range from 20 to -30 ppm. The X-band EPR spectrum of $[\mathbf{1-Ph}]^+$ recorded at 10 K in fluorobenzene proved more informative with observations of a rhombic signal that was simulated with g values of $g_1 = 2.20$, $g_2 = 3.50$, $g_3 = 1.80$ with large ^{59}Co hyperfine coupling interaction ($A_1 = 403$ MHz, $A_2 = 1143$ MHz, $A_3 = 432$ MHz), indicative of a cobalt centered radical (Figure 6). With these data, combined with a solution magnetic moment of $2.1(1) \mu\text{B}$ (Evans' method, 25°C , $\text{THF-}d_8$), $[\mathbf{1-Ph}]^+$ is best described as a low spin $S = \frac{1}{2}$ Co(II) complex with a cobalt-based SOMO.

The solid-state structure of $[\mathbf{1-Br}]^+$ was likewise determined by single crystal X-ray diffraction (Figure 7a). The weak field Br-ligand does not have a significant influence on the solid-state structure $[\mathbf{1-Br}]^+$ and, analogous to the structures of $[\mathbf{1-Ph}]^+$ and $[\mathbf{1-BPin}]^+$, exhibits an idealized square planar geometry around the cobalt center. The solution magnetic moment of $1.8(2) \mu\text{B}$ (Evans' method, 25°C , $\text{THF-}d_8$) again supports a low spin $S = \frac{1}{2}$ Co(II) complex. The X-band EPR spectrum (10 K, fluorobenzene) exhibits a rhombic signal which was simulated with a large g_2 value of 4.55 and a small g_3 value of 1.12 (Figure 6b). A large ^{59}Co hyperfine coupling interaction was found only on g_2 ($A_2 = 1690$ MHz).

Analogous reactivity was observed with iodobenzene (Scheme 5). Addition of 2 equiv of iodobenzene to a fluorobenzene solution of $[\mathbf{1-N_2}]^+$ resulted in a rapid color change to orange. ^1H NMR and EPR spectroscopies confirmed the formation of $[\mathbf{1-Ph}]^+$ along with a new cobalt complex structurally similar to $[\mathbf{1-Br}]^+$. Recrystallization of this mixture from a concentrated fluorobenzene solution at -35°C yielded a mixture of orange and yellow crystals. Bulk separation of the two species by crystallization was not achieved, prohibiting bulk analyses of the new species. Nevertheless, the formation of $[(i\text{PrPNP})\text{CoI}][\text{BArF}^{24}]$ ($[\mathbf{1-I}]^+$) was confirmed by single crystal X-ray crystallography of an orange crystal. The solid-state representation of complex $[\mathbf{1-I}]^+$ is shown in Figure 7b, with structural features similar to $[\mathbf{1-Br}]^+$.

In both reactions $[\mathbf{1-Ph}]^+$ and $[\mathbf{1-X}]^+$ ($X = \text{Br}, \text{I}$) were observed in a 1:1 ratio as judged by integration of the ^1H NMR signals of the crude reaction mixtures (Scheme 5).¹⁵ Budzelaar and coworkers have studied oxidative addition reactions of Ar-X substrates to $(\text{PDI})\text{Co}(\text{N}_2)$ complexes ($\text{PDI} = \text{pyridine diimine}$), which proceeds through a halide atom abstraction mechanism and therefore yields $(\text{PDI})\text{Co}(\text{Ar})/(\text{PDI})\text{Co}(\text{X})$ mixtures of a ratio $<1:1$ due to the side reactivity of the aryl radical.¹⁴ The equimolar formation $[\mathbf{1-Ph}]^+$ and $[\mathbf{1-X}]^+$ ($X = \text{Br}, \text{I}$) in this case stands in contrast to Budzelaar's observation, potentially arguing for a bimetallic transition state involved in product formation.

All observations taken together, the divergent reactivity of $[\mathbf{1-N_2}]^+$ towards the studied reagents might be explained by similar mechanisms (Scheme 6). The first step is a fast and reversible oxidative addition of the reagent to form an equilibrium between Co(I) and Co(III) species. The latter can be observed by low temperature ^1H NMR spectroscopy in the cases of H_2 and HBPIn. Except for $[\mathbf{1-(H)_2L}]^+$, the Co(III) complexes undergo comproportionation with Co(I) to form the observed cationic Co(II) complexes. This bimetallic one-electron reaction accounts for the formation of $[\mathbf{1-BPin}]^+$ as well as the equimolar formation $[\mathbf{1-X}]^+$ ($X = \text{Br}, \text{I}$) and $[\mathbf{1-Ph}]^+$. Because reversible oxidative addition

of aryl halides appears unlikely, comproportionation is likely faster than oxidative addition in this case. In this mechanistic picture, $[(iPrPNP)Co(H)][BArF^{24}]$, which is presumably formed during the reaction of $[1-N_2]^+$ with HBPin, is either inherently unstable towards release of H_2 and regeneration of $[1-N_2]^{+14}$ or reacts with HBPin to form $[1-BPin]^+$ and H_2 directly. Either way, the latter was observed in the reaction mixture as intermediary formed $[1-(H)_2L]^+$ at low temperature. Therefore, the difference in reactivity between neutral and cationic $(iPrPNP)Co(I)$ complexes does not necessarily arise from a different mechanism of oxidative addition, but rather from the stability of $(iPrPNP)Co(III)$ species towards comproportionation with $Co(I)$.

CONCLUDING REMARKS

In summary, oxidative addition of non-polar and polar reagents to cationic $[(iPrPNP)Co(N_2)][BArF^{24}]$ was studied. With H_2 , two-electron oxidative addition to form a $Co(III)$ dihydride occurred while addition of B_2Pin_2 , HBPin, and aryl halides resulted in one-electron chemistry and formation of $Co(II)$ complexes, likely due to comproportionation of initially formed $Co(III)$ species with $Co(I)$. This reactivity stands in contrast to neutral complexes ligated to the same PNP pincer ligand, which perform net two-electron oxidative addition with B_2Pin_2 and HBPin to form stable $Co(III)$ complexes. This study underlines the crucial importance of studying oxidative additions to 1st-row transition metal complexes to inform catalyst design, since the reaction outcome highly depends on many factors, including the charge of the complex, the ligand environment and reagents used. Detailed studies on the hydrogenation activity of cationic cobalt complexes are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Considerations.

All air- and moisture-sensitive manipulations were carried out using vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere (nitrogen) dry box unless otherwise noted. All glassware was stored in a pre-heated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.²⁶ Hydrogen gas was purchased from Airgas National Welders and passed through a column of MnO_2 supported on vermiculite and 3 Å molecular sieves prior to use on a Schlenk manifold. HBpin was purchased from Sigma Aldrich and used as received. B_2Pin_2 was received from Allychem and recrystallized from Et_2O at $-35\text{ }^\circ C$ prior to use. Fluorobenzene, phenyl bromide and phenyl iodide (Sigma Aldrich) were dried over CaH_2 and distilled under reduced pressure prior to use. The following compounds were prepared according to literature procedures: $(iPrPNP)CoCl$,^{5a} $(tBuPNP)CoCl$,¹⁰ $Na[BArF^{24}]$.²⁷

1H NMR spectra were recorded on either Bruker AVANCE 300 or 500 spectrometers operating at 300.13 MHz, and 500.46 MHz, respectively. ^{31}P NMR spectra were recorded on a Bruker AVANCE 500 spectrometer operating at 202 MHz. All 1H chemical shifts are reported in ppm relative to $SiMe_4$ using the 1H ($THF-d_8$: 1.73 ppm) chemical shifts of the residual protonated solvent as a standard. ^{31}P NMR spectra were referenced to 85% H_3PO_4

as an external standard. ^1H NMR data for diamagnetic compounds are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), coupling constants (Hz), integration, assignment. ^1H NMR data for paramagnetic compounds are reported as follows: chemical shift, peak width at half height (Hz). Continuous wave EPR spectra were recorded at room temperature on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB.²⁹ Elemental analyses were performed at Robinson Microlit Laboratories, Inc., in Ledgewood, NJ. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker SMART APEX DUO diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073 \text{ \AA}$) and a Cu X-ray tube ($\lambda = 1.54178 \text{ \AA}$). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

All DFT calculations were performed with the ORCA package in the gas phase.³⁰ Geometry optimizations and single-point calculations were carried out at the B3LYP level of DFT.³¹ This hybrid functional often outperforms pure gradient-corrected functionals in the accurate representation of transition metal complexes, especially those involving significant metal–ligand covalency.³² Alrichs' all-electron Gaussian basis sets were employed for all calculations,³³ wherein the triple- ζ basis set def2-TZVP, which includes one set of polarization functions, was used to describe metal atoms and all atoms directly coordinated to a metal center. The double- ζ basis set def2-SV(P), which includes one set of polarizing d -functionals on all nonhydrogen atoms, was used for all other atoms. Auxiliary basis sets were chosen to match the orbital basis.³⁴ The RIJCOSX approximation was used to accelerate the calculations.³⁵ Throughout this manuscript, computational results are described using the broken symmetry approach introduced by Ginsberg³⁶ and Noodleman *et al.*³⁷ Because several broken symmetry solutions are spin-unrestricted Kohn-Sham equations may be obtained, the general notation for broken symmetry (m,n)³⁸ has been adopted, where m (n) denotes the number of spin-up (spin-down) electrons at the two interacting fragments.³⁹ Representations of canonical orbitals and the corresponding spin density plots were generated with the program *Chimera*.⁴⁰

Preparation of $[(\text{iPrPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]$ ($[\text{1-N}_2]^+$).

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with a solution of $(\text{iPrPNP})\text{CoCl}$ (125 mg, 0.288 mmol, 1.0 equiv) in PhF (ca. 5 mL). A suspension of $\text{Na}[\text{BArF}^{24}]$ (256 mg, 0.288 mmol, 1.0 equiv) in PhF (ca. 3 mL) was added, the resulting mixture was stirred for 10 min at RT, filtered through Celite (eluent: PhF) and the filtrate was concentrated to a volume of ca. 10 mL. Pentane (ca. 3 mL) was added and the resulting

mixture was cooled to $-35\text{ }^{\circ}\text{C}$ overnight to yield 352 mg (88%, 0.254 mmol) of $[(\text{iPrPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ as a dark violet crystalline solid. Crystals suitable for single crystal X-ray diffraction were grown from a PhF solution at $-35\text{ }^{\circ}\text{C}$. Anal Calcd for $\text{C}_{57}\text{H}_{52}\text{BCoF}_{25}\text{N}_3\text{P}_2$: C, 49.41; H, 3.78; N, 3.03. Found: C, 49.67; H, 3.79; N, 3.30. IR (KBr): 2081 cm^{-1} (ν_{N_2}). ^1H NMR (300 MHz, $\text{THF}-d_8$, $25\text{ }^{\circ}\text{C}$): δ 7.92 – 7.73 (m, 8H), 7.59 (s, 4H), 3.55 (br s, 80 Hz), 1.93 (br s, 46 Hz). ^1H NMR (500 MHz, $\text{THF}-d_8$, $-60\text{ }^{\circ}\text{C}$): δ 7.74 (s, 8H), 7.58 (s, 4H), 3.68 (s, 4H), 2.40 (s, 4H), 1.37 (s, 12H), 1.13 (s, 12H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{THF}-d_8$, $-60\text{ }^{\circ}\text{C}$): δ 67.1

Preparation of $[(\text{tBuPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]$ ($[\text{2-N}_2]^+$).

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with a solution of $(\text{tBuPNP})\text{CoCl}$ (107 mg, 0.219 mmol, 1.0 equiv) in PhF (ca. 3 mL). A suspension of $\text{Na}[\text{BArF}^{24}]$ (186 mg, 0.219 mmol, 1.0 equiv) in PhF (ca. 3 mL) was added, the resulting mixture was stirred for 10 min at RT, filtered through celite (eluent: PhF) and the filtrate was concentrated to a volume of ca. 10 mL. Pentane (ca. 3 mL) was added and the resulting mixture was cooled to $-35\text{ }^{\circ}\text{C}$ overnight to yield 250 mg (85%, 0.186 mmol) of $[(\text{tBuPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]$ as a dark pink-purple crystalline solid. Crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of pentane into a concentrated PhF solution at $-35\text{ }^{\circ}\text{C}$. Anal Calcd for $\text{C}_{55}\text{H}_{55}\text{BCoF}_{24}\text{N}_3\text{P}_2$: C, 49.09; H, 4.12; N, 3.12. Found: C, 48.83; H, 4.02; N, 3.05. IR (KBr): 2078 cm^{-1} (ν_{N_2}).

Observation of $[(\text{iPrPNP})\text{Co}(\text{H})_2\text{L}][\text{BArF}^{24}]$ ($[\text{1-(H)}_2\text{L}]^+$).

In a N_2 -filled glovebox a J-Young NMR-tube was charged with a solution of $[(\text{iPrPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ (15 mg, 0.011 mmol) in $\text{THF}-d_8$ (0.5 mL). The tube was sealed, brought outside of the glovebox and attached to a Schlenk line and the contents of the tube were frozen in liquid nitrogen. Following evacuation of the headspace H_2 (1 atm) was admitted at $-196\text{ }^{\circ}\text{C}$. The tube was sealed and allowed to warm to RT. Inversion of the tube induced an immediate color change to yellow. ^1H NMR (500 MHz, $\text{THF}-d_8$, $25\text{ }^{\circ}\text{C}$): δ 7.79 (s, 8H), 7.73 (t, $J = 7.1\text{ Hz}$, 1H), 7.57 (s, 4H), 7.46 (d, $J = 7.7\text{ Hz}$, 2H), 4.03 – 3.83 (bs, 4H), 2.56 – 2.26 (bs, 4H), 1.49 – 1.22 (bs, 12H), 1.22 – 1.03 (bs, 12H), -23.61 – -29.49 (bs, 2H). ^1H NMR (500 MHz, $\text{THF}-d_8$, $-60\text{ }^{\circ}\text{C}$): δ 7.88 (s, 8H), 7.80 (t, $J = 7.7\text{ Hz}$, 1H), 7.71 (s, 4H), 7.51 (d, $J = 7.9\text{ Hz}$, 2H), 4.12 (dt, $J = 18.1, 4.8\text{ Hz}$, 2H), 3.98 (dt, $J = 17.9, 3.4\text{ Hz}$, 2H), 2.52 (h, $J = 6.7\text{ Hz}$, 2H), 2.33 (p, $J = 7.2\text{ Hz}$, 2H), 1.58 (q, $J = 7.6\text{ Hz}$, 6H), 1.47 (q, $J = 6.2\text{ Hz}$, 6H), 1.07 (q, $J = 7.7\text{ Hz}$, 6H), 0.69 (q, $J = 7.1\text{ Hz}$, 6H), -22.10 (td, $J = 56.6, 41.8\text{ Hz}$, 1H), -31.32 (td, $J = 63.1, 42.0\text{ Hz}$, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{THF}-d_8$, $-60\text{ }^{\circ}\text{C}$): δ 76.1.

Preparation of $[(\text{iPrPNP})\text{Co}(\text{BPin})][\text{BArF}^{24}]$ ($[\text{1-BPin}]^+$) with B_2Pin_2 .

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with $[(\text{iPrPNP})\text{Co}(\text{N}_2)][\text{BArF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ (30 mg, 0.022 mmol, 1.0 equiv). A solution of B_2Pin_2 (11 mg, 0.043 mmol, 2.0 equiv) in PhF (ca. 3 mL) was added and the resulting mixture was stirred for 4 h at RT, during which a color change from dark violet to red was observed. All volatiles were removed under vacuum and the residue was dissolved in Et_2O (ca. 2 mL). All volatiles were removed under vacuum and the remaining orange-yellow solid was washed with pentane ($3\times$ ca. 3 mL) and dried to yield 30 mg (98%, 0.022 mmol) of $[(\text{iPrPNP})\text{Co}(\text{BPin})][\text{BArF}^{24}]$ as

an orange-yellow solid. Crystals suitable for single crystal X-ray diffraction were grown from a PhF solution at $-35\text{ }^{\circ}\text{C}$. Anal Calcd for $\text{C}_{57}\text{H}_{59}\text{B}_2\text{CoF}_{24}\text{NO}_2\text{P}_2$: C, 49.30; H, 4.28; N, 1.01. Found: C, 48.95; H, 4.27; N, 0.99. Magnetic Susceptibility (Evans' method, $25\text{ }^{\circ}\text{C}$, THF- d_8): $\mu_{\text{eff}} = 2.2(1)\text{ }\mu_{\text{B}}$. ^1H NMR (500 MHz, THF- d_8 , $25\text{ }^{\circ}\text{C}$): δ 13.54 (45 Hz), 13.33 (387 Hz), 7.78 (10 Hz), 7.55 (7 Hz), 4.41 (142 Hz), 2.66 (452 Hz), 1.19 (5.9 Hz), -2.47 (495 Hz).

Preparation of $[(^i\text{PrPNP})\text{Co}(\text{BPin})][\text{BARF}^{24}]$ ($[\text{1-BPin}]^+$) with HBPIn.

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with $[(^i\text{PrPNP})\text{Co}(\text{N}_2)][\text{BARF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ (30 mg, 0.022 mmol, 1.0 equiv) and PhF (ca. 3 mL). HBPIn (13 μL , 0.097 mmol, 4.0 equiv) was added and the resulting mixture was stirred for 4 h at RT, during which a color change from dark violet to red was observed. All volatiles were removed under vacuum and the residue was dissolved in Et_2O (ca. 2 mL). All volatiles were removed under vacuum and the remaining orange-yellow solid was washed with pentane ($3\times$ ca. 3 mL) and dried to yield 29 mg (95%, 0.021 mmol) of $[(^i\text{PrPNP})\text{Co}(\text{BPin})][\text{BARF}^{24}]$ as an orange-yellow solid. All characterization data matched the material obtained with B_2Pin_2 .

^1H NMR Monitoring of the reaction between $[\text{1-N}_2]^+$ and HBPIn.

In a N_2 -filled glovebox a J-Young NMR-tube was charged with a solution of $[(^i\text{PrPNP})\text{Co}(\text{N}_2)][\text{BARF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ (12 mg, 0.009 mmol) in THF- d_8 (0.5 mL). HBPIn (1.9 μL , 0.013 mmol, 1.5 equiv) was added and the tube was sealed before mixing the reagents. A ^1H NMR spectrum taken at $-60\text{ }^{\circ}\text{C}$ after reacting for 60 min at RT exhibited signals corresponding to $[\text{1-(H)}_2\text{L}]^+$ and a second diamagnetic species tentatively assigned as $[(^i\text{PrPNP})\text{Co}(\text{H})(\text{BPin})\text{L}][\text{BARF}^{24}]$. ^1H NMR (500 MHz, THF- d_8 , $-60\text{ }^{\circ}\text{C}$): δ 7.59 (d, $J = 7.7\text{ Hz}$, 2H), 7.49 (t, $J = 6.4\text{ Hz}$, 1H), 4.08 (d, $J = 17.2\text{ Hz}$, 2H), 3.86 (d, $J = 18.2\text{ Hz}$, 2H), 2.72 – 2.59 (m, 2H), 2.57 – 2.40 (m, 2H), 1.53 – 1.41 (m, 6H), 0.96 – 0.85 (m, 6H), 0.85 – 0.73 (m, 6H), -17.08 (t, $J = 55.1\text{ Hz}$, 1H) (two signals not located, some signals are overlapping with signals from $[\text{1-(H)}_2\text{L}]^+$).

Preparation of $[(^i\text{PrPNP})\text{Co}(\text{Ph})][\text{BARF}^{24}]$ ($[\text{1-Ph}]^+$) and $[(^i\text{PrPNP})\text{CoBr}][\text{BARF}^{24}]$ ($[\text{1-Br}]^+$).

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with a solution of $[(^i\text{PrPNP})\text{Co}(\text{N}_2)][\text{BARF}^{24}]\cdot\text{C}_6\text{H}_5\text{F}$ (30 mg, 0.022 mmol, 1.0 equiv) in PhF (ca. 3 mL). PhBr (5.7 μL , 0.046 mmol, 2.1 equiv) was added and the resulting mixture was stirred for 15 min at RT, during which a color change from dark violet to bright orange was observed. All volatiles were removed under vacuum and the remaining dark orange solid was washed with pentane ($3\times$ ca. 3 mL) and dried to yield 28 mg (95%, 0.021 mmol) of a 1/1 mixture of $[(^i\text{PrPNP})\text{Co}(\text{Ph})][\text{BARF}^{24}]$ and $[(^i\text{PrPNP})\text{CoBr}][\text{BARF}^{24}]$ as an orange solid. To obtain analytically pure compounds the product mixture was dissolved in PhF (ca. 1 mL) and stored at $-35\text{ }^{\circ}\text{C}$ to yield orange crystals and a yellow solution. After separation of the crystals from the mother liquor, pentane (ca. 1 mL) was added to the mother liquor and the resulting mixture was stored at $-35\text{ }^{\circ}\text{C}$ to yield $[(^i\text{PrPNP})\text{Co}(\text{Ph})][\text{BARF}^{24}]$ as yellow crystals suitable for single crystal X-ray diffraction. The orange crystals were recrystallized from PhF at $-35\text{ }^{\circ}\text{C}$ to yield $[(^i\text{PrPNP})\text{Co}(\text{Br})][\text{BARF}^{24}]$ as orange crystals suitable for single crystal X-ray diffraction. Analysis for $[(^i\text{PrPNP})\text{Co}(\text{Ph})][\text{BARF}^{24}]$: Anal Calcd for

$C_{57}H_{52}BCoF_{24}NP_2$: C, 51.14; H, 3.92; N, 1.05. Found: C, 51.09; H, 3.65; N, 1.00. Magnetic Susceptibility (Evans' method, 25 °C, THF- d_8): $\mu_{\text{eff}} = 2.1(1) \mu_B$. 1H NMR (500 MHz, THF- d_8 , 25 °C): δ 16.78 (32 Hz), 16.56 (532 Hz), 11.25 (506 Hz), 9.98 (25 Hz), 8.02 (254 Hz), 7.72 (7.8 Hz), 7.48 (6.3 Hz), 1.13 (495 Hz), -24.61 (264 Hz). Analysis for $[(iPrPNP)Co(Br)][BArF^{24}]$: Anal Calcd for $C_{51}H_{47}BBrCoF_{24}NP_2$: C, 45.66; H, 3.53; N, 1.04. Found: C, 45.84; H, 3.62; N, 1.09. Magnetic Susceptibility (Evans' method, 25 °C, THF- d_8 °C): $\mu_{\text{eff}} = 1.8(2) \mu_B$. 1H NMR (500 MHz, THF- d_8 , 25 °C): δ 12.09 (59 Hz), 7.77 (8.4 Hz), 7.54 (5.5), 3.92 (290 Hz), 2.80 (382 Hz), 0.68 (127 Hz), -0.30 (761 Hz).

Preparation of $[(iPrPNP)Co(Ph)][BArF^{24}]$ ([1-Ph]⁺) and $[(iPrPNP)CoI][BArF^{24}]$ ([1-I]⁺).

In an N_2 -filled glovebox, a 20 mL scintillation vial was charged with a solution of $[(iPrPNP)Co(N_2)][BArF^{24}] \cdot C_6H_5F$ (30 mg, 0.022 mmol, 1.0 equiv) in PhF (ca. 3 mL). PhI (4.8 μ L, 0.043 mmol, 2.0 equiv) was added and the resulting mixture was stirred for 15 min at RT, during which a color change from dark violet to bright orange was observed. All volatiles were removed under vacuum and the remaining dark orange solid was washed with pentane (3 $\times$ ca. 3 mL) and dried to yield 28 mg (93%, 0.021 mmol) of a 1/1 mixture of $[(iPrPNP)Co(Ph)][BArF^{24}]$ and $[(iPrPNP)CoI][BArF^{24}]$ as an orange solid. Crystals of $[(iPrPNP)Co(I)][BArF^{24}]$ suitable for single crystal X-ray diffraction were grown from a PhF solution at -35 °C.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Solid-state molecular structure of $[(i^{\text{Pr}}\text{PNP})\text{Co}(\text{N}_2)]^+ [\text{BArF}^{24}]^-$ ($[\mathbf{1-N}_2]^+$) at 30% probability ellipsoids. Hydrogen atoms and the $[\text{BArF}^{24}]^-$ anion are omitted for clarity. Selected bond distances ($\text{\AA}$) and angles (deg): N1–Co1 1.950(3), N2–N3 1.092(5), N2–Co1 1.767(3), P1–Co1 2.1847(9), P2–Co1 2.1840(10), C1–C2 1.500(5), C6–C7 1.509(5); N2–Co1–N1 178.16(13), N2–Co1–P2 94.28(10), N1–Co1–P2 85.68(8), N2–Co1–P1 94.57(10), N1–Co1–P1 85.57(8), P2–Co1–P1 170.64(4).

Figure 2. Hydride region of the ^1H NMR spectrum of $[1-(\text{H})_2\text{L}]^+$ in $\text{THF-}d_8$ from -60 to 25 °C.

Figure 3.

Solid-state molecular structure of $[(^i\text{PrPNP})\text{Co}(\text{BPin})][\text{BArF}^{24}]$ at 30% probability ellipsoids. Hydrogen atoms and the $[\text{BArF}^{24}]$ anion are omitted for clarity. Selected bond distances (Å) and angles (deg): B1–Co1 1.983(8), N1–Co1 1.958(6), P1–Co1 2.1778(19), P2–Co1 2.178(2), C1–C2 1.514(9), C6–C7 1.500(10); B1–Co1–N1 174.3(3), B1–Co1–P1 91.8(2), N1–Co1–P1 87.08(18), B1–Co1–P2 94.1(2), N1–Co1–P2 86.95(18), P1–Co1–P2 174.01(8).

Figure 4.

a) X-band EPR spectrum of **[1-BPin]⁺**. The spectrum was recorded in C₆H₅F at 10 K. Collection parameters for experimental spectrum: microwave frequency = 9.379 GHz, power = 2.0 mW, modulation amplitude = 4 G. Simulation parameters: $g_1 = 2.21$, $g_2 = 3.04$, $g_3 = 1.95$, $g_{\text{strain}} = (0.06, 0.19, 0.08)$, $A_1 = 2$ MHz, $A_2 = 896$ MHz, $A_3 = 320$ MHz, $A_{\text{strain}} = (290, 119, 0)$, $H_{\text{strain}} = (154, 0, 0)$. b) DFT computed spindensity plot for **[1-BPin]⁺** obtained from Mulliken population analysis in the gas-phase at the B3LYP level of theory.

Figure 5.

Solid-state molecular structure of $[(1\text{PrPNP})\text{Co}(\text{Ph})][\text{BArF}_2^{24}]$ at 30% probability ellipsoids. Hydrogen atoms and the $[\text{BArF}_2^{24}]$ anion are omitted for clarity. Selected bond distances (Å) and angles (deg): Co1–N1 1.993(6), Co1–P2 2.1987(11), C11–Co1 1.925(6), C7–C8 1.505(9); C11–Co1–N1 180.00(6), C11–Co1–P2 94.09(4), N1–Co1–P2 85.91(4), P2–Co1–P2A 171.83(8).

Figure 6.

a) X-band EPR spectrum of a) **[1-Ph]⁺** and b) **[1-Br]⁺**. The spectra were recorded in C₆H₅F at 10 K. a) Collection parameters for experimental spectrum of **[1-Ph]⁺**: microwave frequency = 9.379 GHz, power = 2.0 mW, modulation amplitude = 4 G. Simulation parameters: $g_1 = 2.20$, $g_2 = 3.50$, $g_3 = 1.80$, $g_{\text{strain}} = (0.09, 0.19, 0.06)$, $A_1 = 403$ MHz, $A_2 = 1143$ MHz, $A_3 = 432$ MHz, $A_{\text{strain}} = (0, 50, 0)$, $H_{\text{strain}} (69, 0, 1)$. b) Collection parameters for experimental spectrum of **[1-Br]⁺**: microwave frequency = 9.378 GHz, power = 0.6 mW, modulation amplitude = 4 G. Simulation parameters: $g_1 = 2.35$, $g_2 = 4.55$, $g_3 = 1.12$, $g_{\text{strain}} = (0.19, 0.35, 0.22)$, $A_1 = 10$ MHz, $A_2 = 1690$ MHz, $A_3 = 0$ MHz, $A_{\text{strain}} = (41, 0, 0)$, $H_{\text{strain}} (0, 1240, 253)$.

Figure 7.

Solid-state molecular structure of a) [(iPrPNP)CoBr][BArF²⁴] and b) [(iPrPNP)CoI][BArF²⁴] at 30% probability ellipsoids. Hydrogen atoms and the [BArF²⁴] anion are omitted for clarity. a) Selected bond distances (Å) and angles (deg): Br1–Co1 2.3222(6), Co1–N1 1.956(3), Co1–P2 2.2123(10), Co1–P1 2.2131(10), C7–C8 1.507(5), C12–C13 1.500(5); N1–Co1–P2 85.95(8), N1–Co1–P1 85.89(9), P2–Co1–P1 171.27(4), N1–Co1–Br1 177.77(9), P2–Co1–Br1 94.29(3), P1–Co1–Br1 93.98(3); b) Selected bond distances (Å) and angles (deg): Co1–N1 1.968(4), Co1–P2 2.2103(16), Co1–P1 2.2130(16), Co1–I1 2.5092(8), C7–C8 1.505(8), C12–C13 1.497(8); N1–Co1–P2 85.99(14), N1–Co1–P1 85.82(14), P2–Co1–P1 171.10(6), N1–Co1–I1 177.65(13), P2–Co1–I1 94.27(5), P1–Co1–I1 94.06(4).

(a) Previous Work: Oxidative Addition to a Neutral (PNP)Co(I) Complex **(b) This Work: Oxidative Addition to a Cationic (PNP)Co(I) Complex** **Scheme 1.**

Comparison of the Oxidative Addition of H₂ and HBPIn to a (a) Neutral and (b) Cationic (iPrPNP)Co(I) Complexes

Scheme 2.
Synthesis of [(ⁱPrPNP)Co(N₂)] [BArF²⁴]

Scheme 3. Oxidative Addition of H₂ to [(*i*PrPNP)Co(N₂)] [BArF²⁴]

Scheme 4.
Synthesis of $[(i\text{PrPNP})\text{Co}(\text{BPin})][\text{BArF}^{24}]$

Scheme 5.

Oxidative Addition of Aryl Halides to $[(iPr)PNP]Co(N_2)[BArF^{24}]$.

Scheme 6.

Proposed Mechanism for the Formation of $[(iPrPNP)Co(II)]^+$ Complexes from Oxidative Addition to $Co(I)$.