Carbene Character in a Series of Neutral PC_{carbene}P Cobalt(I) Complexes – Radical Carbenes Versus Nucleophilic Carbenes

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ABSTRACT: Cobalt(I) complexes supported by a series of PC_{carbene}P pincer ligands of varying donicity, differing in the aryl group linking the phosphine arms with the anchoring carbon donor, are described. Addition of the proligands to cobalt bromide results in the formation of a series of cobalt(II) tetrahedral complexes, **L_n-1**, which serve as excellent precursors to the corresponding PC_{alkyl}P and PC_{carbene}P complexes. Square planar cobalt PC_{carbene}P complexes, **L2^R-3-X** (X = Cl, Br), are readily synthesized by addition of a bulky aryloxide radical to the corresponding PC_{alkyl}P complex, **L1-2-Br** or via addition of **L2^R** to ClCo(PPh₃)₃ in the presence of trityl radical or by addition of NaHBET₃ and trityl radical to isolated **L2^R-1**. For the **L2^{NMe2}** PC_{carbene}P complexes, salt metathesis reactions with either CsOH·H₂O, LiCH₂TMS, or LiNH₂ result in the corresponding hydroxo, alkyl, and amine complexes, **L2^{NMe2}-3-R** (R = OH, CH₂TMS, NH₂). Reaction of **L2^{NMe2}-3-OH** with benzoic acid affords the κ²-O₂CPh derivative. The nature of the carbene bond in either ligand platform as well as the effects of the X-type capping ligand on the Co=C bond are explored computationally and show that triplet structures are relatively more stable in for the less electron donating ligand **L1** while singlet Co(I) carbenes dominate for the more electron rich **L2** derivatives. For **L2^{NMe2}** complexes, the effect of the *trans* ligand X was also probed. Pi donors imbue the carbene with singlet character while the strongly σ donating alkyl derivative exhibits significant triplet character.

Introduction

Aryl linked PC_{carbene}P pincer ligands (Chart) are an intriguing family of pincer ligands because of the potential for ligand cooperativity involving the anchoring carbene carbon in the chemistry associated with the activation of various small molecules.¹ The first ligand of this type, **1**, incorporates relatively less basic -PPh₂ groups as the pincer arms and was reported some time ago by Roper *et al.* when they observed its serendipitous self-assembly in the coordination

sphere of the ruthenium complex $[\text{Ru}=\text{CBr}_2(\text{PPh}_3)_2(\text{CO})_2\text{Br}]^+[\text{BBr}_4]^-$ through sequential $\text{S}_{\text{E}}\text{Ar}$ reactions.² The modern era of the study of these ligands began in 2012 when our group intentionally prepared the more electron rich $-\text{P}(\text{iPr})_2$ substituted version **II** (Chart) and explored its chemistry with group 9 and 10 metals (Ir,³⁻⁵ Rh,^{6, 7} Ni,⁸⁻¹⁰ Pt¹¹). In addition, Young et al. have utilized the original ligand **I** for a number of studies involving Rh¹²⁻¹⁴ and the first-row congeners based on Co^{15, 16} while Iluc *et al.* have used **II** to elaborate the Pd chemistry of these $\text{PC}_{\text{carbene}}\text{P}$ ligand systems.¹⁷⁻¹⁹

While these extensive studies have uncovered a multitude of reactions in which the carbene carbon is actively involved, the ligands **I** and **II** exhibit some limitations due to the flexibility and puckering engendered through steric interactions between the aryl C-H bonds *ortho* to the carbene carbon (Chart). For example, side reactions involving $\text{C}_{\text{carbene}}-\text{C}_{\text{ipso}}$ bond cleavage or oxidation of the phosphine arms can breach the integrity of the ligand structure.^{5, 20} We envisioned that further rigidification and/or electronic modification could suppress these processes and therefore prepared ligands with less sterically bulky linker arms (benzothiophene linked ligand **L1**,²¹ Chart) or with phenyl arms linked in the position *ortho* to the carbene carbon by a dimethyl methylene bridge as in ligands **L2^H** and **L2^{NMe2}**.^{20, 22} The latter ligands are planarized and more rigid by incorporation of this structural feature, and the NMe_2 groups *para* to the carbene carbon in **L2^{NMe2}** further boosts the overall electron donating ability of the ligand. The benzothiophene ligand **L1** is less donating,⁷ but is more planar than ligands **I** and **II**, since the smaller ring size of the linking group widens the $\text{C}_{\text{ipso}}-\text{C}_{\text{carbene}}-\text{C}_{\text{ipso}}$ bond angle enough to relieve the steric interactions that are present in ligands **I** and **II**.

Chart 1. $\text{PC}_{\text{carbene}}\text{P}$ Metal Complexes.

What becomes apparent when collectively considering these studies is that the character of the anchoring carbene is highly dependent on the nature and oxidation state of the metal as well as the structure and substitution of the aryl linker. The carbene carbon can variously behave as a nucleophile, a radical, or an electrophile, which modifies the way in which the cooperativity engendered by the carbene manifests itself in the context of stoichiometric or catalytic reactivity with small molecules. Since the structural rigidity and immunity to *beta*-hydrogen elimination processes afforded by the aryl linkers tends to focus any cooperativity on the

anchoring carbene carbon, understanding the factors that dictate the electronic character of this locus is important for harnessing this ligand feature for useful chemistry.

With this in mind, we have used the ligands **L1** and **L2^R** (R = H, NMe₂) to prepare a series of cobalt PC_{carbene}P complexes of general formula (Ln)Co-X. Using spectroscopic data and computational studies, we assess the nature of the carbene in these systems as a function both the PCP ligand structure and, in the series of complexes supported by the most electron rich ligand **L2^{NMe2}**, the nature of X.

Results and Discussion

Ligands **L1** and **L2^R** were prepared as described previously²⁰⁻²² and reacted with CoBr₂ in THF at 60°C, smoothly affording the paramagnetic tetrahedral Co(II) complexes **Ln-1**, which were isolated as blue/green solids in moderate to high yields (Scheme 1). These compounds feature

Scheme 1. Synthesis of Tetrahedral PCP Cobalt(II) Dibromides, Ln-1.

Two distinctive peaks in the UV-vis spectra at approximately 680 and 750 nm, consistent with other tetrahedral cobalt(II) high spin complexes.²³ As paramagnetic compounds, NMR spectroscopy gives rise to broad, paramagnetically shifted spectra that provide spectral fingerprints but little other information. Magnetic moments measured using the Evans method give values of 4.491 (**L1-1**), 4.474 (**L2^H-1**) and 4.158 (**L2^{NMe2}-1**) μ_B , consistent with an $S = 3/2$ electron configuration; the values are somewhat higher than the expected spin only values due to strong spin orbit coupling effects in tetrahedral Co(II) compounds.^{23, 24} The bulk purity of the compounds was established by elemental analyses and the structures of the molecules confirmed by X-ray crystal structure analyses. Figure 1 shows the structure of **L2^{NMe2}-1** while those of **L1-1** and **L2^H-1** are shown in Figure S1. The compounds have C_s symmetry with large P-Co-P angles of 119.98(3)° for **L1-1**, and 123.01(3)° and 124.4(6)° for the two **L2^R** supported compounds, enforced by the large bite angles of these ligands in their chelating, bidentate mode of bonding.

These tetrahedral cobalt(II) compounds serve as excellent precursors to PC_{alkyl}P and PC_{carbene}P complexes. For example, PC_{alkyl}P cobalt(II) complex, **L1-2-Br**, is readily synthesized following

Figure 1. ORTEP illustration of **L2^{NMe2}-1**, with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms and co-crystallized solvent has been omitted for clarity). Select bond distances (Å) and angles (°): Co1-Br1, 2.3752(13); Co1-Br2, 2.3445(12); Co1-P1, 2.4273(17); Co1-P2, 2.4487(17); Co1-H1A, 3.376; Co1-H1B, 2.2016; Br1-Co1-P1, 106.83(5); Br1-Co1-P2, 107.45(6); Br2-Co1-P1, 101.58(5); Br2-Co1-P2, 106.92(5); P1-Co1-P2, 122.16(6).

addition of KHMDS to a solution of **L1-1** in THF at room temperature yielding a paramagnetic brown powder in 54% yield (Scheme 2). Alternatively, KHMDS can be added to a solution of **L1** in THF with later addition of CoBr₂ after stirring for 5h at room temperature with similar overall yields (~ 86%) in comparison to the two-step process wherein **L1-1** is isolated. Complex **L1-2-Br** is red in color and features a distinctive peak in the UV-visible spectrum at 510 nm, indicative of a geometry change from tetrahedral to square planar.²³ The ¹H NMR spectrum is broad and provides little information concerning structure of the complex, but the magnetic moment

Scheme 2. Synthesis of L1 PC_{alkyl}P and PC_{carbene}P Bromides.

Figure 2. ORTEP illustration of **L1-3-Br**, with thermal ellipsoids drawn at the 50% probability level (select hydrogen atoms have been omitted for clarity). Select bond distances (Å) and angles (°): Co1-Br1, 2.3530(5); Co1-C1, 1.867(3); Co1-P1, 2.1945(9); Co1-P2, 2.2037(9); C1-Co1-Br1, 175.0(1); P1-Co1-Br1, 92.40(3); P1-Co1-P2, 173.86(4); P2-Co1-Br1, 93.27(3).

of the complex is 2.187 μB which implies an $S = 1/2$ ground state, consistent with a low spin d^7 complex.²⁴ Bulk purity was established by elemental analysis and an X-ray crystallographic structure determination (Figure S2) revealed a slightly distorted square-planar geometry at the cobalt center. The Co–C1 distance of 1.963 Å is comparable to square planar $\text{PC}_{\text{aryl}}\text{P}$ cobalt(II) complexes (1.91–1.95 Å) prepared by Kirchner *et al.*²⁵ as well as previously synthesized $\text{PC}_{\text{sp}^3}\text{P}$ nickel (II) bromide featuring **L1** (1.965(7) Å).²⁰

$\text{PC}_{\text{alkyl}}\text{P}$ -ligated cobalt bromide **L1-2-Br** can undergo hydrogen atom abstraction as shown in Scheme 2 by treatment with the stable 2,4,6-tri-*tert*-butylphenoxy radical ($\text{ArO}^\bullet$) in THF. This furnished the anticipated product, a Co(I) $\text{PC}_{\text{carbene}}\text{P}$ **L1-3-Br** as indicated by ligand resonances in the ^1H NMR spectrum indicative of C_{2v} symmetry, and the appearance of a broad signal at 180.58 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum corresponding to the carbene carbon at the ligand anchor point. However, broadness in the spectrum, a paramagnetically shifted $^{31}\text{P}\{^1\text{H}\}$ NMR peak at -76.50 ppm alongside a magnetic moment of 0.992 μB indicate a significant contribution from the triplet Co(II) PCP structure, an observation corroborated DFT computations that show a small singlet-triplet gap for this compound (see below). Accordingly, a signal in the EPR spectrum (THF, 156 K, Figure S4) is observed and exhibits a g value of ≈ 2.00 , consistent with an organic centered radical.^{17, 26} The structure was determined via X-ray crystallography (Figure 2) and the cobalt center exhibits a C_{2v} square-planar geometry, with the aryl groups of the ligand backbone becoming more planar compared to $\text{PC}_{\text{alkyl}}\text{P}$ **L1-2-Br**. The Co(1)–C(1) bond distance of 1.867(3) Å is more than 0.1 Å shorter than the saturated analogue but is comparable to previously reported cobalt carbenes (1.8–1.9 Å).^{15, 27}

Two ligand attachment protocols were employed for the linked ligands **L2^R** ($\text{R} = \text{H}, \text{NMe}_2$), one leading to bromides **L2^R-3-Br** (method A, Scheme 3) and the other to the analogous chlorides **L2^R-3-Cl** (method B). In the first protocol, the tetrahedral dibromides **L2^R-1** were treated with NaHBET_3 in the presence of Gomberg's dimer, a source of the triphenylmethane radical.

Although not studied in detail, it is likely that the borohydride reduces the Co(II) starting material to a Co(I) intermediate with release of H₂ (detected by ¹H NMR spectroscopy), **Scheme 3. Synthesis of Square Planar PC_{carbene}P Cobalt(I) Halides, L^{2R}-3-X (R = H, NMe₂; X = Br, Cl).**

triggering a C-H oxidative addition to a Co(III) hydride, which loses further dihydrogen.²⁸ This forms the Co(II) PC_{alkyl}P intermediates **L^{2R}-2-Br**, which in the case of R = H was detected by ³¹P NMR spectroscopy in reactions monitored by this technique (**L^{2H}-2-Br**, 68.4 ppm, Figure S19); indeed, crystals obtained from incomplete reaction mixtures confirmed the intermediacy of this species (Figure S2) The radical then abstracts the remaining dibenzylic hydrogen atom from the ligand and the diamagnetic PC_{carbene}P Co(I) bromides are formed in reasonable yields.

The second protocol begins with the commercially available Co(I) starting material ClCo(PPh₃)₃ and free ligands **L^{2R}**; heating to 80°C in toluene leads directly to the products **L^{2R}-3-Cl** in good to excellent yields (Scheme 3B). In the case of **L^{2H}**, addition of Gomberg's dimer is required to push the reaction to full conversion. Again, a PC_{alkyl}P intermediate **L^{2H}-2-Cl** was detectable and characterized by both ³¹P NMR spectroscopy (68.4 ppm) and X-ray crystallography (Figure S2), suggesting that C-H oxidative addition followed by loss of H• (H₂) is the principal pathway for product formation. Evidently, in the case of the more electron rich ligand **L^{2NMe2}**, these PC_{alkyl}P intermediates are too fleeting to observe in solution. Attempts to generate these intermediates through addition of H₂ to the PC_{carbene}P compounds were unsuccessful; these reactions led to decomposition of the products of H₂ addition.

These four PC_{carbene}P compounds were fully characterized and exhibit the expected C_{2v} square planar structures. The carbene carbon resonances are triplets at 173-175 ppm for **L^{2H}-3-X** and 161-162 ppm for the more electron rich **L^{2NMe2}-3-X** derivatives. X-ray-quality crystals of **L^{2R}-3-Br** (R = H, NMe₂, Figure 3) and **L^{2NMe2}-3-Cl** (Figure S3) were obtained via slow diffusion of pentane into a saturated THF solution at -30 °C. Complexes **L^{2H}-3-Br** and **L^{2NMe2}-3-Br** assume a nearly ideal square-planar geometry illustrating the ability of **L^{2R}** to rigidify the PC_{carbene}P pincer system. The Co1–C1 bond lengths in **L^{2H}-3-Br** (1.8493(13) Å) and **L^{2NMe2}-3-Br** (1.866(3)) Å are shorter than the PC_{alkyl}P Co1–C1 bond in **L^{2H}-2-Br** (≈1.916 Å, disordered) and comparable to Young's cationic cobalt carbene, in which the Co=C bond length is 1.892(3) Å.¹⁵

We used DFT calculations to characterize the electronic structure and Co=C bonding in these halide complexes. As expected, DFT methods accurately replicate the key X-ray structure

Figure 3. ORTEP illustration of a side view of **L2^H-3-Br** (top) and **L2^{NMe2}-3-Br** (bottom). Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (°) **L2^H-3-Br**: Co1-Br1, 2.3707(4); Co1-C1, 1.8493(13); Co1-P1, 2.2056(4); Co1-P2, 2.1866(4); C1-Co1-Br1, 169.46(4); P1-Co1-Br1, 96.840(12); P1-Co1-P2, 168.843(16); P2-Co1-Br1, 92.790(12). **L2^{NMe2}-3-Br**: Co1-Br1, 2.3922(4); Co1-C1, 1.866(3); Co1-P1, 2.1857(7); Co1-P2, 2.1800(7); C13-Co1-Br1, 170.40(10); P1-Co1-Br1, 96.21(2); P1-Co1-P2, 166.44(3); P2-Co1-Br1, 94.70(2).

distances in these complexes (see SI). However, the calculated singlet-triplet gaps are sensitive to the functional. We used B3LYP* and HLE16 since these functionals are expected to perform well for first-row transition metals and their spin-state energies. For **L1-3-Br** the singlet-triplet energy gap is 7.8 kcal mol⁻¹ (positive value is a lower energy triplet) with the HLE16 functional and 13.5 kcal mol⁻¹ with the B3LYP* functional. This indicates that the dominate form, consistent with the experimental paramagnetically shifted NMR peak and magnetic moment, is the Co^{II} complex with a radical L1.

The L2 ligand compared to the L1 ligand reduces the singlet-triplet gap. For **L2^H-3-Br** HLE16 gives a singlet-triplet gap value of 3.0 kcal mol⁻¹ while for the more electron donating **L2^{NMe2}-3-Br**, the gap value is -4.8, which indicates a lower energy singlet spin state. Therefore, incorporation of the NMe₂ donor provides an inversion of the spin state and favors the diamagnetic Co(I) formulation of the complex. The chloro version of **L2^{NMe2}-3** has a similar singlet-triplet triplet gap of -4.4 kcal mol⁻¹; nonetheless, the nature of the X ligand *trans* to the pincer carbon donor does have an influence on the singlet-triplet gap (see below). It is instructive to note that while B3LYP* is generally reliable for the relative spin state energies, this functional predicts that the triplet state is lower in energy for both **L2^{NMe2}-3-Br** and **L2^{NMe2}-3-Cl**, in contradiction to experimental observations.

Figure 4. Top) LUMO of **L2^{NMe2}-3-Br**, composed of the 3d_{z2} orbital of the cobalt metal center. Bottom) HOMO of **L2^{NMe2}-3-Br**, composed of the anti-bonding π orbital between the 3d_{xz} and the π -system of the ligand manifold. Hydrogens have been omitted for clarity.

The singlet-triplet gap sensitivity to the ligand and H versus NMe₂ group can be understood by inspection of the frontier orbitals that significantly determine the gap energy. Figure 4 shows the HOMO and LUMO orbitals of the singlet **L2^{NMe2}-3-Br** system. The **L2^{NMe2}-3-Br** structure has a HOMO-LUMO gap of 0.94 eV. The HOMO is composed of a d _{π} -p antibonding combination for the Co=C. The LUMO is the 3d_{z2} of the cobalt. In the triplet state the unpairing of the HOMO orbital leads to a single electron localizing on the Co metal center and leaving a single electron that is shared between the Co and carbon centers, which provides radical like contribution to the ligand. We also calculated the singlet-triplet gaps for the “free” ligands L1, L2^H, and L2^{NMe2}, which also gives insight to Fischer-like versus Schrock-like carbene bonding. Consistent with the change in singlet-triplet gaps of the complexes, L1 and L2^H ligands (without Co) have a triplet ground state and L2^{NMe2} has a singlet ground state.

Figure 4. Synthesis of **L2^{NMe2}-3-X** (X = OH, CH₂TMS, NH₂) by salt metathesis and **L2^{NMe2}-3-OOCPh** by reaction of **L2^{NMe2}-3-OH** with benzoic acid. For the X-ray structures shown, thermal ellipsoids are shown at the 50% probability level. Selected bond distances (Å) and angles (°) for **L2^{NMe2}-3-OH**: Co1-O1, 1.870(2); Co1-C1, 1.858(3); Co1-P1, 2.1812(9); Co1-P2, 2.1760(9); C1-Co1-O1, 175.98(14); P1-Co1-O1, 92.57(9); P1-Co1-P2, 170.78(4); P2-Co1-O1, 96.61(9). **L2^{NMe2}-3-CH₂TMS**: Co1-C2, 2.051(4); Co1-C1, 1.880(4); Co1-P1, 2.1785(12); Co1-P2, 2.1742(12); C2-Si1, 1.847(4); C1-Co1-C2, 169.84(16); P1-Co1-C2, 95.54(12); P1-Co1-P2, 167.98(5); P2-Co1-C2, 96.39(12); Co1-C2-Si1, 127.4(2). **L2^{NMe2}-3-NH₂**: Co1-Cl1, 2.260(4); Co1-N3, 1.807(8); Co1-C1, 1.852(2); Co1-P1, 2.1656(5); Co1-P2, 2.1740(6); C1-Co1-Cl1, 174.4(1); C1-Co1-N3, 173.1(2); P1-Co1-N3, 95.3(2); P1-Co1-P2, 170.76(3); P2-Co1-N3, 93.9(2). **L2^{NMe2}-3-OOCPh**: Co1-C1, 1.8456(18); Co1-O1, 2.1485(15); Co1-O2, 2.1609(15); Co1-P1, 2.1854(8); Co1-P2, 2.1922(7); C1-Co1-O1, 153.47(7); C1-Co1-O2, 145.54(7); P1-Co1-O1, 92.26(4); P1-Co1-O2, 97.50(5); P2-Co1-O1, 93.10(4); P2-Co1-O2, 93.65(5); O1-Co1-O2, 60.97(5); P1-Co1-P2, 168.84(2); P1-Co1-C1, 85.49(6); P2-Co1-C1, 85.35(6).

In order to probe the effect of the non-pincer X donor on the carbene character and bonding, a series of compounds based on the most electron rich **L2^{NMe2}** ligand framework were synthesized; this chemistry is summarized in Figure 5. Salt metathesis reactions between **L2^{NMe2}-3-Cl** and $\text{CsOH} \cdot \text{H}_2\text{O}$, $\text{LiCH}_2\text{SiMe}_3$ or LiNH_2 afforded the complexes **L2^{NMe2}-3-X** (X = OH, CH₂SiMe₃ and NH₂). The hydroxo derivative **L2^{NMe2}-3-OH** was treated with one equivalent of benzoic acid to access the κ^2 carboxylate compound **L2^{NMe2}-3-OOCPh**. All of these compounds were fully characterized, and the selected spectroscopic data are given in the Figure, as well as ORTEP depictions of their molecular structures. In this **L2^{NMe2}-3-X** series, a variety of p donor (X = Cl, Br, OH, NH₂), s donor (CH₂SiMe₃) and bidentate (κ^2 OOCPh) ligands in the position *trans* to the carbene carbon of the PC_{carbene}P pincer ligand are featured. While several examples of monomeric or bridging cobalt(II/III) hydroxide complexes are known,²⁹⁻³³ cobalt(I) hydroxide

complexes are rare. Despite the difference in the cobalt oxidation state, the Co1-O1 bond distance of **L2^{NMe2}-3-OH** (1.870(2) Å) is comparable to the monomeric Co(II) Co-OH complex TpCoOH (1.859(3) Å).²⁹

Synthesis of the alkyl derivative **L2^{NMe2}-3-CH₂SiMe₃** was similarly straightforward; the key NMR parameters for this compound are distinct from the others in that that carbene carbon appears about 5 ppm downfield of the others at 165.56 ppm, while the ³¹P signature is the most upfield of the series at 35.53 ppm. The methylene cobalt bond (Co1-C2) is 2.053(5) Å, comparable to related PNP cobalt(II) trimethyl silyl pincer complexes (2.005(3) Å).³⁴ The production of **L2^{NMe2}-3-NH₂** was somewhat more problematic synthetically due to the reversibility of the salt metathesis reaction between **L2^{NMe2}-3-Cl** and LiNH₂. No reaction occurred in non-coordinating solvents such as toluene. Nevertheless, spectroscopic data for the amido product was obtainable, and analysis of single crystals grown from worked up solutions of the reaction allowed for extraction of metrical parameters for **L2^{NMe2}-3-NH₂**. The amido derivative co-crystallized with **L2^{NMe2}-3-Cl** and exhibits positional disorder in the X position which is modeled with an occupancy for Cl of 0.392(5) and NH₂ 0.608(5); details of how this structure was refined can be found in the SI (Figure S25). The Co1-C1 distance in **L2^{NMe2}-3-NH₂** is 1.852 (2) Å, comparable to the other carbene complexes. The Co1-Cl1 bond distance [2.260(4) Å] remains consistent with **L2^{NMe2}-3-Cl** while the Co1-N3 bond is 1.807(6) Å, shortened in comparison to those in Co amido complexes of sterically more bulky amido ligands (1.88 – 2.1 Å³⁵⁻³⁸).

As anticipated based on the NMR characterization, the HLE16 calculated singlet-triplet gaps for the **L2^{NMe2}-3-NH₂**, **L2^{NMe2}-3-OH**, and **L2^{NMe2}-3-OOCPh** all show ground state singlets with a gap between -4 to -8 and kcal mol⁻¹. Surprisingly, for the **L2^{NMe2}-3-CH₂SiMe₃** structure, only the HLE16 functional predicted a singlet ground state, and only by 0.1 kcal mol⁻¹. All other functionals tested gave singlet-triplet values between 3-7 kcal mol⁻¹ favoring the triplet. These observations indicate that when X is a p donor, the singlet is stabilized relative to the triplet. In the strongly σ donating alkyl example, the triplet becomes accessible; indeed a strong signal is observable in the EPR spectrum of **L2^{NMe2}-3-CH₂SiMe₃** and the Co1-C1 distance in **L2^{NMe2}-3-CH₂SiMe₃** is 1.880(4)Å, and is the longest such bond in this series, consistent with significant contribution from the triplet in which this bond should assume somewhat more single bond character relative to the singlet.

Conclusions

Synthetic routes to a variety of PC_{carbene}P cobalt complexes are reported. Chlorido and bromo derivatives of three pincer ligands that range from poorly donating (**L1**) to more electron rich (**L2^{H/NMe2}**) show that the resulting cobalt complexes have varying singlet-triplet gaps, with singlets being favored for the more electron rich ligands and the triplet being lower in energy for the less electron donating benzothiophene-based pincer. Further studies on a variety of **L2^{NMe2}-3-X** derivatives show that the nature of the X ligand can also strongly affect the relative stabilities of the singlet vs the triplet. For p donor ligands, the singlet is favored but strong s donors bring the triplet down in energy such that it contributes significantly to the ground state structure. Together these observations have implications for the reactivity of these compounds

because of the variable radical character of the anchoring pincer ligand carbon as a function of the ligand's bridging units and/or X group and offer another lever for tuning the properties of this family of compounds.

Experimental Section

General Considerations: Storage and manipulation of all compounds were performed under an argon atmosphere either in an IT glove box or using a double manifold high vacuum line using standard techniques. Passage of argon through an OxisorBW scrubber (Matheson Gas Products) removed any residual oxygen and moisture. Toluene, hexanes, pentane and tetrahydrofuran were dried and purified using a Grubbs/Dow solvent purification system and stored in 500 mL thick-walled glass vessels over sodium/benzophenone ketal and distilled under reduced pressure. C₆D₆ was dried over sodium/benzophenone ketal. All dried solvents were degassed, and vacuum distilled prior to use. ¹H and ¹³C NMR spectrometry chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant ¹³C resonances for all deuterated solvents. Chemical shift assignments are based on ¹H, ¹³C{¹H}, ³¹P{¹H}, ¹H-¹³C-HSQC and ¹H-¹³C-HMBC NMR experiments performed on Ascend-500 or Avance-600 MHz spectrometers. UV-Vis absorption spectra were collected using an Agilent Technologies Cary 60 spectrophotometer. IR spectra were collected using a Thermo-Nicolet Nexus 470 spectrophotometer. L1,²¹ L2^H,²⁰ L2^{NMe2},²² 2,4,6-tri-*tert*-butylphenoxy radical,³⁹ and Gomberg's dimer⁴⁰ were prepared per literature procedures. All other reagents were purchased from Sigma-Aldrich and used as received. All elemental and high-resolution mass spectrometry analyses were obtained by the Instrumentation Facility of the Department of Chemistry, University of Calgary. Diffraction patterns were collected with Cu K α radiation on a Bruker Smart diffractometer equipped with Apex II detector, fixed-CHI goniometer, and sealed-tube (Cu) source or with Mo K α radiation on a Nonius Kappa CCD diffractometer.

Synthesis of PCP^{Benzothiophene}Co(II)Br₂ (L1-1): A 50 mL thick-walled reaction vessel was charged with L1 (0.526 g, 1.026 mmol) and CoBr₂ (0.226 g, 1.033 mmol) and dissolved in 10 mL of THF. The reaction solution was heated at 60 °C over 48h. Solvent was removed in vacuo and replaced with 10 mL of toluene. The solution was filtered through a 0.1 μ m PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. Solvent was removed in vacuo and the resulting residue triturated with 5 mL pentane and dried to yield a teal powder (0.425 g, 0.581 mmol, 57%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal toluene and pentane and cooling the system at -30 °C for 3 days. ³¹P{¹H} NMR (203 MHz, benzene-*d*₆) δ silent. ¹H NMR (500 MHz, Benzene-*d*₆) δ 13.40 (d, *J* = 6.7 Hz, 1H), 5.87 (s, 1H), 1.86 (s, 24H, CH(CH₃)₂), 0.30 (s, 1H). ¹³C NMR (126 MHz, Benzene-*d*₆) δ 124.49, 110.39, 80.56 (br). UV-vis (THF) λ_{max} , nm: 681.01, 748.01. μ_{eff} (Benzene-*d*₆): 4.419 μ_B . HRMS (APCI) Calcd: 730.9563, Found: 730.9588. Elemental analysis: Calcd (%): C, 47.62; H, 5.24. Found: C, 46.72; H, 5.25.

Synthesis of PCP^{Linked}Co(II)Br₂ (L2^H-1): In a 50 mL thick-walled vessel L2^H (0.204 g, 0.463 mmol) and CoBr₂ (0.101 g, 0.462 mmol) was dissolved in 20 mL of THF. The reaction mixture was heated at 60 °C for 48h. Solvent was removed in vacuo and replaced with 10 mL of toluene. The solution was filtered through a 0.1 μ m PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. The resulting powder was triturated with 5 mL of pentane and dried

under high vacuum to yield a pale blue powder (0.286 g, 0.434 mmol, 94%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal toluene and pentane and cooling the system at $-30\text{ }^{\circ}\text{C}$ for 3 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, benzene- d_6) δ silent. ^1H NMR (500 MHz, Benzene- d_6) δ 22.23 (s, 2H, CH_2), 10.22 (s, 12H, $\text{CH}(\text{CH}_3)_2$), 7.94 (s, 2H, Ar-H), 6.73 (s, 2H, Ar-H), 5.97 (s, 2H, Ar-H), 2.16 (s, 4H, $\text{CH}(\text{CH}_3)_2$), 0.12 (d, $J = 135.8\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), -0.35 (s, 6H, CH_3). ^{13}C NMR (126 MHz, Benzene- d_6) δ 260.29, 217.27 (d, $J = 66.9\text{ Hz}$), 212.88, 156.45, 154.40, 82.12, 30.98, 21.18, 18.93, 1.25. UV-vis (THF) λ_{max} , nm: 678.99, 761.02. μ_{eff} (Benzene- d_6): 4.474 μ_{B} . HRMS (APCI) Calcd: 578.1272 Found: 578.1279. Elemental analysis: Calcd (%): C, 51.01; H, 6.42. Found: C, 50.82; H, 6.63.

Synthesis of $\text{PCP}^{\text{NMe}_2}\text{Co(II)Br}_2$ (L2^{NMe_2} -1): A 50 mL thick-walled vessel was charged with L^{NMe_2} (0.500 g, 0.949 mmol), CoBr_2 (0.198 g, 0.905 mmol) and 20 mL of THF. The reaction solution was heated at $60\text{ }^{\circ}\text{C}$ over 18h. Solvent was removed in vacuo and the resulting residue taken up in 5 mL of toluene. The solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. The resulting powder was triturated with 2 mL of pentane and dried under high vac to yield a dark blue powder (0.619 g, 0.830 mmol, 92%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal toluene and pentane and cooling the system at $-30\text{ }^{\circ}\text{C}$ for 3 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, benzene- d_6) δ silent. ^1H NMR (500 MHz, Benzene- d_6) δ 12.54 (s, 2H, Ar-H), 10.56 (s, 12H, $\text{CH}(\text{CH}_3)_2$), 3.79 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.89 – 1.38 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 0.57 – -0.05 (m, 4H, $\text{CH}(\text{CH}_3)_2$), -0.26 (s, 6H, CH_3). ^{13}C NMR (126 MHz, Benzene- d_6) δ 260.84, 235.70, 146.33, 69.82, 42.72, 29.73, 21.23, 0.89. UV-vis (THF) λ_{max} , nm: 678.01, 752.99. μ_{eff} (Benzene- d_6): 4.158 μ_{B} . HRMS (APCI) Calcd: 745.1377 Found: 745.1377. Elemental analysis: Calcd (%): C, 51.56; H, 7.03; N, 3.76. Found: C, 51.08; H, 7.28; N, 3.55.

Synthesis of $\text{PCP}^{\text{Benzothiophene}}\text{Co(II)Br}$ (L1-2-Br): A 50 mL thick-walled reaction vessel was charged with L1 (0.252 g, 0.492 mmol), KHMDS (0.100 g, 0.501 mmol), and 5 mL of THF. The reaction mixture was stirred over 48h before adding CoBr_2 (0.109 g, 0.498 mmol) alongside an additional 5 mL of THF. The reaction was heated at $60\text{ }^{\circ}\text{C}$ for 18h. Volatiles were removed under vacuum and replaced with 5 mL of toluene. The toluene solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. The resulting residue was triturated with 5 x 2 mL pentane and dried under vacuum to yield a red-brown powder (0.274 g, 0.421 mmol, 86%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal toluene and pentane and cooling the system at $-30\text{ }^{\circ}\text{C}$ for 3 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, benzene- d_6) δ silent. ^1H NMR (500 MHz, Toluene- d_8) δ 52.19 (br. s, 1H, CH) 52.19 (br. s, 1H, CH), 40.48 (br. s, 2H, Ar-H), 26.37 (br. s, 12H, $\text{CH}(\text{CH}_3)_2$), 16.68 (s, 2H, Ar-H), 10.19 (s, 2H, Ar-H), 9.36 (br. s, 4H, $\text{CH}(\text{CH}_3)_2$), 4.21 (s, 2H, Ar-H), -0.90 (br. s, 12H, $\text{CH}(\text{CH}_3)_2$). UV-vis (THF) λ_{max} , nm: 510.98. μ_{eff} (Benzene- d_6): 2.187 μ_{B} . HRMS (APCI) Calcd: 570.11. Found: 570.11 ($\text{M}^+ - \text{Br}$). Elemental analysis: Calcd. (%): C, 53.5; H, 5.73; N: 0.00. Found: C, 53.44; H, 5.73; N, 0.04.

Synthesis of $\text{PC-P}^{\text{Benzothiophene}}\text{Co(II)Br}$ (L1-3-Br): To a 50 mL round bottom flask was added L1-2-Br (0.203 g, 0.312 mmol) and dissolved in 5 mL of THF. A solution of 2,4,6-tri-*tert*-butylphenoxy radical (0.083 g, 0.317 mmol) in 5 mL of THF was added dropwise to the reaction solution and allowed to stir for 22h. Solvent was removed in vacuo and the resulting residue washed with 5 mL of pentane and dried under vacuum. Residual 2,4,6-tri-*tert*-butylphenol was removed via sublimation at $65\text{ }^{\circ}\text{C}$ under dynamic vacuum to yield a red-brown powder (0.175 g, 0.269 mmol,

86%). Crystals suitable for analysis by single-crystal XRD studies were grown by layering minimal THF with pentane and cooling the system at $-30\text{ }^{\circ}\text{C}$ for 5 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, Benzene- d_6) δ -76.50. ^1H NMR (500 MHz, Benzene- d_6) δ 11.59 (d, J = 8.2 Hz, 2H, Ar-H), 9.73 (t, J = 7.8 Hz, 2H, Ar-H), 6.96 (s, 2H, Ar-H), 5.99 (d, J = 8.0 Hz, 2H, Ar-H), 5.75 (p, J = 7.6, 7.1 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 2.38 (d, J = 7.1 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.10 (d, J = 7.2 Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, Benzene- d_6) δ 180.58 (s, Co=C), 154.56 (s, Ar-C), 152.97 (s, Ar-C), 149.40 (s, Ar-C), 131.74 (s, Ar-CH), 130.99 (s, Ar-CH), 129.76 (Ar-CH), 127.43 (Ar-CH), 24.74 (s, $\text{CH}(\text{CH}_3)_2$), 22.31 (s, $\text{CH}(\text{CH}_3)_2$), 21.07 (s, $\text{CH}(\text{CH}_3)_2$). μ_{eff} (Benzene- d_6): 0.992 μ_{B} . HRMS (APCI) Calcd: 648.0255. Found: 648.0267.

Alternative Synthesis of $\text{PCP}^{\text{Benzothiophene}}\text{Co(II)Br}$ (L1-3-Br): To a 50 mL round bottom flask was added L1-2-Br (0.100 g, 0.154 mmol) and TEMPO (0.025 g, 0.160 mmol) and dissolved in 10 mL THF. The solution was stirred for 18h at room temperature before solvent was removed in vacuo and the resulting residue triturated with 10 mL of pentane and dried. Residual TEMPO-H was removed via sublimation at $60\text{ }^{\circ}\text{C}$ under static vacuum to yield a bright red powder (0.057 g, 0.088 mmol, 57%). The solid can be further purified via recrystallization following slow vapour diffusion of equal amounts of THF and pentane over 5 days.

Synthesis of $\text{PCP}^{\text{Linked}}\text{Co(I)Cl}$ (L2^H-3-Cl): To a 50 mL thick-walled reaction vessel was added $\text{ClCo}(\text{PPh}_3)_3$ (0.197 g, 0.224 mmol), Gomberg's Dimer (0.109 g, 0.224 mmol), and L2^H (0.102 g, 0.232 mmol). The solids were dissolved in *ca.* 10 mL of toluene and heated at $80\text{ }^{\circ}\text{C}$ over 18h. Volatiles were removed in vacuo and the resulting residue triturated with 2 x 5 mL pentane. The resulting solid was sonicated in 5 mL pentane and the suspension filtered through a 2 mL fine filter frit. Residual triphenylmethane was removed via sublimation at $80\text{ }^{\circ}\text{C}$ under dynamic vacuum to yield a red powder (0.114 g, 0.214 mmol, 92 %). ^{31}P NMR (203 MHz, Benzene- d_6) δ 32.83. ^1H NMR (500 MHz, Benzene- d_6) δ 9.05 (tt, J = 7.6, 1.9 Hz, 2H, Ar-H), 7.18 (m, 2H, Ar-H), 5.65 (dd, J = 7.9, 1.1 Hz, 2H, Ar-H), 4.23 (dt, J = 10.9, 7.3, 3.6 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.74 (qd, J = 7.1, 4.9 Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.09 (s, 6H, $\text{C}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, Benzene- d_6) δ 174.61 – 173.53 (m, Co=C), 137.45 (s, Ar-CH), 136.79 (s, Ar-CH), 135.92 (t, J = 5.5 Hz, Ar-C), 134.21 (d, J = 19.5 Hz, Ar-C), 132.27 (t, J = 15.1 Hz, Ar-C), 124.87 (s, Ar-CH), 47.86 (s, $\text{C}(\text{CH}_3)_2$), 24.13 (t, J = 9.7 Hz, $\text{CH}(\text{CH}_3)_2$), 21.00 – 20.70 (m, $\text{CH}(\text{CH}_3)_2$), 19.60 (s, $\text{CH}(\text{CH}_3)_2$), 14.74 (s, $\text{C}(\text{CH}_3)_2$). HRMS (APCI) (M+H)⁺ Calcd: 533.1699. Found: 533.17. Elemental analysis: $3^{\text{Linked}}_{\text{Cl}} + 4 \text{ eq. HCPH}_3$ Calcd (%): C, 82.71; H, 6.94; N, 0.00. Found C, 82.92; H, 6.65; N, -0.13.

Synthesis of $\text{PCP}^{\text{Linked}}\text{Co(I)Br}$ (L2^H-3-Br): A 50 mL 2-necked round bottom flask was charged with L2^H-1 (0.073 g, 0.111 mmol) and Gomberg's Dimer (0.054 g, 0.111 mmol) and was dissolved in *ca.* 6 mL of toluene. At $-78\text{ }^{\circ}\text{C}$ NaHBEt_3 (115 μL , 0.115 mmol) was added dropwise. The solution was allowed to warm to room temperature and was stirred over 18h. Volatiles were removed in vacuo and the residue re-dissolved in 5 mL toluene. The solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed. The solid was rinsed with 2 x 2 mL pentane and dried. The sample was further purified following recrystallization at $-30\text{ }^{\circ}\text{C}$ by dissolving the product in minimal THF and layering with an equivalent amount of pentane, yielding dark red crystals (0.038 g, 0.066 mmol, 59 %). Crystals suitable for x-ray analysis were grown by vapour diffusion using minimal THF and pentane at $-30\text{ }^{\circ}\text{C}$ over 5 days. ^{31}P NMR (203 MHz, Benzene- d_6) δ 30.53. ^1H NMR (500 MHz, Benzene- d_6) δ 9.18 (d, J = 7.9 Hz, 2H, Ar-H), 7.09 (d, J = 7.7 Hz, 2H, Ar-H), 5.53 (d, J = 7.8 Hz, 2H, Ar-H), 4.45 (q, J = 7.2 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.77 (p, J = 7.5 Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.08 (s, 6H, $\text{C}(\text{CH}_3)_2$). ^{13}C NMR (126 MHz, Benzene- d_6) δ 174.99 (d, J = 25.3 Hz, Co=C), 137.77 (s, Ar-CH), 137.03 (s, Ar-CH), 136.82 (s, Ar-C), 132.54

(s, Ar-C), 129.92 (s, Ar-C), 125.57 (s, Ar-CH), 48.45 (s, C(CH₃)₂), 24.53 (d, *J* = 10.6 Hz, CH(CH₃)₂), 21.08 (s, CH(CH₃)₂), 19.58 (s, CH(CH₃)₂), 13.62 (s, C(CH₃)₂). HRMS (APCI) Calcd: 576.1121. Found: 576.111. Elemental analysis: Calcd (%): C, 58.24; H, 6.98; N, 0.00. Found C, 58.24; H, 7.35; N, 0.09.

Synthesis of PCP^{NMe2}Co(I)Cl (L2^{NMe2}-3-Cl): In a 100 mL thick-walled reaction vessel ClCo(PPh₃)₃ (0.813 g, 0.923 mmol) and L2^{NMe2} (0.512 g, 0.972 mmol) were dissolved in 20 mL of toluene. The reaction vessel was degassed before heating at 80 °C over 18h. The resulting solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. The resulting residue triturated with 5 mL pentane. The resulting solid was sonicated in 5 mL of pentane and the suspension filtered through a 2 mL filter frit. The collected powder was washed with an additional 5 mL of pentane. The solid was dried under vacuum to yield a red-brown powder (0.388 g, 0.627 mmol, 68%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal THF and pentane and cooling the system at -30 °C for 3 days. ³¹P{¹H} NMR (203 MHz, benzene-*d*₆) δ 46.01. ¹H NMR (500 MHz, Benzene-*d*₆) δ 6.94 (q, *J* = 3.0 Hz, 2H, Ar-H), 5.72 (d, *J* = 2.4 Hz, 2H, Ar-H), 4.00 (ddp, *J* = 10.5, 7.1, 3.5, 3.1 Hz, 4H, CH(CH₃)₂), 2.06 (d, *J* = 1.6 Hz, 12H, N(CH₃)₂), 1.86 (q, *J* = 7.4 Hz, 12H, CH(CH₃)₂), 1.79 (q, *J* = 6.7 Hz, 12H, CH(CH₃)₂), 1.39 (s, 6H, C(CH₃)₂). ¹³C NMR (126 MHz, Benzene-*d*₆) δ 161.69 (t, *J* = 24.9 Hz, Co=C), 148.11 (vt, *J* = 2.5 Hz, Ar-C), 135.26 (vt, *J* = 6.5 Hz, Ar-C), 134.06 (vt, *J* = 14.9 Hz, Ar-C), 133.91 (vt, *J* = 29.8 Hz, Ar-C), 119.36 (s, Ar-CH), 117.95 (s, Ar-CH), 46.19 (vt, *J* = 2.1 Hz, C(CH₃)₂), 40.16 (s, N(CH₃)₂), 24.51 (vt, *J* = 8.9 Hz, CH(CH₃)₂), 21.15 (s, C(CH₃)₂), 20.59 (vt, *J* = 2.6 Hz, CH(CH₃)₂), 19.53 (s, CH(CH₃)₂). UV-vis (THF) λ_{max}, nm: 538.0, 912.0. HRMS (APCI) Calcd: 618.2453. Found: 618.2464. Elemental analysis: Calcd. (%): C, 62.08; H, 8.14; N, 4.52. Found: C, 61.84; H, 8.56; N, 4.34.

Synthesis of PCP^{NMe2}Co(I)Br (L2^{NMe2}-3-Br): In a 100 mL 2-necked round bottom flask was dissolved L2^{NMe2}-1 (0.150 g, 0.201 mmol) and Gomberg's Dimer (0.098 g, 0.201 mmol) in 15 mL toluene. At -78 °C add NaHBET₃ (0.3 mL, 0.300 mmol) dropwise. The reaction solution was allowed to stir for 30 minutes at -78 °C before being warmed to room temperature and stirred for an additional hour. Solvent was removed in vacuo and the resulting residue washed with 2 x 5 mL of pentane. The sample was suspended in 1 mL of pentane and filtered through a small filter frit, washing with an additional 2 mL of pentane. The solid was dried under high vacuum. Residual triphenylmethane was removed via sublimation under dynamic vacuum at room temperature to yield a red-brown solid (0.096 g, 0.145 mmol, 72%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal THF and pentane and cooling the system at -30 °C for 3 days. ³¹P{¹H} NMR (203 MHz, benzene-*d*₆) δ 45.78. ¹H NMR (500 MHz, Benzene-*d*₆) δ 6.96 (s, 2H, Ar-H), 5.76 – 5.52 (m, 2H, Ar-H), 4.20 (s, 4H, CH(CH₃)₂), 2.02 (d, *J* = 7.5 Hz, 12H, N(CH₃)₂), 1.88 (p, *J* = 7.9 Hz, 12H, CH(CH₃)₂), 1.80 (t, *J* = 7.3 Hz, 12H, CH(CH₃)₂), 1.39 (d, *J* = 7.4 Hz, 6H, C(CH₃)₂). ¹³C NMR (126 MHz, Benzene-*d*₆) δ 162.25 (s, Co=C), 148.33 (s, Ar-C), 135.58 (s, Ar-C), 133.69 (s, Ar-C), 119.37 (s, Ar-CH), 117.96 (s, Ar-CH), 46.40 (s, C(CH₃)₂), 40.02 (s, C(CH₃)₂), 24.76 (s, CH(CH₃)₂), 20.57 (s, C(CH₃)₂), 20.33 (s, CH(CH₃)₂), 19.32 (s, CH(CH₃)₂). HRMS (APCI) (M+H)⁺ Calcd: 663.20374. Found: 663.20689. Elemental analysis: Calcd (%): C, 57.92; H, 7.60; N, 4.22. Found C, 57.97; H, 8.10; N, 4.15.

Synthesis of PCP^{NMe2}Co(I)OH (L2^{NMe2}-3-OH): To a 50 mL thick-walled reaction vessel was added L2^{NMe2}-3-Cl (0.229 g, 0.370 mmol) alongside CsOH·H₂O (0.443 g, 2.63 mmol) and dissolved in 15 mL of toluene. The reaction mixture was heated at 80 °C over 18h. The solution was filtered

through a 0.1 μm PTFE syringe filter into a 50 mL 2-necked round bottom flask. To the solution was added 1 mL of degassed water and the solvent was removed in vacuo. The resulting residue was suspended in pentane and collected on a small filter frit. The resulting solid was dried over 5 days at ambient temperature to yield a bright red powder (0.209 g, 0.348 mmol, 94%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal THF and pentane and cooling the system at $-30\text{ }^{\circ}\text{C}$ for 10 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, benzene- d_6) δ 48.12. ^1H NMR (500 MHz, Benzene- d_6) δ 6.88 – 6.82 (m, 2H, Ar-H), 5.95 (d, J = 2.4 Hz, 2H, Ar-H), 3.71 (s, 1H, OH), 3.43 (dp, J = 10.2, 4.1, 3.0 Hz, 4H, CH(CH $_3$) $_2$), 2.24 (s, 12H, N(CH $_3$) $_2$), 1.73 (dq, J = 18.6, 7.0 Hz, 24H, CH(CH $_3$) $_2$), 1.46 (s, 6H, C(CH $_3$) $_2$). ^{13}C NMR (126 MHz, Benzene- d_6) δ 160.59 (t, J = 25.0 Hz, CoC), 146.87 (vt, J = 2.4 Hz, Ar-C), 138.05 (vd, J = 12.2 Hz Ar-C), 134.20 (vd, J = 19.6 Hz, Ar-C), 129.15 – 128.72 (m, Ar-C), 118.71 (s, Ar-CH), 117.66 (s, Ar-CH), 45.04 (vt, J = 2.2 Hz, C(CH $_3$) $_2$), 40.18 (s, N(CH $_3$) $_2$), 24.03 (vt, J = 7.7 Hz, CH(CH $_3$) $_2$), 23.08 (s, C(CH $_3$) $_2$), 20.26 (vt, J = 3.1 Hz, CH(CH $_3$) $_2$), 19.53 (s, CH(CH $_3$) $_2$). Infrared: ν Co-OH stretch, 3883.932 cm^{-1} . HRMS (APCI) Calcd: 600.2781. Found: 600.2803. Elemental analysis: Calcd (%): C, 63.99; H, 8.55; N, 4.66. Found C, 64.46; H, 8.03; N, 3.49.

Synthesis of PCP^{NMe $_2$} Co(I)OOCPh, (L^{NMe $_2$} -3-OOCPh): To a 50 mL thick-walled reaction vessel was added 4 (0.058 g, 0.096 mmol) and benzoic acid (0.028 g, 0.229 mmol) and dissolved in 5 mL toluene. The reaction was heated at $80\text{ }^{\circ}\text{C}$ over 18h. The resulting solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo to give a dark red powder (0.025 g, 0.035 mmol, 37 %). The resulting solid was dissolved in 2 mL of pentane and recrystallized at $-30\text{ }^{\circ}\text{C}$ over 3 days yielding crystals suitable for analysis by X-ray crystallography. ^{31}P NMR (203 MHz, C $_6$ D $_6$) δ 54.31. ^1H NMR (500 MHz, C $_6$ D $_6$) δ 7.84 (s, 1H, (*para*) Ph-H), 7.04 – 6.97 (m, 4H, (*ortho/meta*) Ph-H), 6.85 (s, 2H, Ar-H), 5.87 (s, 2H, Ar-H), 3.67 (s, 4H, CH(CH $_3$) $_2$), 2.20 (s, 12H, N(CH $_3$) $_2$), 1.79 (q, J = 6.7 Hz, 12H, CH(CH $_3$) $_2$), 1.66 (q, J = 7.4 Hz, 12H, CH(CH $_3$) $_2$), 1.46 (s, 6H, C(CH $_3$) $_2$). ^{13}C NMR (126 MHz, C $_6$ D $_6$) δ 160.79 (vt, Co=C), 148.12 (s, Ar-C), 136.15 (s, Ar-C), 132.38 (s, Ar-C), 131.54 (s, Ar-C), 128.35 (s, (*para*) Ph-CH), 118.73 (s, Ar-CH), 117.86 (s, Ar-CH), 45.17 (s, C(CH $_3$) $_2$), 40.15 (s, N(CH $_3$) $_2$), 24.51 (s, CH(CH $_3$) $_2$), 22.79 (s, C(CH $_3$) $_2$), 19.54 (s, CH(CH $_3$) $_2$), 18.89 (s, CH(CH $_3$) $_2$). *(*ortho/meta*) Ph-CH carbon peaks are located under the C $_6$ D $_6$ solvent peak. Confirmed by HSQC*. HMRS (APCI) Calcd: 705.31103. Found: 705.3124.

Synthesis of PCP^{NMe $_2$} Co(I)CH $_2$ SiMe $_3$, L^{NMe $_2$} -3-CH $_2$ SiMe $_3$: A 50 mL round bottom flask was charged with 3^{NMe $_2$} Cl (0.115 g, 0.186 mmol) and LiCH $_2$ Si(CH $_3$) $_3$ (0.036 g, 0.382 mmol) and dissolved in 6 mL of toluene. The reaction solution was stirred for 18h at room temperature. Solvent was removed in vacuo and replaced with a solvent mixture of 1:5 benzene:pentane. The resulting solution was filtered through a 0.1 μm PTFE syringe filter into a 50 mL round bottom flask and solvent removed in vacuo. The resulting residue was triturated with 2 mL of pentane and dried under high vac to yield a dark brown powder (0.089 g, 0.133 mmol, 72%). Crystals suitable for analysis by single-crystal XRD studies were grown by vapor diffusion using minimal benzene and pentane at room temperature over 10 days. $^{31}\text{P}\{^1\text{H}\}$ NMR (203 MHz, Benzene- d_6) δ 35.44. ^1H NMR (500 MHz, Benzene- d_6) δ 7.03 (d, J = 9.4 Hz, 2H, Ar-H), 5.52 (s, 2H, Ar-H), 4.47 (s, 4H, CH(CH $_3$) $_2$), 2.05 (s, 12H, N(CH $_3$) $_2$), 1.91 – 1.83 (m, 12H, CH(CH $_3$) $_2$), 1.74 (d, J = 6.4 Hz, 12H, CH(CH $_3$) $_2$), 1.37 (s, 6H, C(CH $_3$) $_2$), 0.01 (s, 2H, CH $_2$), -0.07 (s, 9H, Si(CH $_3$) $_3$). ^{13}C NMR (126 MHz, Benzene- d_6) δ 165.56 (vt, J = 25.4 Hz, Co=C), 147.40 (Ar-C), 134.42 (d, J = 18.9 Hz, Ar-C), 133.87 (vt, J = 5.8 Hz, Ar-C), 129.05 (d, J = 8.2 Hz, Ar-C), 120.89 (Ar-CH), 119.71 (Ar-CH),

48.34 (d, $J = 2.6$ Hz, $\text{C}(\text{CH}_3)_2$), 40.27 ($\text{N}(\text{CH}_3)_2$), 25.18 (t, $J = 7.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 21.62 (d, $J = 2.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.91 ($\text{CH}(\text{CH}_3)_2$), 17.73 ($\text{C}(\text{CH}_3)_2$), 5.54 ($\text{Si}(\text{CH}_3)_3$), 0.15 (CH_2Si). HRMS (APCI) Calcd: 670.3406. Found: 670.3379.

Synthesis of $\text{PCP}^{\text{NMe}_2}\text{Co}(\text{I})\text{NH}_2$, ($\text{L}^{\text{NMe}_2}\text{-3-NH}_2$): To a 50 mL thick-walled reaction vessel was added $\text{L}^{\text{NMe}_2}\text{-3-Cl}$ (0.015 g, 0.025 mmol) alongside LiNH_2 (0.060 g, 2.613 mmol) and dissolved in 5 mL of THF. The reaction was heated at 75°C over 5 days resulting in a bright red solution. Solvent was removed under high vacuum and the residue redissolved in C_6D_6 and filtered through a glass filter pad into a 50 mL round bottom flask. Solvent was removed under vacuum and the resulting residue titrated with 2 mL pentane. The solid was dissolve in pentane and filtered through a $0.1\ \mu\text{m}$ PTFE syringe filter into a 50 mL round bottom flask and solvent removed to yield a bright red solid in 26% yield by NMR (0.005 g, 0.008 mmol). X-ray quality crystals were grown from a THF:pentane mixture at -30°C over 5 days. The crystals show a 50:50 mixture of $\text{L}^{\text{NMe}_2}\text{-3-Cl}$ and $\text{L}^{\text{NMe}_2}\text{-3-NH}_2$. ^{31}P NMR (203 MHz, C_6D_6) δ 58.46. ^1H NMR (500 MHz, C_6D_6) δ 6.90 (q, $J = 3.1$ Hz, 2H, Ar-H), 6.09 (d, $J = 2.4$ Hz, 2H, Ar-H), 3.31 – 3.20 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 2.33 (s, 12H, $\text{N}(\text{CH}_3)_2$), 1.63 (dq, $J = 16.2, 6.9$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.49 (s, 6H, $\text{C}(\text{CH}_3)_2$), -1.45 (t, $J = 9.2$ Hz, 2H, NH_2). ^{13}C NMR (126 MHz, C_6D_6) δ 159.19 (t, $J = 25.7$ Hz, $\text{Co}=\text{C}$), 147.17 (t, $J = 2.3$ Hz, Ar-C), 136.44 (t, $J = 16.6$ Hz, Ar-C), 134.28 (t, $J = 6.7$ Hz, Ar-C), 134.13 (s, Ar-C), 117.94 (s, Ar-CH), 117.20 (s, Ar-CH), 44.10 (s, $\text{C}(\text{CH}_3)_2$), 40.29 (s, $\text{N}(\text{CH}_3)_2$), 24.92 – 24.60 (m, $\text{C}(\text{CH}_3)_2$), 20.45 (t, $J = 3.1$ Hz, $\text{CH}(\text{CH}_3)_3$), 19.37 (s, $\text{CH}(\text{CH}_3)_3$). ^{31}P NMR (203 MHz, THF) δ 58.52. ^1H NMR (500 MHz, THF) δ 6.81 (s, 2H, Ar-H), 6.06 (s, 2H, Ar-H), 3.25 (s, 4H, $\text{CH}(\text{CH}_3)_2$), 2.68 (s, 12H, $\text{N}(\text{CH}_3)_2$), 1.48 (dq, $J = 13.9, 7.1$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$), 1.37 (s, 6H, $\text{C}(\text{CH}_3)_2$), -2.01 (d, $J = 9.5$ Hz, 2H, NH_2). ^{13}C NMR (126 MHz, THF) δ 158.93 (t, $J = 25.6$ Hz, $\text{Co}=\text{C}$), 147.56 (s, Ar-C), 136.10 (t, $J = 16.3$ Hz, Ar-C), 134.41 (s, Ar-C), 134.27 (t, $J = 6.8$ Hz, Ar-C), 117.90 (s, Ar-CH), 117.01 (s, Ar-CH), 44.14 (s, $\text{C}(\text{CH}_3)_2$), 40.38 (s, $\text{N}(\text{CH}_3)_2$), 24.77 (s, $\text{CH}(\text{CH}_3)_2$), 24.47 (s, $\text{C}(\text{CH}_3)_2$), 20.27 (d, $J = 3.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 19.26 (s, $\text{CH}(\text{CH}_3)_2$). HRMS (APCI) Calcd: 599.29685. Found: 599.29502.

Supporting Information

The Supporting Information is given below.

Experimental details, NMR, IR, EPR, and UV-vis spectra, and computational details (PDF)

Computational coordinates (.xyz)

Accession Codes

CCDC codes 2114067-2114081 contain the crystallographic data for the 15 structurally characterized compounds reported. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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Carbene Character in a Series of Neutral PC_{carbene}P Cobalt(I) Complexes – Radical Carbenes Versus Nucleophilic Carbenes

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Selected ORTEP Diagrams

Figure S1. ORTEP diagrams for complexes L1-1 and L2^H-1.

L1-1; thermal ellipsoids are shown at the 50% probability level. Most hydrogen atoms are omitted for clarity. Only one molecule per asymmetric unit is shown. Select bond lengths (Å) and angles (degrees): Co-Br1 2.3820(5), Co1-Br2 2.3697(5), Co1-P1 2.4636(7), Co1-P2 2.4551(8), Br1-Co1-P1 106.15(2), Br1-Co1-P2 108.81(2), Br2-Co1-P1 109.57(2), Br2-Co1-P2 101.36(2), Br2-Co1-Br1 110.91(2), P1-Co1-P2 119.98(3). L2^H-1; thermal ellipsoids are shown at the 50% probability level. Most hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (degrees): Co-Br1 2.3600(5), Co1-Br2 2.3750(5), Co1-P1 2.4536(8), Co1-P2 2.4329(8), Br1-Co1-P1 102.11(2), Br1-Co1-P2 110.55(2), Br2-Co1-P1 109.57(2), Br2-Co1-P2 98.58(2), Br2-Co1-Br1 113.51(2).

Figure S2. ORTEP illustrations of L1-2-Br (top), L2^H-2-Br (bottom, left), and L2^H-2-Cl (bottom, right).

L1-2-Br; thermal ellipsoids are drawn at the 50% probability level (select hydrogen atoms have been omitted for clarity). Co1-C1A refined with an occupancy factor of 0.55. Co1-C1B refined with an occupancy factor of 0.45. Select bond distances (Å) and angles (degrees): Co1-Br1 2.3596(3), Co1-C1A 1.987(4), Co1-C1B 1.938(6), Co1-P1 2.2202(5), Co1-P2 2.2105(5), C1A-Co1-Br1 163.9(3), C1B-Co1-Br1 176.3(4), P1-Co1-Br1 93.970(15), P1-Co1-P2 172.41(2), P2-Co1-Br1 93.244(14). L2^H-2-Cl; thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (degrees): Co1-Cl1 2.2395(5), Co1-C1A 1.947(5), Co1-C1B 1.921(5), Co1-P1 2.1892(5), Co1-P2 2.2039(5), C1A-Co1-Cl1 177.9(3), C1B-Co1-Cl1 163.8(3), P1-Co1-Cl1 93.391(16), P1-Co1-P2 169.541(16), P2-Co1-Cl1 96.835(17).

Figure S3: ORTEP diagram for complex $L2^{NMe_2}\text{-3-Cl}$.

Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Select bond distances (Å) and angles (degrees): Co1-Cl1 2.2525(5), Co1-C1 1.8447(16), Co1-P1 2.1742(5), Co1-P2 2.1721(5), C1-Co1-Cl1 171.95(6), P1-Co1-Cl1 96.06(2), P1-Co1-P2 166.31(2), P2-Co1-Cl1 94.424(19).

Selected Electron Paramagnetic Resonance (EPR) Spectra

Figure S4: X-Band EPR Spectrum of Complex L1-3-Br (Toluene, 160.1 K)

Table S1. Xenon (EPR) Absolute Number of Spins Results.

Sample	$X_{\min}$	$X_{\max}$	Spins/mm ³	M	Spins
L2 ^{NMe2} -3-CH ₂ TMS	3.274×10^3	3.387×10^3	1.374×10^{11}	2.281×10^{-7}	3.884×10^{13}
L2 ^{NMe2} -3-Cl	3.349×10^3	3.390×10^3	1.333×10^{10}	2.214×10^{-8}	3.770×10^{12}
L2 ^{NMe2} -3-OH	3.316×10^3	3.339×10^3	8.871×10^9	1.473×10^{-8}	2.508×10^{12}

Selected NMR Spectra

Figure S5: ^1H NMR spectrum of L1-1 in $\text{benzene-}d_6$

Figure S6: ¹H NMR spectrum of L2^H-1 in benzene-*d*₆

Figure S7: ¹H NMR (top) and ¹³C{¹H} NMR (bottom) spectra of L2^{NMe2}-1 in benzene-*d*₆

Figure S9: ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of L1-3-Br in benzene- d_6

Figure S10: ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of $\text{L2}^{\text{H}}\text{-3-Cl}$ in benzene- d_6

Figure S11: ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of L2^H-3-Br in benzene-*d*₆

Figure S12: 1H NMR and $^{31}P\{^1H\}$ NMR (top) and $^{13}C\{^1H\}$ NMR (bottom) spectra of $L2^{NMe_2-3-Cl}$ in benzene- d_6

Figure 13: ^1H NMR and $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of L2^{NMe}-3-Br in benzene- d_6

Figure 14: HSQC spectrum of L2^{NMe}-3-Br in benzene-*d*₆

Figure S15: 1H NMR and $^{31}P\{^1H\}$ NMR (top) and $^{13}C\{^1H\}$ NMR (bottom) spectra of $L2^{NMe_2}$ -3-OH in benzene- d_6

Figure S16: 1H NMR, $^{31}P\{^1H\}$ NMR (top) and $^{13}C\{^1H\}$ NMR (bottom) spectra of $L2^{NMe_2}$ -3-OOCPh in benzene- d_6

Figure S17: ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of L2^{NMe2}-3-CH₂TMS in benzene-*d*₆

Figure S18: ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR (top) and $^{13}\text{C}\{^1\text{H}\}$ NMR (bottom) spectra of $\text{L2}^{\text{NMe}_2}\text{-3-NH}_2$ in $\text{THF-}d_8$

Figure S19: ³¹P{¹H} NMR spectra of the reactivity of L2^H-1 with NaBEt₃ and “·CPh₃” featuring intermediate formation of L2^H-2-Br (68.42 ppm) and proposed Co(I) reduced complex (-8.33 ppm) [left]. ³¹P{¹H} NMR spectra of the reactivity of L2^H with ClCo(PPh₃)₃ featuring intermediate formation of L2^H-2-Cl (66.42 ppm), proposed Co(I) reduced complex (-7.80 ppm), and triphenylphosphine (-5.65 ppm) [right].

Selected Ultra-Violet Spectra

Figure S20: UV-Vis spectrum (300.0 – 1100.0 nm) of L1-1. Scan rate 9600.000 nm/min. Data interval 2.00 nm. Average time 0.0125 sec. Dual beam.

Figure S21: UV-Vis spectrum (300.0 – 1100.0 nm) of L2^H-1. Scan rate 9600.000 nm/min. Data interval 2.00 nm. Average time 0.0125 sec. Dual beam.

Figure S22: UV-Vis spectrum (300.0 – 1100.0 nm) of L2^{NMe2}-1. Scan rate 9600.000 nm/min. Data interval 2.00 nm. Average time 0.0125 sec. Dual beam.

Figure S23: UV-Vis spectrum (300.0 – 1100.0 nm) of L1-2-Br. Scan rate 9600.000 nm/min. Data interval 2.00 nm. Average time 0.0125 sec. Dual beam.

Selected Infrared Spectra

Figure S24: Infrared Spectrum of L2^{NMe2}-3-OH, KBr Pellet

Crystal Data Collection and Refinement Parameters

Solved as a fluorine adduct

$R_1 = 4.42\%$

$wR_2 = 11.22\%$

Residual electron density
 $\sim 0.8 \text{ e}\text{\AA}^{-3}$

Disorder along Co-F bond.

Split fluorine atom to
nitrogen and chlorine

$R_1 = 4.02\%$

$wR_2 = 9.29\%$

Residual electron density
 $\sim 0.5 \text{ e}\text{\AA}^{-3}$

Two regions of residual
electron density $\sim 1 \text{ \AA}$ from
nitrogen.

Added hydrogen atoms to
nitrogen (NH_2)

$R_1 = 3.97\%$

$wR_2 = 9.04\%$

Residual electron density
 $\sim 0.4 \text{ e}\text{\AA}^{-3}$

No substantial regions of
residual electron density.

Figure S25: Crystallographic structural determination method for complex $\text{L2}^{\text{NMe}_2}\text{-3-NH}_2$.

Table S2. Crystal data collection and refinement parameters for compounds L_n-1

Identification code	L1-1-Br	L1-1-Cl	L2 ^H -1-Br
Empirical formula	C ₂₉ H ₃₈ Br ₂ CoP ₂ S ₂	C ₂₉ H ₃₈ Cl ₂ CoP ₂ S ₂	C ₂₈ H ₄₂ Br ₂ CoP ₂
Formula weight	731.4	642.48	659.30
Temperature/K	172.78	173.15	173
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	14.03540(10)	13.9927(5)	26.1325(8)
b/Å	12.69840(10)	12.5862(7)	10.9851(3)
c/Å	17.6811(2)	17.4895(8)	21.6717(7)
α/°	90	90	90
β/°	97.5220(10)	98.177(2)	106.1940(10)
γ/°	90	90	90
Volume/Å ³	3124.13(5)	3048.8(2)	5974.4(3)
Z	4	4	8
ρ _{calc} /cm ³	1.555	1.400	1.466
μ/mm ⁻¹	9.645	0.998	3.371
F(000)	1484.0	1340.0	2696.0
Crystal size/mm ³	0.18 × 0.14 × 0.12	0.358 × 0.294 × 0.148	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.352 to 143.564	6.112 to 56.632	1.622 to 54.998
Index ranges	-16 ≤ h ≤ 17, -15 ≤ k ≤ 15, -21 ≤ l ≤ 20	-18 ≤ h ≤ 17, -16 ≤ k ≤ 14, -22 ≤ l ≤ 23	-32 ≤ h ≤ 29, -14 ≤ k ≤ 14, -28 ≤ l ≤ 26
Reflections collected	34951	23274	91479
Independent reflections	6080 [R _{int} = 0.0340]	7509 [R _{int} = 0.0630, R _{sigma} = 0.0699]	13709 [R _{int} = 0.0683, R _{sigma} = 0.0523]
Data/restraints/parameters	6080/ 73 / 354	7509/0/333	13709/0/615
Goodness-of-fit on F ²	1.032	1.051	1.003
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0323, wR ₂ = 0.0842	R ₁ = 0.0519, wR ₂ = 0.1048	R ₁ = 0.0354, wR ₂ = 0.0638
Final R indexes [all data]	R ₁ = 0.0360, wR ₂ = 0.0865	R ₁ = 0.0862, wR ₂ = 0.1167	R ₁ = 0.0693, wR ₂ = 0.0734
Largest diff. peak/hole / e Å ⁻³	0.69/-0.28	0.62/-0.45	0.72/-0.80

*Note 1^{NMe2} contains 2 molecules alongside benzene co-crystallized.

Table S3. Crystal data collection and refinement parameters for compounds L2^{NMe2}-1-Br and L_n-2-X.

Identification code	L2 ^{NMe2} -1-Br	L1-2-Br	L2 ^H -2-Cl
Empirical formula	C ₈₂ H ₁₂₂ Br ₄ Co ₂ N ₄ P ₄	C ₂₉ H ₃₇ BrCoP ₂ S ₂	C ₂₈ H ₄₁ ClCoP ₂
Formula weight	1725.21	650.48	533.93
Temperature/K	173.0	173.15	173.0
Crystal system	triclinic	Monoclinic	Triclinic
Space group	P-1	P2 ₁ /n	P-1
a/Å	13.121(4)	13.3195 (9)	10.9499(14)
b/Å	13.412(4)	13.3225 (8)	11.1362(14)
c/Å	24.978(7)	19.1065 (13)	13.6741(17)
α/°	89.703(8)	90	97.995(2)
β/°	76.408(8)	103.8936 (9)	108.079(2)
γ/°	82.348(8)	90	114.6060(10)
Volume/Å ³	4233(2)	2945.4 (3)	1370.0(3)
Z	2	4	2
ρ _{calc} /cm ³	1.354	1.467	1.294
μ/mm ⁻¹	2.398	2.207	0.855
F(000)	1792.0	1340.0	566.0
Crystal size/mm ³	0.3 × 0.2 × 0.1	0.455 × 0.328 × 0.107	0.481 × 0.242 × 0.216
Radiation	MoKα (λ = 0.71073)	Mo Ka (0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	1.678 to 50	3.38 to 56.526	3.296 to 56.6
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -29 ≤ l ≤ 29	-17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -25 ≤ l ≤ 24	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	110427	27223	26938
Independent reflections	14885 [R _{int} = 0.0689, R _{sigma} = 0.0462]	7232 [R _{int} = 0.0269, R _{sigma} = 0.0224]	6805 [R _{int} = 0.0227, R _{sigma} = 0.0208]
Data/restraints/parameters	14885/1140/986	7232 / 0 / 326	6805/13/309
Goodness-of-fit on F ²	1.052	1.035	1.049
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0596, wR ₂ = 0.1390	R ₁ = 0.0283, wR ₂ = 0.0693	R ₁ = 0.0298, wR ₂ = 0.0743
Final R indexes [all data]	R ₁ = 0.0882, wR ₂ = 0.1583	R ₁ = 0.0374, wR ₂ = 0.0733	R ₁ = 0.0383, wR ₂ = 0.0792
Largest diff. peak/hole / e Å ⁻³	2.46/-1.04	0.61/-0.52	0.45/-0.31

Table S4. Crystal data collection and refinement parameters for compounds L2^H-2-Br and Ln-3-Br

Identification code	L2 ^H -2-Br	L1-3-Br	L2 ^H -3-Br
Empirical formula	C ₂₈ H ₄₁ BrCoP ₂	C ₂₉ H ₃₆ BrCoP ₂ S ₂	C ₂₈ H ₄₀ BrCoP ₂
Formula weight	578.39	649.48	577.38
Temperature/K	173.0	173.15	173.0
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2 ₁ /n	P-1
a/Å	11.0188(17)	13.2417(7)	11.0699(13)
b/Å	11.1579(17)	11.8759(5)	11.1657(13)
c/Å	13.760(2)	19.0433(9)	13.1023(16)
α/°	98.534(2)	90	69.1410(10)
β/°	108.349(2)	104.230(3)	84.2960(10)
γ/°	114.560(2)	90	64.8410(10)
Volume/Å ³	1381.9(4)	2902.8(2)	1367.2(3)
Z	2	4	2
ρ _{calc} /cm ³	1.390	1.486	1.403
μ/mm ⁻¹	2.197	2.239	2.220
F(000)	602.0	1336.0	600.0
Crystal size/mm ³	0.4 × 0.25 × 0.2	0.39 × 0.35 × 0.21	0.325 × 0.277 × 0.167
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.296 to 56.674	6.602 to 54.968	3.332 to 56.56
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -24 ≤ l ≤ 24	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	27275	41555	27016
Independent reflections	6883 [R _{int} = 0.0210, R _{sigma} = 0.0204]	6650 [R _{int} = 0.1044, R _{sigma} = 0.0720]	6784 [R _{int} = 0.0222, R _{sigma} = 0.0194]
Data/restraints/parameters	6883/13/309	6649/0/324	6784/0/299
Goodness-of-fit on F ²	1.022	1.023	1.029
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0265, wR ₂ = 0.0617	R ₁ = 0.0439, wR ₂ = 0.0864	R ₁ = 0.0223, wR ₂ = 0.0542
Final R indexes [all data]	R ₁ = 0.0349, wR ₂ = 0.0648	R ₁ = 0.0826, wR ₂ = 0.0993	R ₁ = 0.0285, wR ₂ = 0.0567
Largest diff. peak/hole / e Å ⁻³	0.48/-0.47	0.59/-0.46	0.41/-0.43

Table S5. Crystal data collection and refinement parameters for compounds L2^{NMe2}-3-X

Identification code	L2 ^{NMe2} -3-Cl	L2 ^{NMe2} -3-Br	L2 ^{NMe2} -3-OH
Empirical formula	C ₃₂ H ₅₀ ClCoN ₂ P ₂	C ₃₂ H ₅₀ BrCoN ₂ P ₂	C ₃₂ H ₅₁ CoN ₂ OP ₂
Formula weight	619.06	663.52	600.61
Temperature/K	173.0	173.0	173.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c
a/Å	10.9201(2)	10.9504(5)	9.1706(3)
b/Å	14.0043(3)	14.0425(6)	17.3516(5)
c/Å	22.0003(5)	22.1697(8)	20.3999(6)
α/°	90	90	90
β/°	103.9790(10)	104.1810(10)	98.845(2)
γ/°	90	90	90
Volume/Å ³	3264.83(12)	3305.2(2)	3207.52(17)
Z	4	4	4
ρ _{calc} /g/cm ³	1.259	1.333	1.244
μ/mm ⁻¹	5.961	1.848	5.328
F(000)	1320.0	1392.0	1288.0
Crystal size/mm ³	0.348 × 0.326 × 0.223	0.41 × 0.388 × 0.321	0.498 × 0.226 × 0.225
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2θ range for data collection/°	7.55 to 140.004	3.464 to 56.622	6.722 to 144.572
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -29 ≤ l ≤ 29	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -25 ≤ l ≤ 25
Reflections collected	33478	20275	47769
Independent reflections	6198 [R _{int} = 0.0348, R _{sigma} = 0.0250]	8201 [R _{int} = 0.0312, R _{sigma} = 0.0423]	6276 [R _{int} = 0.0519, R _{sigma} = 0.0300]
Data/restraints/parameters	6198/0/357	8201/0/357	6276/0/357
Goodness-of-fit on F ²	1.035	1.014	1.077
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0316, wR ₂ = 0.0824	R ₁ = 0.0414, wR ₂ = 0.0882	R ₁ = 0.0598, wR ₂ = 0.1782
Final R indexes [all data]	R ₁ = 0.0350, wR ₂ = 0.0846	R ₁ = 0.0691, wR ₂ = 0.0999	R ₁ = 0.0674, wR ₂ = 0.1877
Largest diff. peak/hole / e Å ⁻³	0.29/-0.30	0.67/-0.41	1.18/-0.36

Table S6. Crystal data collection and refinement parameters for compounds L2^{NMe2}-3-X

Identification code	L2 ^{NMe2} -3-CH ₂ TMS	L2 ^{NMe2} -3-NH ₂ /Cl	L2 ^{NMe2} -3-OOCPh
Empirical formula	C ₃₆ H ₆₁ CoN ₂ P ₂ Si	C ₃₂ H _{51.22} Cl _{0.39} CoN _{2.61} P ₂	C ₃₉ H ₅₅ CoN ₂ O ₂ P ₂
Formula weight	670.82	607.21	704.72
Temperature/K	173.0	173.0	73.0
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /c	P2 ₁ /c
a/Å	9.9578(7)	9.0243(4)	11.006(4)
b/Å	14.1680(10)	17.5396(9)	22.735(6)
c/Å	14.5109(8)	20.6964(11)	15.309(5)
α/°	68.750(4)	90	90
β/°	88.141(4)	98.5140(10)	102.305(12)
γ/°	72.666(4)	90	90
Volume/Å ³	1814.8(2)	3239.8(3)	3743(2)
Z	2	4	4
ρ _{calc} /cm ³	1.228	1.245	1.251
μ/mm ⁻¹	0.621	0.685	0.579
F(000)	724.0	1300.0	1504.0
Crystal size/mm ³	0.338 × 0.21 × 0.068	0.22 × 0.21 × 0.171	0.229 × 0.156 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.058 to 56.664	3.085 to 55.754	4.5 to 56.558
Index ranges	-13 ≤ h ≤ 12, -17 ≤ k ≤ 18, -18 ≤ l ≤ 19	-11 ≤ h ≤ 11, -23 ≤ k ≤ 23, -27 ≤ l ≤ 25	-14 ≤ h ≤ 14, -30 ≤ k ≤ 30, -20 ≤ l ≤ 20
Reflections collected	17381	23459	58977
Independent reflections	8958 [R _{int} = 0.0773, R _{sigma} = 0.1385]	7715 [R _{int} = 0.0365, R _{sigma} = 0.0434]	9280 [R _{int} = 0.0605, R _{sigma} = 0.0432]
Data/restraints/parameters	8958/0/396	7715/3/373	9280/194/471
Goodness-of-fit on F ²	1.000	1.046	1.015
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0698, wR ₂ = 0.1428	R ₁ = 0.0396, wR ₂ = 0.0827	R ₁ = 0.0390, wR ₂ = 0.0839
Final R indexes [all data]	R ₁ = 0.1428, wR ₂ = 0.1801	R ₁ = 0.0630, wR ₂ = 0.0906	R ₁ = 0.0650, wR ₂ = 0.0947
Largest diff. peak/hole / e Å ⁻³	0.89/-0.47	0.37/-0.26	0.40/-0.23

Computational Details

All the calculations were conducted using the Gaussian16 program suite. Structures were optimized at both the HLE16¹ and M06-L functional levels, while additional B3LYP*² single-point calculations were performed on the M06-L³ optimized structures. The LANL2DZ^{4,5} basis set and corresponding electron-core potential (ECP) was employed for cobalt while all other atoms used the 6-31G(d,p) basis. All calculations were performed in using the SMD continuum solvent method with THF.⁶

Table S6. Structural energies of the different carbene structures in Hartrees. E_{SCF} are the electronic energies, E_{ZPE} are the zero-point energy corrections, H includes the enthalpic corrections, and G includes the Gibbs corrections.

Structure	Spin	E _{SCF}	E _{ZPE}	H	G
UM06-L/6-31G(d,p)[LANL2DZ(Co)]					
L1-3-Br	S=0	-2764.113121	-2763.535814	-2763.495794	-2763.607175
	S=1	-2764.130641	-2763.554455	-2763.514136	-2763.627503
L2 ^H -3-Br	S=0	-1932.078831	-1931.465422	-1931.427471	-1931.533516
	S=1	-1932.087635	-1931.475424	-1931.437309	-1931.544612
L2 ^{NMe2} -3-Br	S=0	-2199.998013	-2199.23897	-2199.191836	-2199.317793
	S=1	-2199.996638	-2199.238622	-2199.191471	-2199.317799
L2 ^{NMe2} -3-Cl	S=0	-2647.013599	-2646.254467	-2646.207446	-2646.332819
	S=1	-2647.013338	-2646.254773	-2646.208031	-2646.332503
L2 ^{NMe2} -3-CH ₂ TMS	S=0	-2635.301391	-2634.406455	-2634.351668	-2634.491256
	S=1	-2635.305807	-2634.412	-2634.357139	-2634.498548
L2 ^{NMe2} -3-NH ₂	S=0	-2242.72474	-2241.942987	-2241.895617	-2242.020832
	S=1	-2242.717531	-2241.936677	-2241.889245	-2242.015746
L2 ^{NMe2} -3-OH	S=0	-2262.599448	-2261.828802	-2261.781781	-2261.90724
	S=1	-2262.59515	-2261.826212	-2261.779696	-2261.904002
L2 ^{NMe2} -3-OOCPh	S=0	-2607.015439	-2606.153769	-2606.100261	-2606.240818
	S=1	-2607.010141	-2606.148839	-2606.095319	-2606.237183

Table S7. Structural energies of the different carbene structures in Hartrees. E_{SCF} are the electronic energies, E_{ZPE} are the zero-point energy corrections, H includes the enthalpic corrections, and G includes the Gibbs corrections. ^a Calculations were performed with the B3LYP* functional on M06-L optimized structures. HLE16 energies are from HLE16 optimized structures.

Structure	Spin	^a E _{B3LYP*}	E _{HLE16}
B3LYP*/6-31G(d,p)[LANL2DZ(Co)]//UM06-L/6-31G(d,p)[LANL2DZ(Co)] and HLE16/6-31G(d,p)[LANL2DZ(Co)]			
L1-3-Br	S=0	-2763.035931	-2824.886961
	S=1	-2763.057467	-2824.899333
L2 ^H -3-Br	S=0	-1931.185988	-1980.532665
	S=1	-1931.197536	-1980.53743
L2 ^{NMe2} -3-Br	S=0	-2198.954113	-2256.475135
	S=1	-2198.958079	-2256.467451
L2 ^{NMe2} -3-Cl	S=0	-2645.881324	-2709.295959
	S=1	-2645.885908	-2709.288918
L2 ^{NMe2} -3-CH ₂ TMS	S=0	-2634.083038	-2701.055509

	S=1	-2634.093417	-2701.055425
L2 ^{NMe2} -3-NH ₂	S=0	-2241.662388	-2300.220847
	S=1	-2241.653716	-2300.20855
L2 ^{NMe2} -3-OH	S=0	-2261.531149	-2320.390798
	S=1	-2261.530499	-2320.381106
L2 ^{NMe2} -3-OOCPh	S=0	-2605.749755	-2674.62125
	S=1	-2605.746529	-2674.61529

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