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Phosphine-Ligated Cobalt(II) Acetylacetonate Complexes

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Cobalt(II) acetylacetonate complexes bearing a phosphine ligand can be key intermediates or precursors to cobalt-based catalysts; however, they have been rarely studied, especially from a molecular structure point of view. This work is focused on the understanding of how different phosphines react with $Co(acac)_2$ (acac = acetylacetonate). To do so, a variety of analytical tools, including NMR and IR spectroscopy, X-ray crystallography, mass spectrometry, and elemental analysis, have been used to study the reactions and characterize the isolated products. These results have shown that the monodentate ligand, $HPPh_2$, binds to $Co(acac)_2$ weakly and reversibly to produce $Co_2(acac)_4(HPPh_2)$, whereas the bidentate ligand, 1,2-bis(diphenylphosphino)ethane (dppe), interacts with $Co(acac)_2$ more strongly to yield a 1D coordination polymer of $Co(acac)_2(dppe)$. 2-(Dicyclohexylphosphino)methyl-1 H-pyrrole ($^{Cy}PN^{H}$), which is a pyrrole-tethered phosphine, forms an unusual 5-coordinate cobalt complex, $Co(acac)_2(^{Cy}PN^{H})$, in which the pyrrole moiety participates in a bifurcated hydrogen–bonding interaction with the $[acac]^-$ ligands. In contrast, another bidentate ligand, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), fails to react with $Co(acac)_2$, presumably due to its wide bite angle and difficulty in bridging two metals.

1. Introduction

Cobalt(II) acetylacetonate, $Co(acac)_2$, is an inexpensive (≈$1.5 per g) and versatile reagent, which has been frequently used to prepare cobalt-based nanostructures,[1] thin films,[2] coordination polymers,[3] and metal complexes.[4] It can also serve as a stand-alone catalyst[5] or, more commonly, as a key precursor to carbene-,[6] pyridine-,[7] or phosphine-ligated[8–11] cobalt catalysts for numerous synthetic applications. To understand the exact function of $Co(acac)_2$ in these processes, it is imperative to know, at the molecular level, how $Co(acac)_2$ interacts with molecules with different donor properties.

It is well known that the anhydrous form of $Co(acac)_2$ adopts a tetrameric structure (**Figure 1**), relying on the oxygen atoms to bridge two metals so that the octahedral geometry at each cobalt center is satisfied.[12] Crystals grown from halogenated solvents such as $CHCl_3$, CH_2Cl_2, and $ClCH_2CH_2Cl$ typically show a trimeric structure (Figure 1) along with the co-crystallized solvent molecules.[13] The $Co(acac)_2$ clusters can be further broken down by water,[14] alcohols,[13,15] or pyridine[16] (added as a solvent or reagent), giving *trans*-$Co(acac)_2L_2$ as the crystallographically characterized products. Adducts of $Co(acac)_2$ and nitrogen-based bidentate ligands are also known in the literature.[17] The two prototypical examples are $Co(acac)_2(TMEDA)$ and $Co(acac)_2(TEEDA)$, both featuring a mononuclear, propeller-like structure as illustrated in Figure 1.

While informative, the solid-state structures probed by single-crystal or powder X-ray diffraction may not necessarily reflect all or even the major species in solution. Spectrophotometric and NMR studies of the reaction of $Co(acac)_2$ with pyridine (in C_6H_6 or C_6D_6) have suggested that $Co(acac)_2(py)_2$ is in equilibrium with $Co_2(acac)_4(py)$, $Co(acac)_2(py)$, and free pyridine.[18] $Co(acac)_2(py)_2$ becomes the dominant species only when pyridine is added in large excess. The complexity of the system is further exemplified by an early study showing that $Co(acac)_2$ reacts with pyridine (in C_6H_6) to produce three unique crystals: orange orthorhombic crystals of $Co(acac)_2(py)_2$, red triclinic crystals of $Co_2(acac)_4(py)_2$, and purple triclinic crystals of $Co_2(acac)_4(py)(H_2O)$.[16]

Our interests in phosphine-ligated cobalt(II) acetylacetonate complexes are primarily driven by their potential to act as precursors to cobalt hydrides,[19] which in turn can be used to prepare a variety of pincer complexes.[20] Structurally well-defined compounds of the type $Co(acac)_2(phosphine)_x$ ($x = 0.5$, 1, 2, or >2) are surprisingly rare, considering that $Co(acac)_2$ mixed with a phosphine ligand is routinely employed as a (pre)catalyst.[8–11] In some cases, using the premade $Co(acac)_2(phosphine)_x$ as the catalyst can give more reproducible yields than using the mixture of $Co(acac)_2$ and a phosphine ligand.[9b] To synthesize the desired Co(II) complexes such as $Co(acac)_2(dppe)$[21,17a] and $Co(acac)_2\{o\text{-}C_6H_4(PPh_2)_2\}$,[22] the diphosphine ligand is often treated with ≈1 equiv of $Co(acac)_2$, although very limited data are available to support the composition or establish the structure of the isolated product. Of particular note is that the closely related trivalent complexes (i.e., $[Co(acac)_2(monophosphine)_2]^+$[23] and $[Co(acac)_2(diphosphine)]^+$[24,23a]) are better characterized, likely due to their low-spin, diamagnetic nature (18-electron complexes with a d^6 metal ion).

The objective of this work was thus to provide a more definitive structural elucidation of the Co(II) complexes derived from

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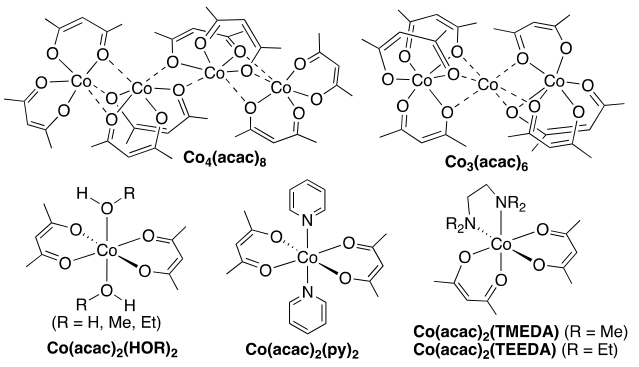


Figure 1. Selected examples of crystallographically characterized $Co(acac)_2$ complexes with or without an exogenous ligand.

$Co(acac)_2$ and different phosphine ligands. The selection of ligands (**Figure 2**) was based on our longer-term plans to study the corresponding Co(I) hydride species for catalytic hydrophosphination, hydroboration, hydrogenation, and transfer hydrogenation reactions. They are also representative of phosphines with different coordination modes and properties (e.g., monodentate, bidentate, hemilabile, bifunctional, and wide bite angle). For the target phosphine-ligated cobalt(II) acetylacetonate complexes, particular attention was paid to investigating their behaviors not only in the solid state but also in solution.

2. Results and Discussion

2.1. Reaction of $Co(acac)_2$ with $HPPh_2$

Our initial efforts were focused on isolating discrete metal complexes from the 1:4 mixture of $Co(acac)_2$ and $HPPh_2$ in THF. This specific metal-to-ligand ratio reflects the composition of $HCo(HPPh_2)_4$, a hydride complex that we targeted for a different research project. The $Co(acac)_2$-to-$HPPh_2$ ratio was subsequently changed to 2:1, 1:1, and 1:2 to match those in $Co_2(acac)_4$ L, $Co(acac)_2$ L, and $Co(acac)_2L_2$, respectively, as the potential products. Despite repeated trials (by varying the reaction time and temperature), the crude product always appeared oily but nevertheless could be extracted with pentane, followed by cooling at –30 °C to yield a precipitate. Elemental and IR analyses of the isolated solid product (Table S1, Supporting Information) indicated that it was $Co(acac)_2$ or $Co(acac)_2$ mixed with $HPPh_2$ ($\leq$0.5 equiv). These results suggest that the binding of $HPPh_2$ to $Co(acac)_2$, if present, is weak.

For a better understanding of how $Co(acac)_2$ reacts with $HPPh_2$, the ^1H NMR spectrum of $Co(acac)_2$ in CD_2Cl_2 was first recorded (**Figure 3**), which displayed a broad CH_3 resonance at -1.85 ppm ($w_{1/2} = 940$ Hz). The CH resonance for the acetylacetonate ligand was not located. Adding 0.5 equiv of $HPPh_2$ to this solution caused a downfield shift of the CH_3 resonance to 1.31 ppm. The proton resonances for the phosphine were found at 7.38 ($w_{1/2} = 45$ Hz), 6.19 ($w_{1/2} = 42$ Hz), 5.01 ($w_{1/2} = 52$ Hz), and –10.05 ppm ($w_{1/2} = 190$ Hz); however, no phosphorus signal was detected. These proton resonances continued to shift downfield upon further addition of $HPPh_2$. It is worth noting that the resonances for the diamagnetic impurity (i.e., acetylacetone or Hacac) were unaffected by $Co(acac)_2$ and $HPPh_2$. Based on these observations, one can conclude that, in CD_2Cl_2, $Co(acac)_2$ interacts with $HPPh_2$ but not with Hacac. Replacing the halogenated solvent with C_6D_6 gave a similar result, although the proton resonances for $Co(acac)_2$ and $HPPh_2$ were shifted less drastically. For example, when the amount of $HPPh_2$ was increased by eightfold, the PH resonance was shifted from –4.06 to –0.91 ppm in C_6D_6 (Figure S4-A, Supporting Information) as opposed to the observed shift from –10.05 to –4.66 ppm in CD_2Cl_2 (Figure 3). The minor differences could be explained by the notion that the extent of $Co(acac)_2$ aggregation is solvent dependent. The more coordinating solvent, THF, is expected to further break down the $Co(acac)_2$ clusters. In fact, *trans*-$Co(acac)_2(THF)_2$ had already been crystallographically characterized, although at ambient temperature the crystals were shown to readily lose the THF molecules.[25] $Co(acac)_2$ dissolved in THF-d_8 displayed a broad resonance at 29.8 ppm ($w_{1/2} = 350$ Hz), which was almost intact when 0.5 equiv of $HPPh_2$ was added (**Figure 4**). Increasing the amount of $HPPh_2$ to 4 equiv, however, led to a new CH_3 resonance emerging nearby at 30.8 ppm. The resonances associated with $HPPh_2$ appeared in the diamagnetic region, albeit broad and shifted from free $HPPh_2$. Taken together, the NMR studies confirm that $HPPh_2$ binds to $Co(acac)_2$ weakly and reversibly, regardless of the solvent used. This analysis also agrees with early studies of triarylphosphines, which were shown to weakly interact with

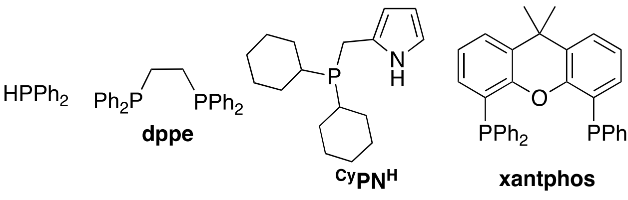


Figure 2. An assortment of phosphines used to react with $Co(acac)_2$.

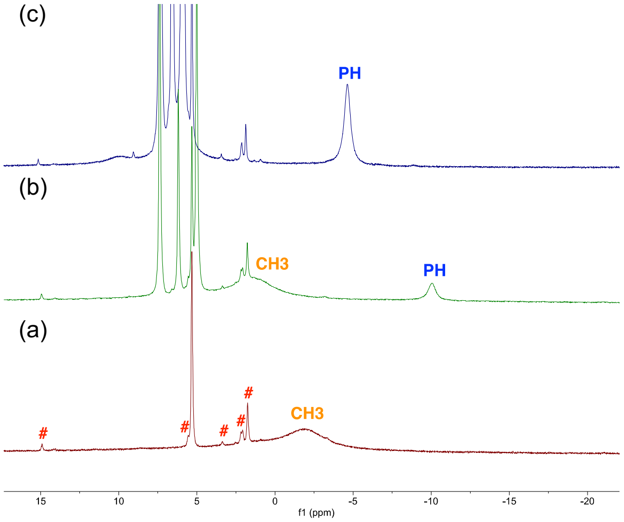


Figure 3. ^1H NMR spectra (23 °C, CD_2Cl_2) of a) $Co(acac)_2$, b) $Co(acac)_2$ mixed with 0.5 equiv of $HPPh_2$, and c) $Co(acac)_2$ mixed with 4 equiv of $HPPh_2$. # denotes the residual acetylacetone (keto and enol forms) present in the commercial sample of $Co(acac)_2$.

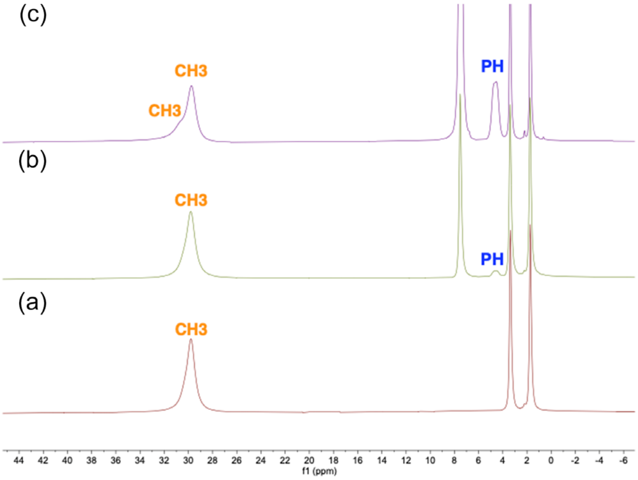


Figure 4. ^1H NMR spectra (23 °C, THF-d_8) of a) $Co(acac)_2$, b) $Co(acac)_2$ mixed with 0.5 equiv of $HPPh_2$, and c) $Co(acac)_2$ mixed with 4 equiv of $HPPh_2$.

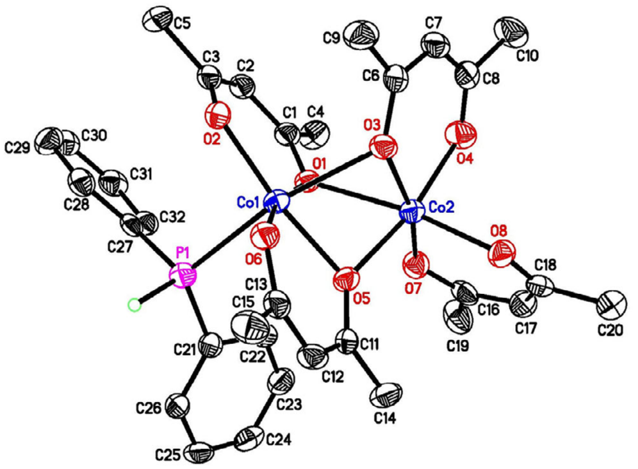


Figure 5. ORTEP of $Co_2(acac)_4(HPPh_2)$ at the 50% probability level. Selected distances (Å) and angles (°): Co(1)–O(1) 2.048(3), Co(1)–O(2) 1.993(3), Co(1)–O(3) 2.297(3), Co(1)–O(5) 2.028(3), Co(1)–O(6) 2.008(3), Co(1)–P(1) 2.5285(16), Co(2)–O(1) 2.254(3), Co(2)–O(3) 2.072(3), Co(2)–O(4) 2.040(3), Co(2)–O(5) 2.132(3), Co(2)–O(7) 2.002(3), Co(2)–O(8) 2.042(3), Co(1)…Co(2) 2.9964(10); O(1)–Co(1)–O(2) 90.49(12), O(5)–Co(1)–O(6) 88.15(12), O(3)–Co(2)–O(4) 89.83(13), O(7)–Co(2)–O(8) 91.12(13).

$Co(acac)_2$ in $CDCl_3$.[26] The more electron-rich monophosphines, such as PMe_3, are expected to bind to $Co(acac)_2$ more tightly. The NMR titration experiment of $Co(acac)_2$ with PMe_3 (0.5–10 equiv) in C_6D_6 (Figure S9, Supporting Information) showed a continuous upfield shift of the PCH_3 resonance from 42.5 to 10.7 ppm, accompanied by a continuous downfield shift of the $Co(acac)_2$ resonances from −1.21 (CH_3) to 28.3 (CH) and 21.8 ppm (CH_3). The chemical shift values and the shifting pattern are reminiscent of the reaction of $Co(acac)_2$ with pyridine,[18b] suggesting that PMe_3 remains in equilibrium with one or more PMe_3-ligated $Co(acac)_2$ complexes.

In an attempt to discern the structure of $HPPh_2$-bound $Co(acac)_2$ species, the two reagents were mixed in THF with a metal-to-ligand ratio of 1:4, diluted with $CHCl_3$–MeOH, and then analyzed by electrospray ionization mass spectrometry (ESI-MS). An ion corresponding to $[Co^{II}(acac)(HPPh_2)]^+$ ($m/z = 344.0363$) was observed (Figure S8, Supporting Information), although extensive oxidation of $HPPh_2$ and the metal led to the detection of $[Co^{II}(acac)(O{=}PHPh_2)]^+$, $[Co^{II}(acac)(O{=}PHPh_2)_2]^+$, and $[Co^{II}Co^{III}(acac)_3(O{=}PPh_2)]^+$ as the major ions. Furthermore, the incorporation of chlorine, presumably from $CHCl_3$, gave an ion consistent with $[Co^{II}Co^{III}(acac)_3(HPPh_2)Cl]^+$. The mass spectral conditions are obviously different from those applied in the synthesis and NMR studies. Nevertheless, the ESI-MS result establishes the possibility of $HPPh_2$ binding to $Co(acac)_2$.

Fortunately, light pink crystals were obtained during the synthesis of a cobalt hydride from $Co(acac)_2$, $HPPh_2$, and $NaBH_4$ (see Supporting Information for details). The X-ray diffraction study revealed that they were crystals of $Co_2(acac)_4(HPPh_2)$ (**Figure 5**). In the previous studies of the reaction between $Co(acac)_2$ and pyridine, $Co_2(acac)_4(pyr)$ was proposed as one of the possible products, although its molecular structure remains unclear.[18] The crystal structure of $Co_2(acac)_4(HPPh_2)$ described here provides a hint at what $Co_2(acac)_4(pyr)$ might look like. In this dinuclear structure, both cobalt centers are situated in an octahedral coordination environment, completed by three μ_2-η^2:η^1-$[acac]^-$ ligands, one η^2-$[acac]^-$ ligand, and one $HPPh_2$ ligand. The $Co_2(acac)_4$ fragment of the molecule is unremarkable, with the Co–O bond lengths falling in the reported range of 1.95–2.30 Å.[13] As expected, the longer Co–O bonds [2.132–2.297 Å] involve bridging oxygen atoms from the neighboring $Co(acac)_2$ unit. The Co–P bond of $Co_2(acac)_4(HPPh_2)$, on the other hand, is unique. Its length [2.5285(16) Å] is only slightly shorter than the sum of the covalent radii of phosphorus [1.07 Å] and high-spin cobalt [1.50 Å].[27] It would rank $Co_2(acac)_4(HPPh_2)$ as a cobalt diphenylphosphine complex with the longest Co–P bond.[28] The long Co–P bond further confirms that $HPPh_2$ binds to $Co(acac)_2$ weakly. Despite this weak phosphine–cobalt interaction, the oxygen donor trans to $HPPh_2$ (i.e., O3) responds by forming a Co–O bond [2.297(3) Å] longer than any other Co–O bonds within the molecule.

2.2. Characterization of $Co(acac)_2(dppe)$

The stability of phosphine-ligated cobalt(II) acetylacetonate complexes can potentially be improved when a diphosphine is employed, either as a chelating ligand or as a bridging ligand. The most studied system is $Co(acac)_2(dppe)$, which can be prepared by mixing $Co(acac)_2$ with 1.05–1.1 equiv of dppe in toluene or THF.[9,21,17a] However, this complex was not well characterized; the only reported data were the two IR bands at 1585 and 1514 cm^{-1}.[17a] In this work, $Co(acac)_2(dppe)$ was synthesized using a strict 1:1 ratio of $Co(acac)_2$ and dppe mixed in THF. The isolated product, a light pink powder, gave elemental analysis data that consistently matched the molecular formula of $Co(acac)_2(dppe)$. Comparing its IR spectrum (Figure S13, Supporting Information) with the spectra of the individual reactants confirmed that the product was not simply a mixture of $Co(acac)_2$ and dppe but a new cobalt complex. A mixture would also result in a composition change following a wash with pentane or THF. This was not the case for our isolated product.

Unlike $Co(acac)_2$ and dppe, which have good solubility in halogenated solvents, $Co(acac)_2(dppe)$ is sparsely soluble in CD_2Cl_2. However, its solubility in THF is modest, allowing NMR analysis to be conducted on a sample dissolved in THF-d_8. The broad CH_3 resonance (Figure S12, Supporting Information) is centered at 30.0 ppm ($w_{1/2} = 316$ Hz), which deviates and sharpens only slightly from the CH_3 resonance of Co(acac)$_2$ in THF-d_8 (29.8 ppm, $w_{1/2} = 350$ Hz). In contrast, the resonances for dppe show significant changes upon coordination: the CH_2 resonance is shifted downfield by 0.56 ppm, and the clustered aromatic resonances become well separated.

The solid sample of Co(acac)$_2$(dppe) can be exposed to air for hours without noticeable decomposition. Its suspension in acetone or solution in THF gradually changed color from pink to green, indicating some air sensitivity. NMR analysis of the decomposed samples suggested that oxidation had occurred to both the phosphine ligand and the metal (Co(acac)$_3$ was detected). Single crystals for the X-ray diffraction study were obtained from a saturated toluene solution kept under argon. To our surprise, the crystal structure (**Figure 6**) revealed a 1D coordination polymer of Co(acac)$_2$(dppe) with dppe acting as a bridging ligand. The Co–O bonds [2.0347(7) and 2.0542(7) Å] are comparable to those in *trans*-Co(acac)$_2$L$_2$[13–16] while the Co–P bonds [2.5475(3) Å] remain relatively long.

The cobalt acetylacetonate complex (diluted in $CHCl_3$–MeOH) was further characterized by ESI-MS (Figure S15, Supporting Information). The molecular ion [Co^{III}(acac)$_2$(dppe)]$^+$ ($m/z = 655.1559$) was observed, likely due to a facile oxidation of Co(II) to Co(III) under the ionization conditions.[29] The most intense ion or base peak was identified as [Co^{II}(acac)(dppe)]$^+$, resulting from dissociation of the negatively charged [acac]$^-$ ligand. Other identifiable ions included [dppe+H]$^+$, [Co$^{II}_2$(acac)$_3$]$^+$, [Co^{II}(acac)(dppe)+O]$^+$, [Co^{II}(dppe)$_2$Cl]$^+$, and [Co^{II}(acac)(dppe)$_2$]$^+$, demonstrating a variety of possibilities to redistribute the supporting ligands to cobalt. More importantly, the ESI-MS data further support our early assumption that diphosphines would bind to Co(acac)$_2$ more tightly than monophosphines. Additionally, 1,2-bis(dicyclohexylphosphino)ethane (dcpe), another diphosphine ligand, was also shown to react with Co(acac)$_2$ to form a discrete compound related to Co(acac)$_2$(dppe) (Figure S16–S19, Supporting Information), although its molecular structure is not yet determined.

2.3. A 5-Coordinate Cobalt(II) Acetylacetonate Complex

As a phosphine ligand, 2-(dicyclohexylphosphino)methyl-1*H*-pyrrole (^{Cy}PN^H) is unique in many ways. It can behave as a monodentate (κ^P) or bidentate (κ^P,κ^N) ligand, and the NH group can participate in hydrogen–bonding interactions or transfer the protic hydrogen to other molecules.[30] The latter property prompted us to investigate its reactivity toward Co(acac)$_2$, in which the basic [acac]$^-$ ligand may deprotonate the NH group to yield κ^P,κ^N-Co(acac)(^{Cy}PN), our target precursor to cobalt hydride species.

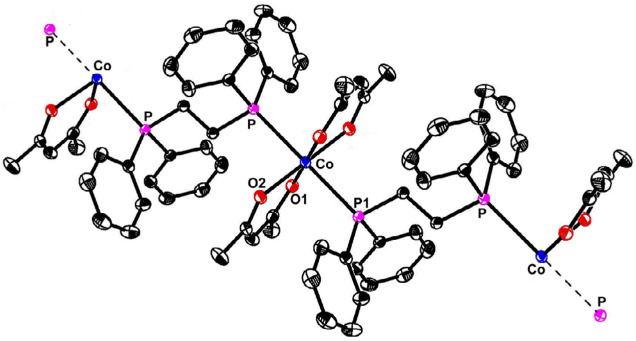


Figure 6. ORTEP of Co(acac)$_2$(dppe) polymer at the 50% probability level. Selected distances (Å) and angles (°): Co–O(1) 2.0542(7), Co–O(2) 2.0347(7), Co–P and Co–P(1) 2.5475(3); O(1)–Co–O(2) 88.47(3), P–Co–P(1) 180.0.

When equimolar amounts of ^{Cy}PN^H and Co(acac)$_2$ were mixed in THF, a dark purple-blue solution was obtained. Evaporating the solvent, followed by a pentane wash, gave a blue powder whose elemental analysis data matched the composition of Co(acac)$_2$(^{Cy}PN^H). The IR spectrum of this material (Figure S22, Supporting Information) clearly showed a new compound with a characteristic N–H stretch observed at 3339 cm^{-1}, which is significantly shifted from the same band for the free ^{Cy}PN^H ($\nu_{N-H} = 3251$ cm^{-1}). The molecular structure (**Figure 7**) was further established by X-ray crystallography using crystals grown from THF-pentane. Interestingly, the cobalt(II) acetylacetonate complex adopts a distorted square pyramidal structure as inferred by the geometry index ($\tau_5 = 0.15$).[31] The ^{Cy}PN^H ligand occupies the axial position while participating in a bifurcated hydrogen–bonding interaction with the two [acac]$^-$ ligands. The O4 atom, which has the shortest interatomic distance with the pyrrole nitrogen, forms the longest bond with cobalt [2.0606(12) Å]. The oxygen donors that are not involved in the hydrogen–bonding interaction form comparatively short bonds with cobalt. The Co–O bonds [1.9835(11) and 1.9993(11) Å] are among the shortest for cobalt(II) acetylacetonate or its derivatives.[13]

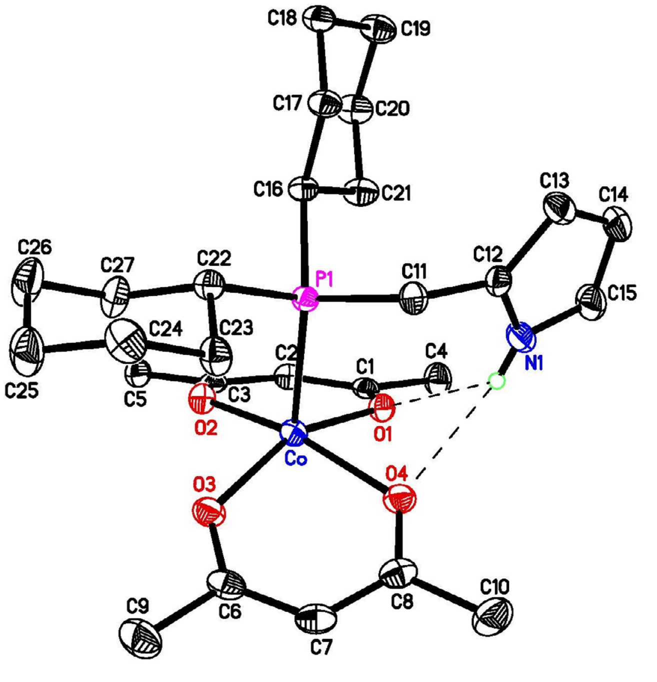
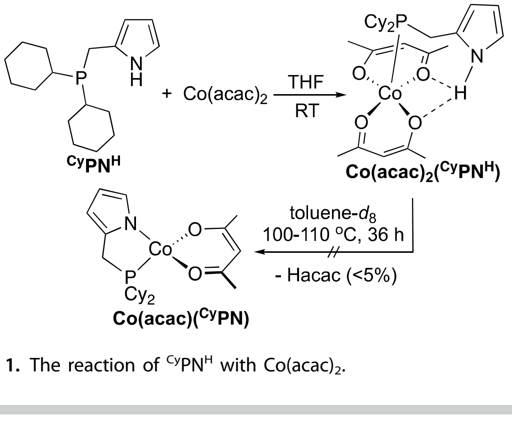


Figure 7. ORTEP of Co(acac)$_2$(^{Cy}PN^H) at the 50% probability level. Selected distances (Å) and angles (°): Co–O(1) 2.0069(11), Co–O(2) 1.9835(11), Co–O(3) 1.9993(11), Co–O(4) 2.0606(12), Co–P(1) 2.4422(5), N(1)…O(1) 3.0923(19), N(1)…O(4) 3.0186(18); O(1)–Co–O(2) 90.58(5), O(3)–Co–O(4) 87.66(5), O(1)–Co–O(3) 155.44(5), O(2)–Co–O(4) 164.17(5).

A more in-depth IR study of $Co(acac)_2(^{Cy}PN^H)$ showed no spectral change to a powder sample exposed to air overnight or washed by pentane or THF, suggesting that this compound can maintain its structural integrity, at least in the solid state. However, the pentane and THF solutions obtained following the wash rapidly changed their color upon exposure to air, from blue to pink. The THF-pentane solution (kept under argon) that produced single crystals of $Co(acac)_2(^{Cy}PN^H)$ also formed colorless-pale pink dichroic crystals, which proved to be the previously known aqua complex, *trans*-$Co(acac)_2(H_2O)_2$.[14] These observations suggest that, in solution, $Co(acac)_2(^{Cy}PN^H)$ is hygroscopic and the $^{Cy}PN^H$ ligand can be readily displaced by water.

The solution behavior of $Co(acac)_2(^{Cy}PN^H)$ was further studied by NMR spectroscopy, for which CD_2Cl_2 was chosen as the deuterated solvent to dissolve this specific compound. Unsurprisingly, no phosphorus resonances were observed. The 42 hydrogens were, however, all located in the chemical shift range of +90 to –20 ppm (Figure S20, Supporting Information). The resonance at 13.58 ppm ($w_{1/2} = 245$ Hz) can be assigned to the CH_3 groups based on its integration value (12 H) relative to other resonances. The broadest resonance at 67.36 ppm ($w_{1/2} \approx 1000$ Hz) can be attributed to the NH resonance, as suggested by its ability to exchange hydrogen with D_2O. Because water and CD_2Cl_2 are not miscible, adding H_2O or D_2O to the CD_2Cl_2 solution of $Co(acac)_2(^{Cy}PN^H)$ created a biphasic system, in which a small amount of pink solid was found at the interface. The NMR signals were all shifted upon the addition of water (Figure S21, Supporting Information). These results can be explained by the displacement of $^{Cy}PN^H$ from cobalt by water to yield *trans*-$Co(acac)_2(H_2O)_2$. The released phosphine undergoes a rapid ligand exchange with the coordinated $^{Cy}PN^H$ ligand in $Co(acac)_2(^{Cy}PN^H)$. The binding of $[acac]^-$ to cobalt appears to be relatively strong. In an attempt to prepare $Co(acac)(^{Cy}PN)$ from $Co(acac)_2(^{Cy}PN^H)$ via an elimination of Hacac, a toluene solution of $Co(acac)_2(^{Cy}PN^H)$ was heated at 100–110 °C for 36 h (**Scheme 1**). The ^1H NMR spectrum showed little change during this period, suggesting that $Co(acac)_2(^{Cy}PN^H)$ is thermally stable as long as the moisture level is kept low.

The facile dissociation of $^{Cy}PN^H$ from $Co(acac)_2(^{Cy}PN^H)$ was also observed during the ESI-MS study (Figure S24, Supporting Information). In this case, the base peak was identified as $[^{Cy}PN^H + H]^+$, and the $Co(acac)_2$ fragment was shown to form ions $[Co^{II}(acac)_2{+}H]^+$ and $[Co^{II}_2(acac)_3]^+$. Once again, oxidation of Co(II) to Co(III) and dissociation of the $[acac]^-$ ligand provided the molecular ion $[Co^{III}(acac)_2(^{Cy}PN^H)]^+$ ($m/z = 534.2172$) and the ion $[Co^{II}(acac)(^{Cy}PN^H)]^+$ ($m/z = 435.1722$), respectively. Other ions that could be readily identified were $[Co^{II}(acac)(^{Cy}PN^H)_2]^+$ (formed by ligand redistribution) and ions with the oxidized phosphine (i.e., $[Co^{II}(acac)(^{Cy}PN^H){+}O]^+$, $[Co^{II}(acac)(^{Cy}PN^H)_2{+}O]^+$, and $[Co^{II}(acac)(^{Cy}PN^H)_2{+}2O]^+$). Overall, the ESI-MS data establish the structure of $Co(acac)_2(^{Cy}PN^H)$ and, compared to $Co(acac)_2(dppe)$, a higher propensity to lose the phosphine ligand.



Scheme 1. The reaction of $^{Cy}PN^H$ with $Co(acac)_2$.

2.4. Search for "$Co(acac)_2$(xantphos)"

Diphosphines with a wide bite angle and a rigid backbone can face some challenges when interacting with $Co(acac)_2$. Their *trans*-spanning property would leave little room for cobalt to accommodate the two $[acac]^-$ ligands. The ligand rigidity would also prevent them from bridging two metals. This was best demonstrated in our investigation of the reactivity of xantphos toward $Co(acac)_2$. A light purple powder was isolated from the 1:1 mixture of $Co(acac)_2$ and xantphos in THF following the same procedure used to prepare $Co(acac)_2(dppe)$. However, the IR spectrum (Figure S25, Supporting Information) showed cumulative bands from the individual reactants instead of a new compound. In addition, washing this material with THF gave a sample with a lighter color and characterization data (IR and elemental analyses) similar to xantphos. This is consistent with the fact that the purple-colored $Co(acac)_2$ has a higher solubility in THF than xantphos, which is a white solid. The lack of reactivity was further supported by ESI-MS analysis of the 1:1 mixture of $Co(acac)_2$ and xantphos (Figure S27, Supporting Information). In contrast to the three phosphine systems described earlier, xantphos shows no affinity for $Co(acac)_2$ or $[Co(acac)]^+$ under the mass spectral conditions.

An important mechanistic implication of our work here is that xantphos is unable to stabilize the catalytically active species until the $[acac]^-$ ligand is removed or partially removed from cobalt. In reactions catalyzed by $Co(acac)_2$/xantphos, this is typically accomplished by introducing oxophilic reagents such as $AlMe_3$,[10a,b] silanes,[10c,e] and boranes.[10d,f,g] However, their reactions with the unsupported $Co(acac)_2$ could be complicated processes, involving reduction/degradation of $Co^{II}Me$ and $Co^{II}H$ type species that may or may not be quickly stabilized by xantphos. This can be the reason why some of the catalytic systems require an excess amount of xantphos (e.g., 1.2–2 equiv with respect to $Co(acac)_2$).[10a,b,f,g]

3. Conclusion

Through this work, we have shown that the reaction of $Co(acac)_2$ with a phosphine ligand is not as straightforward as one might have anticipated. It does not necessarily lead to the formation of $Co(acac)_2$(monophosphine)$_2$ or $Co(acac)_2$(diphosphine). In fact, the reaction outcome depends greatly on the phosphine structure. A monodentate phosphine may only weakly interact with $Co(acac)_2$ to form $Co_2(acac)_4$(monophosphine) reversibly, as demonstrated with $HPPh_2$. A diphosphine ligand can react with

Co(acac)$_2$ to give Co(acac)$_2$(diphosphine) as a 1D coordination polymer, provided that the diphosphine can act as a bridging ligand. In Co(acac)$_2$ clusters and the related acetylacetonate complexes, each cobalt center typically adopts an octahedral geometry. Our study of the ^{Cy}PN^{H} ligand system suggests that it is also possible to form a square pyramidal structure, in which the phosphorus atom binds to cobalt and the pyrrole moiety forms hydrogen bonds with the [acac]$^-$ ligands. These structural variations, besides being interesting in their own right, are expected to have profound impacts on organic reactions catalyzed by Co(acac)$_2$/phosphine, which are being further studied in our laboratory.

4. Experimental Section

General Consideration

Unless otherwise noted, all cobalt complexes described in this work were prepared and handled under an argon atmosphere using standard glovebox and Schlenk techniques. Dry and oxygen-free pentane was collected from an Innovative Technology solvent purification system and used throughout the experiments. Anhydrous and inhibitor-free THF (packed in a Sure/Seal bottle), HPPh$_2$, and PMe$_3$ were purchased from Sigma–Aldrich. 1,2-Bis(dicyclohexylphosphino)ethane (dcpe) was purchased from Strem. The other two diphosphine ligands, dppe and xantphos, were purchased from Ambeed. Anhydrous Co(acac)$_2$ was obtained from two different vendors: Sigma–Aldrich (97% and >99% purity) and Ambeed (96% purity). The source and purity of Co(acac)$_2$ had no effect on the reaction outcome. Tetrahydrofuran-*d*$_8$ (99.5% D), methylene chloride-*d*$_2$ (99.8% D), and toluene-*d*$_8$ (99.5% D) were purchased from Cambridge Isotope Laboratories, Inc. These commercial reagents were used as received without further purification. Benzene-*d*$_6$ (99.5% D) was dried over sodium–benzophenone and distilled under an argon atmosphere. 2-(Dicyclohexylphosphino)methyl-1*H*-pyrrole (^{Cy}PN^{H}) was prepared according to a literature procedure.[30] NMR spectra were recorded on a Bruker AV400, AV500, or NEO400 NMR spectrometer. Chemical shift values in ^{1}H NMR spectra were referenced internally to the residual solvent resonances. Infrared spectra were recorded on a PerkinElmer Spectrum Two FTIR spectrometer equipped with a smart orbit diamond attenuated total reflectance (ATR) accessory. ESI-MS data were acquired using a Thermo Scientific Q Exactive^{TM} mass spectrometer.

Synthesis of Co(acac)$_2$(dppe)

This compound was prepared following a procedure slightly different from those reported by Colborn[17a] and RajanBabu.[21] Under an argon atmosphere, Co(acac)$_2$ (257 mg, 1.00 mmol) was mixed with dppe (398 mg, 1.00 mmol) in anhydrous THF (6 mL) and stirred for 18 h, which resulted in a light pink suspension. The solvent was removed under vacuum, and the residue was washed with pentane (5 mL × 3) and then dried. The desired product was isolated as a light pink powder (536 mg, 82% yield). X-ray quality, pale pink block-shaped crystals were grown from the slow evaporation of a toluene solution at room temperature. ^{1}H NMR (400 MHz, THF-*d*$_8$, δ): 30.0 (br, $w_{1/2} = 316$ Hz, CH$_3$, 12 H), 7.43 (br, Ar*H*, 8 H), 7.13 (br, Ar*H*, 4 H), 6.93 (br, Ar*H*, 8 H), 2.65 (br, C*H*$_2$, 4 H); the C*H* resonance was not located. This compound showed no ^{31}P NMR signal. Selected ATR-IR data (solid, cm^{-1}): 3061, 2987, 2917, 1581, 1515, 1458, 1432, 1404, 1257, 1180, 1017, 924. ESI-MS of Co(acac)$_2$(dppe) diluted in CHCl$_3$–MeOH, *m/z* (relative intensity, ion): 399.1419 (8%, [dppe + H]$^+$), 414.9987 (34%, [Co$^{II}_2$(acac)$_3$]$^+$), 566.1116 (100%, [Co^{II}(acac)(dppe)]$^+$), 572.1061 (12%, [Co^{II}(acac)(dppe)+O]$^+$), 655.1559 (39%, [Co^{III}(acac)$_2$(dppe)]$^+$), 890.1704 (3%, [Co^{II}(dppe)$_2$Cl]$^+$), 954.2460 (12%, [Co^{II}(acac)(dppe)$_2$]$^+$). Anal. Calcd for C$_{36}$H$_{38}$O$_4$P$_2$Co: C, 65.96; H, 5.84. Found: C, 65.70; H, 5.87. The synthesis was repeated. Elemental analysis data for the second batch: C, 65.68; H, 5.72.

Synthesis of Co(acac)$_2$(^{Cy}PN^{H})

An equimolar mixture of Co(acac)$_2$ (129 mg, 0.50 mmol) and ^{Cy}PN^{H} (139 mg, 0.50 mmol) suspended in 10 mL of anhydrous THF was stirred under argon for 20 h, giving a dark purple-blue solution. Removal of the solvent under vacuum afforded a blue residue, which was washed with pentane (5 mL × 3) and then dried. The desired product was isolated as a blue powder (177 mg, 66% yield). X-ray quality, purple/blue-peach dichroic crystals were grown from THF-pentane at −30 °C. Due to the hygroscopic nature of Co(acac)$_2$(^{Cy}PN^{H}), the same sample also produced colorless-pale pink dichroic crystals, which proved to be *trans*-Co(acac)$_2$(H$_2$O)$_2$.[14] ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, δ): 87.96 (1 H), 67.36 (likely N*H*, 1 H, exchangeable with D$_2$O), 58.05 (1 H), 21.55 (1 H), 13.58 (CH$_3$, 12 H), 9.04 (1 H), 7.82 (2 H), 3.74 (2 H), 3.43 (1 H), 2.95 (1 H), 1.68 (1 H), 1.17 (2 H), −0.26 (2 H), −1.96 (2 H), −2.81 (2 H), −7.47 (2 H), −8.45 (2 H), −12.73 (2 H), −13.26 (2 H), −14.56 (2 H). This compound showed no ^{31}P NMR signal. Selected ATR-IR data (solid, cm^{-1}): 3339 (ν_{N-H}), 2929, 2850, 1580, 1518, 1401, 1353, 1264, 1194, 1120, 1017, 926, 851. ESI-MS of Co(acac)$_2$(^{Cy}PN^{H}) diluted in CHCl$_3$–MeOH, *m/z* (relative intensity, ion): 199.1609 (10%, [Cy$_2$PH + H]$^+$), 258.0295 (5%, [Co^{II}(acac)$_2$+H]$^+$), 278.2026 (100%, [^{Cy}PN^{H} + H]$^+$), 414.9990 (4%, [Co$^{II}_2$(acac)$_3$]$^+$), 435.1722 (21%, [Co^{II}(acac)(^{Cy}PN^{H})]$^+$), 451.1673 (7%, [Co^{II}(acac)(^{Cy}PN^{H})+O]$^+$), 534.2172 (10%, [Co^{III}(acac)$_2$(^{Cy}PN^{H})]$^+$), 712.3681 (3%, [Co^{II}(acac)(^{Cy}PN^{H})$_2$]$^+$), 728.3630 (8%, [Co^{II}(acac)(^{Cy}PN^{H})$_2$+O]$^+$), 744.3569 (4%, [Co^{II}(acac)(^{Cy}PN^{H})$_2$+2O]$^+$). Anal. Calcd for C$_{27}$H$_{42}$NO$_4$PCo: C, 60.67; H, 7.92; N, 2.62. Found: C, 60.67; H, 8.01; N, 2.50. The synthesis was repeated. Elemental analysis data for the second batch: C, 60.38; H, 8.05; N, 2.51.

X-ray Structure Determination

Intensity data were collected at 150 K on a Bruker APEX-II CCD diffractometer [for Co$_2$(acac)$_4$(HPPh$_2$) and Co(acac)$_2$(^{Cy}PN^{H})] or Bruker D8 Venture diffractometer [for Co(acac)$_2$(dppe)] using Mo Kα radiation, $\lambda = 0.71073$ Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections. The structure was solved by a combination of direct methods and the difference Fourier technique as implemented in the SHELX suite of programs and refined by full-matrix least squares on F^2 for reflections out to 0.80 Å [for Co$_2$(acac)$_4$(HPPh$_2$)] or 0.75 Å [for Co(acac)$_2$(dppe) and Co(acac)$_2$(^{Cy}PN^{H})] resolution. Nonhydrogen atoms were refined with anisotropic displacement parameters. The *N*- and *P*-bound H-atoms were located directly from the difference map, and their coordinates were refined. All remaining H-atoms were calculated and treated with a riding model. The H-atom isotropic displacement parameters were defined as a * U$_{eq}$ of the adjacent atom (a = 1.5 for CH$_3$ and 1.2 for all others). The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 2432808-2432810.[32]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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