Coordination Chemistry

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A Neutral Tetraphosphacyclobutadiene Ligand in Cobalt(I) Complexes**

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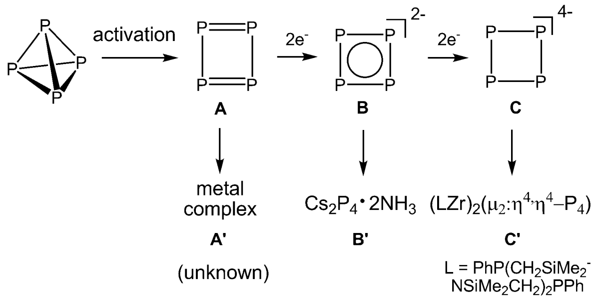
Abstract: *The unusual reactivity of the newly synthesized β-diketiminato cobalt(I) complexes, $[(L^{Dep}Co)_2]$ (**2a**, $L^{Dep} = CH[C(Me)N(2,6\text{-}Et_2C_6H_3)]_2$) and $[L^{Dipp}Co\cdot toluene]$ (**2b**, $L^{Dipp} = CH[CHN(2,6\text{-}{}^iPr_2C_6H_3)]_2$), toward white phosphorus was investigated, affording the first cobalt(I) complexes $[(L^{Dep}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)]$ (**3a**) and $[(L^{Dipp}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)]$ (**3b**) bearing the neutral cyclo-P_4 ligand with a rectangular-planar structure. The redox chemistry of **3a** and **3b** was studied by cyclic voltammetry and their chemical reduction with one molar equivalent of potassium graphite led to the isolation of $[(L^{Dep}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)][K(dme)_4]$ (**4a**) and $[(L^{Dipp}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)][K(dme)_4]$ (**4b**). Unexpectedly, the monoanionic Co_2P_4 core in **4a** and **4b**, respectively, contains the two-electron-reduced cyclo-P_4^{2-} ligand with a square-planar structure and mixed-valent cobalt(I,II) sites. The electronic structures of **3a**, **3b**, **4a**, and **4b** were elucidated by NMR and EPR spectroscopy as well as magnetic measurements and are in agreement with results of broken-symmetry DFT calculations.*

Tetraphosphacyclobutadiene (**A**, Scheme 1) with a rectangular-planar structure is known as a thermochemically unstable isomer in comparison to the P_4 tetrahedron.[1] Because phosphorus atoms are often termed as a "carbon copy" and are considered isolobal to a CH fragment,[2] the instability of **A** is reminiscent to that of the highly reactive cyclobutadiene.



Scheme 1. Various types of cyclo-P_4 ligands and the respective complexes as examples.

The latter possesses four π electrons and can only be studied spectroscopically under extreme experimental conditions such as in an Ar matrix or be isolated as a $[C_4H_4]^{2-}$ ligand entity within metal complexes.[3]

Over the last decades, coordination and subsequent reduction of white phosphorus (P_4) with transition metal complexes has attracted considerable attention, because metal-catalyzed P_4 functionalization has been integral to the ultimate goal of synthesizing organophosphorus derivatives due to increasingly stringent environmental regulations.[4] Numerous phosphorus complexes have thus been prepared, among which the first cyclo-P_4 complex $[Cp^*(CO)_2Nb(\eta^4\text{-}P_4)]$ ($Cp^* = C_5Me_5$),[5a,6] was reported by Scherer in 1989. Although several transition-metal and main-group-element cyclo-P_4 complexes (e.g., **B′**,[5h] Scheme 1) were reported thereafter,[5b–p] these phosphorus ligands are either two-electron-reduced cyclo-P_4^{2-} (**B**) or four-electron-reduced cyclo-P_4^{4-} (**C′**[5l]). There are also examples known such as $[(Cp^*Co)_2(\mu_2{:}\eta^2,\eta^2\text{-}P_2)_2]$ that feature a rectangular-planar P_4 unit with two very long P⋯P distances (> 2.5 Å) and two very short P–P bonds (< 2.10 Å).[7] In fact, the two P_2 units in these complexes show no significant bonding interactions and thus the moiety would be better described as two independent P_2 ligands.[4] The neutral cyclo-P_4 ligand **A** with alternating P=P bonds that would result from a transformation of the P_4 tetrahedron by breaking two P–P bonds should be an important intermediate for **B** and **C**. However, to date and to the best of our knowledge, no substituent-free cyclo-P_4 metal complex (**A′**) has been reported and crystallographically characterized.

Recently, β-diketiminato ligands have been successfully utilized for stabilization of both transition metals and main group elements in unusual oxidation states.[8] These complexes often show interesting reactivity in small-molecule

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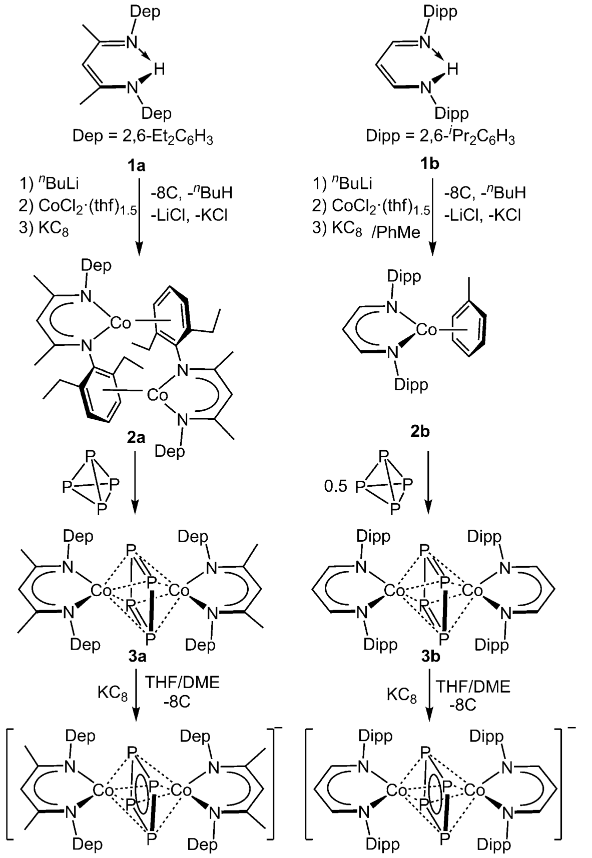
activation chemistry. One striking example of this unusual reactivity is the activation of dinitrogen to form ammonia under mild conditions.[9] In this context, we recently reported the activation of white phosphorus with a toluene-masked β-diketiminato nickel(I), leading to a novel η^3-P_4 complex with a transformed but yet unreduced P_4 unit.[10] The latter prompted us to develop suitable precursors with the aim to isolate complexes of **A** and to investigate its transformation to **B** in a complex. Herein we report the isolation of two cobalt(I) complexes with a neutral cyclo-P_4 ligand and their transformation under reducing conditions to two mixed-valent cobalt(I,II) complexes with a cyclo-P_4^{2-} ligand.

The synthesis of monovalent cobalt complexes $[(\mathrm{L^{Dep}Co})_2]$ (**2a**, $\mathrm{L^{Dep}} = \mathrm{CH[CMeN(2,6\text{-}Et_2C_6H_3)]_2}$) and $[\mathrm{L^{Dipp}Co{\cdot}toluene}]$ (**2b**, $\mathrm{L^{Dipp}} = \mathrm{CH[CHN(2,6\text{-}{}^{i}Pr_2C_6H_3)]_2}$) is straightforward and both compounds can be prepared in a one-pot reaction (Scheme 2). The lithiation of the β-diketiminato ligand $[\mathrm{L^{Dep}H}]$ (**1a**, in THF) and $[\mathrm{L^{Dipp}H}]$ (**1b**, in THF and toluene) with ^{n}BuLi, followed by metathesis with the cobalt dichloride THF complex and subsequent reduction with potassium graphite (KC_8) resulted in the isolation of **2a** and **2b** as dark red crystals in 79% and 72% yield, respectively. Both complexes are paramagnetic as evidenced by their room-temperature magnetic moment in solution (3.57 μ_B in $[D_8]$THF for **2a**, 2.84 μ_B in $[D_6]$benzene for **2b**). The single-crystal X-ray diffraction studies confirm their identities and the molecular structures are shown in Figure 1.



Scheme 2. Synthesis of β-diketiminato cobalt(I) complexes **2a** and **2b**, the formation of cyclo-P_4 complexes **3a** and **3b** as well as cyclo-P_4^{2-} complexes **4a** and **4b**, respectively.

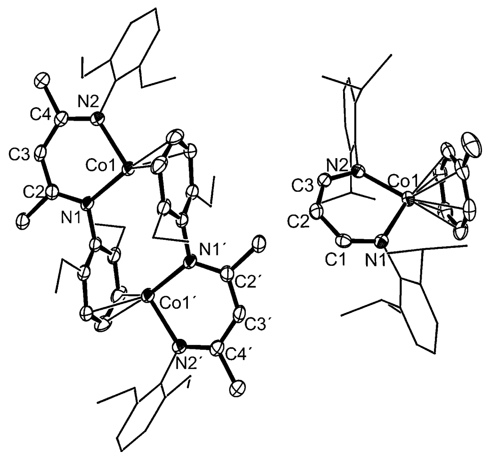


Figure 1. Molecular structure of **2a** (left) and **2b** (right). Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′) in **2a**: $-x+2$, $-y+1$, $-z+1$. Selected distances (Å) and angles (°) for **2a**: Co1–N1 1.977(2), Co1–N2 2.041(2), N1–C2 1.348(3), N2–C4 1.332(3), C2–C3 1.394(3), C3–C4 1.397(3), Co···C_{ring} 2.131(3)–2.537(3), N1-Co1-N2 92.62(8). Selected distances (Å) and angles (°) for **2b**: Co1–N2 2.017(2), Co1–N1 2.017(2), N1–C1 1.321(2), N2–C3 1.320(2), C1–C2 1.391(3), C2–C3 1.385(3), Co···C_{ring} 2.190(2)–2.237(2), N2-Co1-N1 91.09(6). Ellipsoids at 50% probability level.

Complex **2a** crystallizes as a dimer, in which the cobalt ions bind to the β-diketiminato-N atoms as well as to an aryl ring of a second β-diketiminato unit of the dimer in a η^3-coordination mode. A similar structure was reported previously by us for a nickel(I) species.[11a] The toluene complex **2b** is a mononuclear complex with a η^6-toluene. A similar high-spin d^8 cobalt(I) complex with a sterically less encumbering β-diketiminato ligand was reported by Warren and coworkers.[11b]

Treating toluene solutions of **2a** and **2b** with half of an equivalent of P_4 at room temperature led to the formation of $[(\mathrm{L^{Dep}Co})_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)]$ (**3a**) and $[(\mathrm{L^{Dipp}Co})_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)]$ (**3b**), which precipitate from the reaction solution as dark brown solids. Both products can be isolated in good yields (88% for **3a** and 89% for **3b**) upon work-up (Scheme 2). In both cases, when excess white phosphorus was used, the same products were generated exclusively. The composition of **3a** and **3b** was proven by elemental analysis and electrospray ionization (ESI) mass spectrometry. Their molecular structures have been established by single-crystal X-ray diffraction analysis and are shown in Figure 2 (**3a**) and Figure 3 (**3b**).

Both molecular structures of **3a** and **3b** consist of a $[\mathrm{Co_2}(\mu_2{:}\eta^4,\eta^4\text{-}P_4)]$ octahedral core, coordinated by two slightly puckered β-diketiminato ligands. The Co···Co distances in **3a** (3.532 Å) and **3b** (3.491 Å) exclude any significant metal–metal interaction in both complexes. The Co–P distances, ranging from 2.338(1) to 2.367(1) Å, are slightly longer than those observed for $[(\mathrm{Cp^*Co})_2(\mu_2{:}\eta^2,\eta^2$-

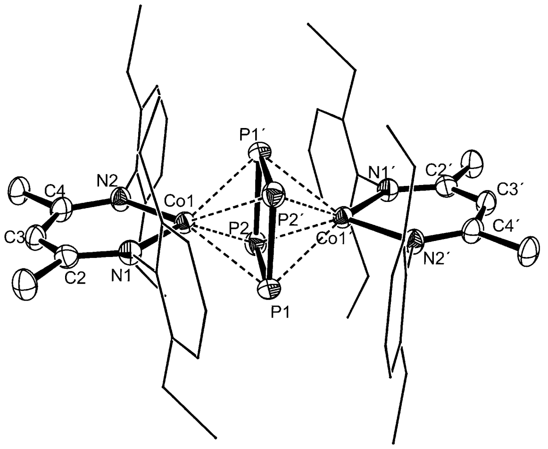


Figure 2. Molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+1$, $-y+1$, $-z$. Selected distances (Å) and angles (°): Co1–N2 1.905(3), Co1–N1 1.915(3), Co1–P1 2.351(1), Co1–P2′ 2.355(1), Co1–P2 2.362(1), Co1–P1′ 2.367(1), P1–P2 2.130(1), P1–P2′ 2.289(2), N2-Co1-N1 94.4(1), P2-P1-P2′ 89.99(5), P1-P2-P1′ 90.01(5). Ellipsoids at 50 % probability level.

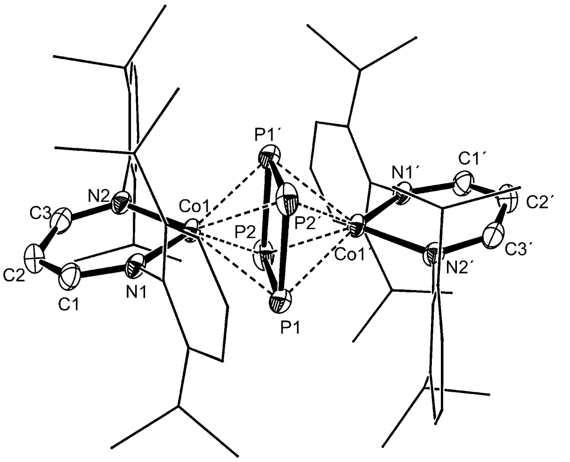


Figure 3. Molecular structure of **3b**. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms with (′): $-x+1/2$, $-y+3/2$, $-z+1$. Selected distances (Å) and angles (°): Co1–N1 1.906(3), Co1–N2 1.907(3), Co1–P1 2.338(1), Co1–P2 2.3415(9), Co1–P2′ 2.346(1), Co1–P1′ 2.3512(9), P1–P2 2.124(1), P1–P2′ 2.298(1), N1-Co1-N2 93.1(1), P2-P1-P2′ 89.96(4), P1-P2-P1′ 90.04(4). Ellipsoids at 50 % probability level.

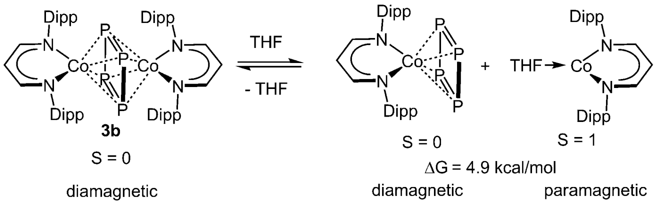
$P_2)_2]$ (2.301(4)–2.309(4) Å).[7a] The most interesting features of **3a** and **3b** are the geometric parameters of the P_4 moieties (Table 1). In both structures, the P_4 units are planar and possess a rectangle structure with two long P–P bonds (2.289(2) Å for **3a** and 2.298(1) Å for **3b**) and two short P–P bonds (2.130(1) Å for **3a** and 2.124(1) Å for **3b**). The former P–P distances are longer than a P–P bond in free P_4 (2.21 Å), whereas the latter are significantly shorter than that.

Both **3a** and **3b** are diamagnetic in the solid state as shown by SQUID magnetization (SQUID = superconducting quantum interference device) and confirmed by solid-state

Table 1: Comparison of the P–P distances and Mayer bond order (MBO) in **3a** and **3b** as well as **4a** and **4b**.

Complex		3a	3b	4a	4b
P–P bond (short)	Exp. (Å)	2.130(1)	2.124(1)	2.163(1) 2.154(1)	2.1739(7)
	Calc. (Å)	2.131	2.132	2.166	2.183
	MBO	1.09	1.03	1.08	1.03
P–P bond (long)	Exp. (Å)	2.289(2)	2.298(1)	2.225(1) 2.230(1)	2.1976(7)
	Calc. (Å)	2.296	2.283	2.226	2.222
	MBO	0.89	0.93	1.08	1.03

^{31}P NMR magic angle spinning (MAS) measurements. The latter revealed a singlet resonance at $\delta = 169$ (**3a**) and 128 ppm (**3b**). However, dissolution of the compounds in THF leads to paramagnetic species. Susceptibility measurements of the solutions (Evans method)[12] at 298 K revealed a magnetic moment of 1.55 (**3a**) and 1.53 μ_B (**3b**). This observation is reminiscent to that of the diamagnetic dinuclear $[(LNi)_2P_4]$ complex (L = β-diketiminato ligand), which partially undergoes reversible dissociation to give paramagnetic [LNi] and $[LNiP_4]$ complex fragments in solutions.[10] Variable-temperature ^{1}H NMR measurements (50 °C to −60 °C) of **3a** and **3b** in $[D_8]$THF showed not only a decrease of the magnetic moments (1.11 μ_B at 213 K for **3a**; 1.08 μ_B at 213 K for **3b**) upon lowering the temperature, but also a drastic change of the chemical shifts of the paramagnetic resonance signals (see Supporting Information (SI), Figures S1 and S2). The paramagnetic behavior of the compounds in THF is in accordance with results of DFT calculations, which revealed a remarkably low Gibbs free energy of 4.9 kcal mol^{-1} for the dissociation of **3b** in THF to give $[L^{Dipp}Co(\eta^4\text{-}P_4)]$ and the paramagnetic $[L^{Dipp}Co(thf)]$ (Scheme 3). In line with that, the $[L^{Dipp}Co(thf)]$ complex fragment could be detected in the high-resolution (HR) ESI mass spectrum of **3b** in THF solutions [$m/z = 520.28483$ (calcd 520.28584)]. The analogous $[L^{Dep}Co(thf)]$ complex fragment could also be observed in THF solutions of **3a** at $m/z = 492.25325$ (calcd 492.25454) by HR-ESI mass spectrometry along with the corresponding $[L^{Dep}Co(\eta^4\text{-}P_4)]$ complex fragment ($m/z = 544.09137$; calcd 544.09207).



Scheme 3. A representation of the reversible dissociation of **3b** in THF solutions to give diamagnetic $[L^{Dipp}Co(\eta^4\text{-}P_4)]$ and the paramagnetic $[L^{Dipp}Co(thf)]$. DFT calculations at the B97D/6-31G(d)[Co, P: aug-cc-pVTZ] level of theory revealed the remarkably low dissociation energy of only 4.9 kcal mol^{-1}.

To shed light on the electronic structure of **3a** and **3b**, broken-symmetry DFT calculations were carried out (see SI). In agreement with experimentally obtained magnetic data, the calculations support that **3a** and **3b** have total low-spin ground states ($S_{\mathrm{tot}} = 0$), with one unpaired spin on each Co center coupled antiferromagnetically to each other ($J = -112\ \mathrm{cm}^{-1}$ for **3a** and $J = -119\ \mathrm{cm}^{-1}$ for **3b**). The geometry of the computed low-spin state also is in excellent agreement with the experimentally observed metric parameters (Table 1).

The Mayer bond order (MBO) suggests the presence of two different bonding situations in the P_4 moiety: single bonds for the longer P–P bonds (MBO < 1) and partial double bond character for the shorter P–P bonds (MBO > 1). Furthermore, the natural bond orbital (NBO) analysis revealed the interaction of each Co center with one shorter P–P moiety, which can be considered as the donation of the π bond to the vacant orbital of the Co center (see SI). The NBO charges of the P atoms show no additional electrons in the P_4 moiety, as all P atoms are neutral (average charge of P is +0.01). Therefore, calculations unambiguously support that the P_4-ligand in complexes of **3a** and **3b** is of type **A** (Scheme 1). Accordingly, **3a** and **3b** represent the first examples of **A′** with a neutral rectangular cyclo-P_4 (**A**). With the coordination of two cobalt(I) ions, the elusive neutral cyclo-P_4 species is now isolated as a ligand in the complexes.

The electrochemical properties of **3a** and **3b** were investigated by using cyclic voltammetry in THF solution, containing 0.3 M $^{n}Bu_4NPF_6$ as electrolyte (at 295 K, for further details see SI). The cyclic voltammogram (CV) of **3a** features one reversible redox event centered at $E_{1/2} = -1.5$ V (vs. Fc/Fc$^+$) and a complicated, possibly more-electron, quasi-reversible electrode process involving structural reorganization at $E_{1/2} = -2.7$ V. In addition, a separate scan indicated an irreversible oxidation at $E_{\mathrm{ox}} = -0.3$ V. In the case of **3b**, two reversible redox events were observed at $E_{1/2} = -1.4$ V and $E_{1/2} = -2.8$ V together with an irreversible oxidation wave at $E_{1/2} = -0.04$ V. The large separation of the redox events implies that the reduction of **3a** and **3b** may yield isolable reduced products. Accordingly, we performed the reduction of **3a** and **3b** with one molar equivalent amount of potassium graphite, KC_8, in THF at room temperature (Scheme 3). As expected, this led to the isolation of $[(L^{\mathrm{Dep}}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)][K(dme)_4]$ (**4a**) and $[(L^{\mathrm{Dipp}}Co)_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)][K(dme)_4]$ (**4b**) as dark brown crystals upon work-up (yield: 90 % for **4a**, 87 % for **4b**), respectively. The crystals of **4a** and **4b** obtained from 1,2-dimethoxyethane (DME) afforded high-quality X-ray diffraction data. The potassium cations in both structures are each coordinated by four DME molecules. Although the anion structure of **4a** is quite similar to its precursor **3a**, the differences between the alternating long P–P and short P–P bonds in **4a** decrease significantly ($\Delta_d = d_{(\mathrm{P-P})\mathrm{long}} - d_{(\mathrm{P-P})\mathrm{short}} = 0.07$ Å in **4a** vs. $\Delta_d = 0.16$ Å in **3a**, Figure 4, Table 1). In case of **4b** the equivalence of P–P bonds is even more pronounced compared with that of **3b** ($\Delta_d = 0.02$ Å for **4b** vs. $\Delta_d = 0.17$ Å for **3b**). This observation is in line with a rotation of the cyclo-P_4 unit about the Co–Co′ axis with respect to the supporting ligands (Figure 4), implying a π-electron delocalization within the P_4 ring. In fact, the P_4 rings in **4a** and **4b** are now close to a square geometry. The P–P distances in **4b** (2.1739(7), 2.1976(7) Å) are comparable to those observed for $[Cp^*(CO)_2Nb(\eta^4\text{-}P_4)]$ (2.136(2)–2.181(2) Å).[5a]

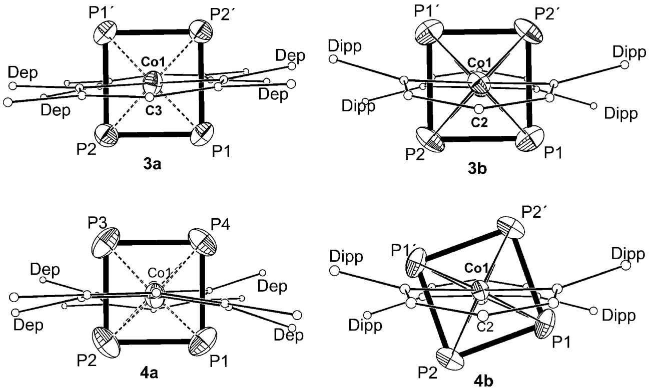


Figure 4. The Co_2P_4 cores viewed along Co1–Co1′ in the molecular structure of **3a**, **4a**, **3b**, and **4b**. Selected distances (Å) and angles (°) for **4a**: Co1–P1 2.3740(9), Co1–P4 2.3747(8), Co1–P2 2.3750(9), Co1–P3 2.3814(9), Co2–P2 2.3577(9), Co2–P3 2.3986(9), Co2–P4 2.4084(9), P1–Co2 2.3495(9), P1–P2 2.163(1), P1–P4 2.225(1), P2–P3 2.230(1), P3–P4 2.154(1), P2-P1-P4 90.12(4), P1-P2-P3 89.64(4), P4-P3-P2 90.23(4), P3-P4-P1 90.01(4). Selected distances (Å) and angles (°) for **4b**: Co1–P1 2.3734(5), Co1–P2 2.3751(5), Co1–P1′ 2.3768(5), Co1–P2′ 2.4046(5), P1–P2 2.1739(7), P1–P2′ 2.1976(7), P2-P1-P2′ 90.85(2), P1-P2-P1′ 89.15(2). Ellipsoids at 50 % probability level.

Both complexes **4a** and **4b** exhibit paramagnetic behavior in [D$_8$]THF solution and reveal magnetic moments of 2.32 μ_B and 2.12 μ_B at room temperature, respectively. Moreover, the solid-state magnetization measurement of **4b** shows a temperature-dependent effective magnetic moment (see Figure S16). Below 80 K the magnetic moment μ_{eff} remains constant at 1.7 μ_B, suggesting an $S = 1/2$ ground state. Upon increasing the temperature from 80 to 300 K, the value increases from 1.7 to 3.4 μ_B owing to gradual spin crossover from the $S = 1/2$ to the $S = 3/2$ spin state (see Figure S17). The EPR spectrum of **4b** in frozen THF solution confirms the 1/2 ground state (Figure S18).

Broken-symmetry calculations were carried out to elucidate the magnetic behavior of **4a** and **4b**. Consistent with the experimentally determined magnetism, the calculations revealed that **4a** and **4b** possess a total low-spin ground state ($S_{\mathrm{tot}} = 1/2$) with one and two unpaired spins on each Co center, antiferromagnetically coupled to each other ($J = -155\ \mathrm{cm}^{-1}$ for **4a** and $J = -161\ \mathrm{cm}^{-1}$ for **4b**). The geometries of the low-spin-state structures of **4a** and **4b** are in agreement with the experimentally observed distances (Table 1). In line with the P–P bond lengths, the MBO suggests that there is only one bonding situation present within the P_4 moiety, since all P–P bonds have the same MBO (1.08 for **4a** and 1.03 for **4b**). The latter reveals also partial π character, indicative of cyclic π-electron delocalization of the P_4 ligand. Furthermore, NBO analyses suggest that the extra electron resides in one of the p orbitals of the π system, whereas another extra electron stems from one of the Co centers (see SI). Thus there are a total of six π electrons in the P_4 moiety. Consistently, NBO charge analyses of **4a** and **4b** show increased negative charges on the P atoms (−0.17 and −0.19, respectively) compared to that of **3a** and **3b** (+0.01 for both). Therefore, the overall conclusion is that the cyclo-P_4 ligands in **4a** and **4b** are two-electron reduced, and thus representatives of type **B** P_4 complexes.

In summary, by utilizing the β-diketiminato ligand-supported cobalt(I) precursors, the dinuclear cobalt complexes **3a** and **3b** bearing the neutral tetraphosphacyclobutadiene ligand could be realized and fully characterized for the first time. Remarkably, the reduction of **3a** and **3b** with one molar equivalent of potassium graphite leads to the mixed-valent monoanionic cobalt(I,II) complex **4a** and **4b**, respectively, with a cyclo-P_4^{2-} unit having six π electrons and a square-planar structure. Further investigations regarding the reactivity of these complexes toward electrophiles with the aim to functionalize the phosphorus moieties in the coordination sphere of cobalt is currently in progress.

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