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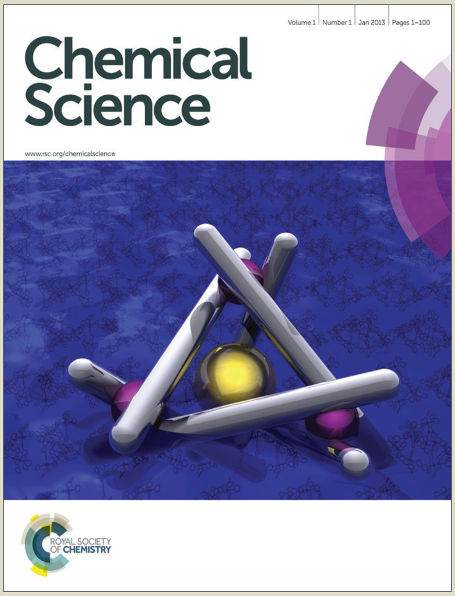

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Edge Article

Oxidative Addition and C-H Activation Chemistry with a PNP Pincer Ligated Cobalt Complex.

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The bis(phosphino)pyridine (PNP) cobalt(I) methyl complex, $(^{iPr}PNP)CoCH_3$ is a rich platform for the oxidative addition of non-polar reagents such as H_2, the C-H bonds of arenes and terminal alkynes. Rare examples of hexacoordinate cobalt(III) compounds including a trihydride, a bis(acetylide) hydride and a trimethyl complex have been isolated and two examples structurally characterized. These findings demonstrate that when placed in an appropriately strong ligand field, two-electron oxidative addition chemistry is possible with first row transition metals.

Introduction

The oxidative addition of dihydrogen and unactivated C-H bonds to reduced transition metals is often an essential substrate activation step in important catalytic transformations including hydrogenation and hydrocarbon functionalization.[1] Such transformations are kinetically and thermodynamically favorable with electron rich second and third row transition metals and are in part responsible for the prevalence of precious metals in homogeneous catalytic reactions that rely on oxidative addition.[2,3] Enabling such two electron reactivity with first row transition metals,[4] where one electron alternatives are common and often disruptive,[5] is a key component in developing catalysts that rely on more earth-abundant and inexpensive elements.

Tris(phosphine) cobalt(III) trihydride complexes, $(R_3P)_3CoH_3$ have been implicated in the context of catalytic olefin hydrogenation but in most cases are poorly characterized due to their instability toward H_2 reductive elimination.[6,7] In only one instance, $((^{i}PrO)_3P)_3CoH_3$, has oxidative addition of H_2 to a Co(I) precursor been described but characterization of the putative Co(III) trihydride was again minimal.[8] Recently, Mock and coworkers have reported H_2 oxidative addition to bis(diphosphine) cobalt(I) acetonitrile complexes to yield the corresponding Co(III) dihydride cations[9] while Caulton and coworkers have prepared a rare three coordinate Co(I) compound with an anionic PNP-pincer ligand that undergoes oxidative addition of H_2 to form the cobalt(III) dihydride.[10] Peters and coworkers have described formation of a cobalt(III) dihydridoborate complex from H_2 addition to a tris(phosphino)cobalt(I) boryl.[11] In this example, the boryl ligand directly participates in the H_2 cleavage reaction. During the preparation of this manuscript, Arnold and coworkers reported oxidative addition of H_2 to a family of pincer-ligated cobalt derivatives.[12]

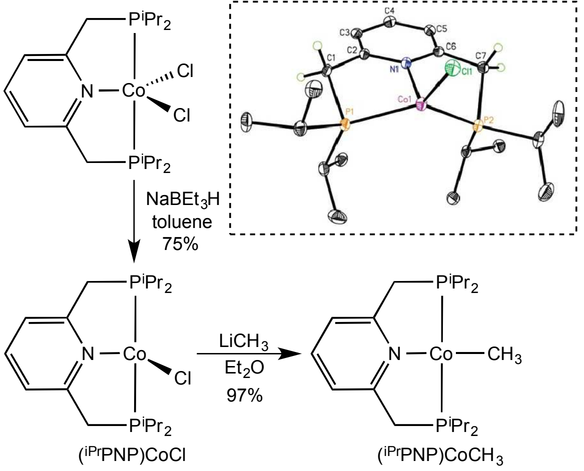
In the context of base metal catalysis, our laboratory has discovered that redox-active[13] bis(imino)pyridine cobalt alkyl complexes are effective precursors for asymmetric alkene hydrogenation[14,15] and isomerization-hydroboration.[16] These compounds, $(PDI^{1-})Co^{II}R$ are best described as low spin cobalt(II) engaged in antiferromagnetic coupling with a bis(imino)pyridine radical anion.[17] Replacing the imine donors with *N*-heterocyclic carbenes generated a more electron rich cobalt center while maintaining the cobalt(II) oxidation state and the one-electron reduced form of the supporting chelate, *e.g.* $(CNC^{1-})Co^{II}CH_3$.[18] Importantly, the catalytic hydrogenation activity was significantly improved, consistent with previous observations in iron catalysis that more electron rich metal pre-catalysts give rise to increased hydrogenation[19] and hydrosilylation[20] activity.

Despite the excellent hydrogenation activity of $(PDI^{1-})Co^{II}R$ and $(CNC^{1-})Co^{II}CH_3$, there has been no experimental evidence for the oxidative addition of H_2. DFT studies on the bis(imino)pyridine cobalt examples[14,21] support σ-bond metathesis pathways, likely due to the Co(II) oxidation state and the presence of a redox-active chelate. We reasoned that introduction of a sufficiently electron donating ligand may facilitate oxidative addition to Co(III) and potentially enable new bond activation processes and catalytic chemistry. Precedent for such reactivity differences has been established in iron chemistry where addition of H_2 to $(PDI^{2-})Fe^{II}N_2$ yielded the η^2-dihydrogen complex[22] while the corresponding PNP derivative formed a stable iron(II) dihydride.[23] During the course of these investigations, Milstein and coworkers reported the attempted synthesis of the desired $(^{iPr}PNP)CoCH_3$ compound but instead isolated a cobalt(II) methyl complex arising from purported H-atom loss from the benzylic position of the chelate.[24] Here we describe the successful synthesis of $(^{iPr}PNP)CoCH_3$ and its utility as a platform for oxidative addition of non-polar substrates such as H_2 and C-H bonds of arenes and terminal alkynes. This approach has enabled the isolation of rare examples of hexacoordinate Co(III) trihydride, bis(acetylide) hydride and trimethyl complexes.

Results and Discussion

In light of Milstein's observations,[24] an alternative route to (^{iPr}PNP)CoCH$_3$ was explored (Scheme 1). Addition of one equivalent of NaBEt$_3$H to a toluene suspension of (^{iPr}PNP)CoCl$_2$ followed by filtration and recrystallization afforded purple crystals identified as (^{iPr}PNP)CoCl in 75% yield. The solid state structure of S = 1 (^{iPr}PNP)CoCl was determined by X-ray diffraction (Scheme 1) and establishes a near tetrahedral geometry with N$_{py}$-Co-Cl and P-Co-P angles of 117.63(8)° and 127.26(3)°, respectively. Both the paramagnetic ^{1}H NMR spectrum and the crystallographic data for the compound support an intact PNP ligand. The target methyl complex, (^{iPr}PNP)CoCH$_3$ was obtained by stoichiometric addition of LiCH$_3$ to (^{iPr}PNP)CoCl and was isolated as a diamagnetic, dark brown powder in 97% yield. The observed diamagnetism of (^{iPr}PNP)CoCH$_3$ as compared to (^{iPr}PNP)CoCl is a result of the increased field strength of the alkyl relative to the halide ligand.[25] The ^{1}H and ^{31}P NMR data are consistent with a diamagnetic C_{2v} symmetric compound with the Co-CH$_3$ resonance appearing as a triplet ($^3J_{P\text{-}H}$ = 10.1 Hz) at -1.22 ppm and observation of a single ^{31}P resonance at 48.5 ppm.

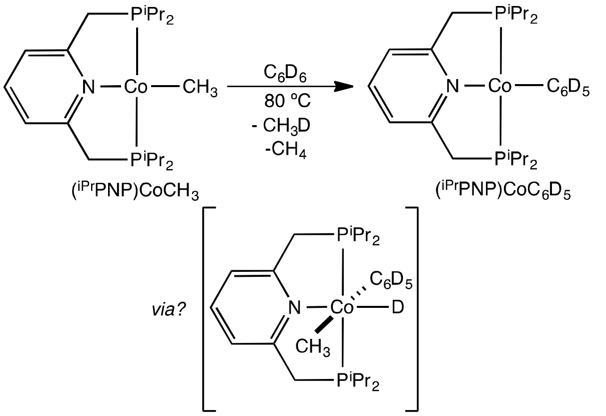
Scheme 1. Synthesis of (^{iPr}PNP)CoCl and (^{iPr}PNP)CoCH$_3$ and solid state structure of (^{iPr}PNP)CoCl at 30% probability ellipsoids.



Notably, (^{iPr}PNP)CoCH$_3$ was stable toward H-atom loss[24] at 23 ºC over extended periods (~weeks) both in the solid state and solution. Warming cyclohexane solutions of (^{iPr}PNP)CoCH$_3$ to 80 ºC for 12 hours also produced no change, demonstrating thermal stability. By contrast, heating the compound in benzene-d_6 under the same conditions resulted in loss of one equivalent of the methane isotopologues, CH$_4$ and CH$_3$D in a 2:1 ratio (^{1}H NMR spectroscopy) with concomitant formation of (^{iPr}PNP)CoC$_6$D$_5$, arising from C-D activation of the solvent (Scheme 2). As will be discussed in more detail, significant decomposition of the cobalt complex accompanies benzene activation. The natural abundance isotopologue, (^{iPr}PNP)CoC$_6$H$_5$ was independently synthesized in 66% yield by treatment of (^{iPr}PNP)CoCl with PhLi and confirmed the identity of the intermolecular C-H activation product. With (^{iPr}PNP)CoC$_6$H$_5$ in hand, thermolysis of the compound was conducted in benzene-d_6 at 80 ºC for 16 hours. No exchange of the aryl ligands was observed suggesting that if oxidative addition is operative, the putative Co(III) diphenyl hydride is not kinetically accessible.

To address the source of CH$_4$, (^{iPr}PNP)CoC$_6$D$_5$ prepared from activation of benzene-d_6 was analyzed by ^{2}H and quantitative ^{13}C NMR spectroscopies and established no incorporation of deuterium into any portion of the PNP chelate. Performing the thermolysis in the presence of an internal ferrocene standard established that at complete conversion of the starting cobalt compound, only 30% of (^{iPr}PNP)CoC$_6$D$_5$ was obtained along with concomitant formation of an unidentified insoluble dark product and free ^{iPr}PNP (~ 20%). The amount of CH$_3$D observed corresponds to the amount of (^{iPr}PNP)CoC$_6$D$_5$. It iss likely that degradation of the chelate accounts for the source of H atoms and ultimately the observed preponderance of CH$_4$.

Scheme 2. Activation of benzene by (^{iPr}PNP)CoCH$_3$.



Activation of C-H bonds by reduced cobalt complexes has been known since the seminal work of Murahashi[26] and typically relies on chelate assistance to facilitate the putative oxidative addition.[27] Combinations of cobalt salts, Grignard activators and neutral donors such as phosphines have since been developed for chelate assisted C-H activation and applied to synthesis.[28] Oxidative addition of unactivated C-H bonds with well-defined organometallic compounds remains rare and limited to Brookhart's cyclopentadienyl cobalt(I) platform that promotes H-D exchange and transfer hydrogenation.[29] Intramolecular activation of benzylic C-H bonds of tethered NHC ligands upon reduction of a Co(I) chloride has also recently been reported by Deng and coworkers.[30]

Benzene activation by diamagnetic (^{iPr}PNP)CoCH$_3$ is also noteworthy in light of Caulton's observations that a related, three coordinate, anionic, amido-based "PNP"-ligated cobalt complex with an S =1 ground state is unreactive towards C-H bonds.[31] The observed intermolecular C-H activation with (^{iPr}PNP)CoCH$_3$ raised the possibility that the reaction proceeds either via a redox neutral σ-bond metathesis[32] or an oxidative-addition reductive elimination pathway. In an attempt to distinguish these possibilities, the synthesis of isolable Co(III) oxidative addition products was explored.

Stirring a diethyl ether solution of (^{iPr}PNP)CoCH$_3$ with 4 atm of H$_2$ followed by recrystallization at -35 ºC under a dihydrogen atmosphere furnished yellow crystals identified as (^{iPr}PNP)CoH$_3$ (Scheme 3). At 23 ºC, a single broad cobalt-hydride resonance was observed at -14.1 ppm by ^{1}H NMR spectroscopy, establishing rapid interchange between the Co-H positions at this temperature. To confirm the identity as a Co(III) trihydride rather than the Co(I) dihydrogen alternative,[33] variable temperature T_1 measurements were carried out (Figure S1 and Table S1). A minimum value of 65 ms was measured at -35 ºC, consistent with a classical cobalt trihydride. It should be noted that quadrupolar

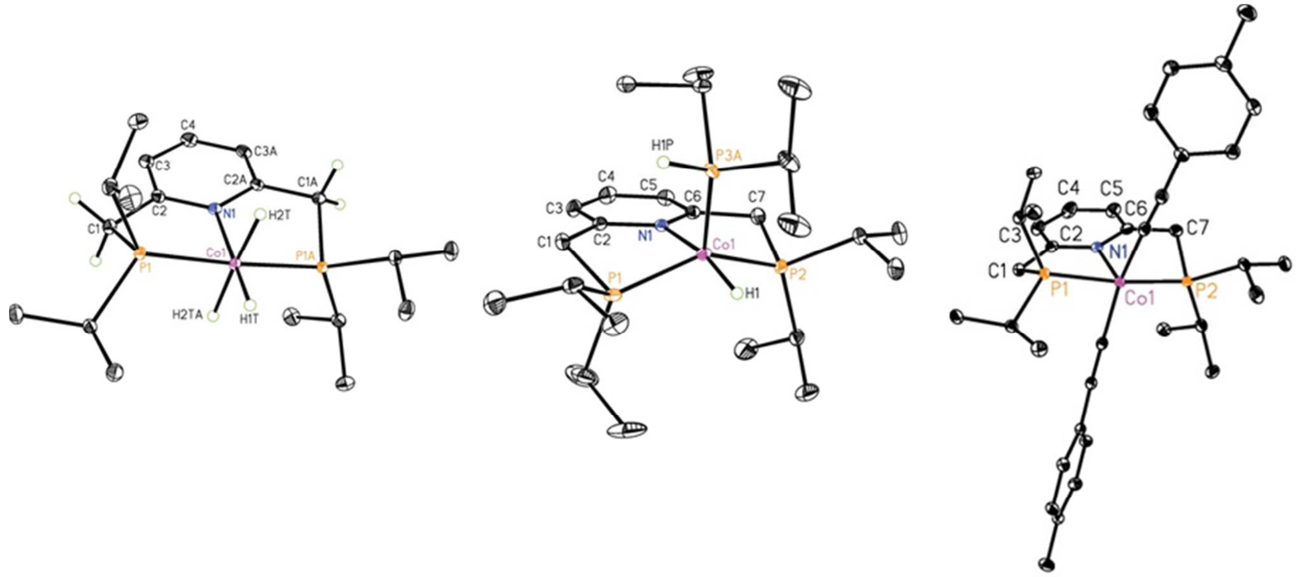
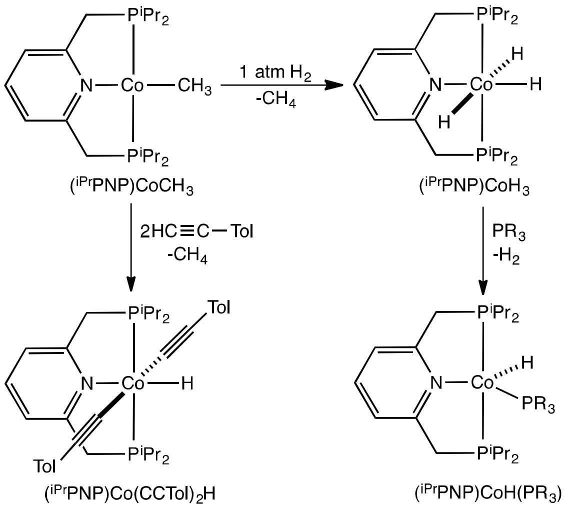


Figure 1. Solid state structures of (^{iPr}PNP)CoH$_3$, (^{iPr}PNP)CoH(HP^{i}Pr$_2$) and (^{iPr}PNP)Co(CCTol)$_2$H at 30% probability ellipsoids. For (^{iPr}PNP)CoH$_3$ and (^{iPr}PNP)CoH(HP^{i}Pr$_2$), hydrogen atoms, except the cobalt-hydrides, omitted for clarity

broadening from the cobalt nucleus has been known to complicate interpretation of T_1 min values.[33,34] However, the value is similar to those reported by Arnold in related pincer-ligated cobalt hydrides.[12] At temperatures below –60 ºC, two distinct cobalt hydride resonances are observed in a 2:1 ratio at -9.73 and -22.92 ppm respectively, also consistent with this formulation.[35] The peaks remain broadened even at the lowest temperatures accessible and prohibiting measurement of H-H and P-H coupling constants. The identity of (^{iPr}PNP)CoH$_3$ was also confirmed by X-ray diffraction (Figure 1), where each of the cobalt hydrides was located and freely refined and is strikingly similar to the iridium congener reported by Nozaki.[36] Performing the synthesis with D$_2$ gas cleanly yielded (^{iPr}PNP)CoD$_3$ with exclusive formation of CH$_3$D and no evidence for deuterium incorporation into the pincer.

Scheme 3. Oxidative addition of H$_2$ and TolCCH with (^{iPr}PNP)CoCH$_3$.



In light of the facile oxidative addition of H$_2$, the catalytic hydrogenation performance of (^{iPr}PNP)CoCH$_3$ was evaluated. With 5 mol% of (^{iPr}PNP)CoCH$_3$, 0.4 mmol of substrate and 4 atm of H$_2$, 5% conversion of cyclohexene to cyclohexane and no hydrogenation of *trans*-methylstilbene was observed after 16 hours at 22 ºC. The poor hydrogenation activity is likely a result of facile H$_2$ oxidative addition to form (^{iPr}PNP)CoH$_3$, which in the presence of a dihydrogen atmosphere, does not undergo reductive elimination to form the requisite Co(I) hydride for olefin insertion. Thus, introduction of a relatively electron rich pincer enables H$_2$ oxidative addition. Although seemingly counterintuitive, this behavior adversely effects catalytic hydrogenation performance. As noted by Goldman and coworkers in rhodium chemistry, it is also possible that the poor catalytic activity may be a result of the poor trans influence of the nitrogen of the central pyridine donor.[37]

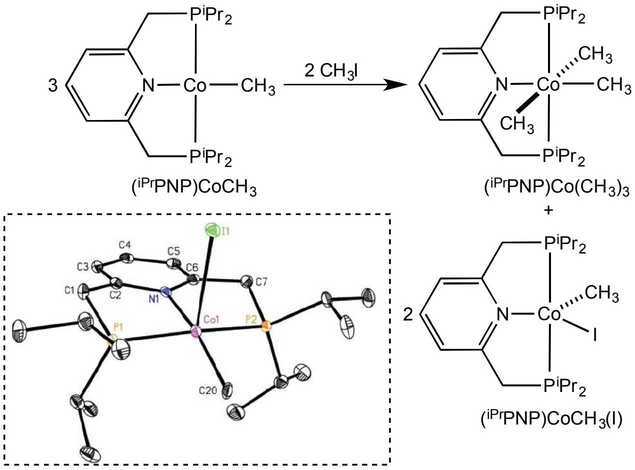
The Co(III) trihydride proved unstable to reductive elimination in the absence of H$_2$. Exposure of a diethyl ether solution of (^{iPr}PNP)CoH$_3$ to N$_2$ resulted in immediate formation of a yellow-brown product identified as (^{iPr}PNP)CoH(HP^{i}Pr$_2$). Recrystallization at -35 ºC resulted in isolation of single crystals in 40% yield (Figure 1). The benzene-d_6 ^{1}H NMR spectrum of (^{iPr}PNP)CoH(HP^{i}Pr$_2$) exhibits a diagnostic doublet of triplets of triplets for the P-H at 4.57 ppm while the cobalt-hydride was located at -25.0 ppm as a triplet of doublets ($^2J_{PH}$ = 59.6, 28.7 Hz). More rational and high yielding independent syntheses of both (^{iPr}PNP)CoH(HP^{i}Pr$_2$) and (^{iPr}PNP)CoH(PMe$_3$) were accomplished by addition of the free phosphine to (^{iPr}PNP)CoH$_3$ (Scheme 3). The identity of (^{iPr}PNP)CoH(PMe$_3$) was also confirmed by X-ray diffraction (Figure S2). It is likely that such ligand degradation processes are operative during the oxidative addition of benzene-d_6 to (^{iPr}PNP)CoCH$_3$ and account for CH$_4$ formation and the overall low yield.

The observation of oxidative addition of H$_2$ to form a rare example of a Co(III) trihydride inspired us to explore if similar products could be isolated from C-H oxidative addition. Stirring two equivalents of TolCCH (Tol = 4-CH$_3$-C$_6$H$_4$) with

(^{iPr}PNP)CoCH$_3$ in diethyl ether at 23 ºC resulted in rapid loss of CH$_4$ and formation of a yellow solid identified as (^{iPr}PNP)Co(CCTol)$_2$H in 84% yield. A diagnostic cobalt-hydride resonance was observed as a triplet ($^2J_{P\text{-}H}$ = 51.0 Hz) at -19.0 ppm in the benzene-d_6 ^{1}H NMR spectrum. The solid state structure was determined by single crystal X-ray diffraction and although the hydride ligand was not located, confirms formation of an idealized octahedral Co(III) complex (Figure 1) with *trans*-acetylide ligands, consistent with the symmetry observed in solution by NMR spectroscopy. Unlike (^{iPr}PNP)CoH$_3$, (^{iPr}PNP)Co(CCTol)$_2$H proved thermally stable for extended periods both in the solid state and in benzene-d_6 solution at 23 ºC. Consistent with this observation, performing the oxidative addition of TolCCD resulted in exclusive liberation of CH$_3$D.

Because (^{iPr}PNP)CoCH$_3$ proved to be a rich platform for promoting two-electron chemistry with non-polar reagents, the oxidative addition of a polar molecule was also studied. Dropwise addition of 0.66 equivalents of CH$_3$I to a diethyl ether solution of (^{iPr}PNP)CoCH$_3$ at -35 ºC resulted in a color change to dark red along with formation of dark red precipitate (Scheme 4). Isolation of diamagnetic red crystals from the soluble portion and analysis by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies established formation of a rare cobalt(III) trimethyl complex, (^{iPr}PNP)Co(CH$_3$)$_3$. In the ^{1}H NMR spectrum (Figure S3), two triplets ($^3J_{P\text{-}H}$ = 6.5 and 7.5 Hz) were located at 0.22 and 0.50 ppm in a 2:1 ratio for the two types of methyl ligands.

Scheme 4. Addition of CH$_3$I to (^{iPr}PNP)CoCH$_3$.



The red, diethyl ether insoluble product was paramagnetic with an S = 1/2 ground state (μ_{eff} = 2.1(1) μB, solid state, 23 ºC). Both X-band EPR spectroscopy (Figure S4) and X-ray crystallography established formation of the cobalt(II) methyl iodide product, (^{iPr}PNP)CoCH$_3$(I). No other products were identified based on NMR or EPR spectroscopies. The observed mixture of products likely arises from initial iodine atom abstraction by (^{iPr}PNP)CoCH$_3$ to form (^{iPr}PNP)CoCH$_3$(I) with liberation of [CH$_3$] radical that combines with (^{iPr}PNP)CoCH$_3$ to ultimately yield (^{iPr}PNP)Co(CH$_3$)$_3$. To conclusively identify the source of the methyl groups in the Co(III) trialkyl product, a deuterium labeling experiment was performed. Following a similar procedure as above, 0.66 equivalents of CD$_3$I were added to a diethyl ether solution of (^{iPr}PNP)CoCH$_3$. Analysis of the benzene soluble product by ^{1}H and ^{2}H NMR spectroscopies established incorporation of deuterium into both methyl positions of (^{iPr}PNP)Co(CH$_3$)$_3$ in a statistical ratio, confirming the source of two of the three methyl groups as arising from CD$_3$I. Similar experiments have been reported by Milstein^{24} using the larger (^{tBu}PNP)CoCH$_3$ complex and exclusive formation of the Co(II) [(^{tBu}PNP)CoCH$_3$][I] product was observed with no evidence for any Co(III) complexes. This disparity is likely a result of the increased steric profile of the tert-butyl ligand relative to the iso-propyl substituted chelate employed here.

Conclusions

In summary, the synthesis of the thermally stable cobalt methyl complex, (^{iPr}PNP)CoCH$_3$ is described. Introduction of an electron donating rather than redox-active pincer type ligand enables oxidative addition of H$_2$ and C-H bonds to yield rare examples of isolable, crystallographically characterized Co(III) products. The application of this fundamental chemistry to new, base metal catalyzed transformations is currently under investigation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Complete experimental procedures, characterization data for all new compounds and computational results. Crystallographic data: CCDC 982446-982451. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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