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Polyphosphides

Selective P₄ Activation by a Highly Reduced Cobaltate: Synthesis of Dicobalt Tetraphosphido Complexes


Abstract: Although the chemistry of transition metal polyphosphide anions has attracted significant attention, there are few reports of studies in which such species have been synthesized directly from white phosphorus. [K(OEt)₂][Co(BIAN)(cod)] (1, BIAN = 1,2-bis(2,6-disopropylphenylimino)acenaphthene, cod = 1,5-cyclooctadiene), which is readily prepared by ligand exchange from [K(thf)][Co(cod)₂], reacts with P₄ to afford [K(OEt)₂][Co(BIAN)₄(μ-η⁴-P₄)] (2a) in 61% yield (isolated product). [K(OEt)₂][Co(BIAN)(μ-η⁴-P₄)₄] (2b) and [K][18-crown-6][MeCN]₂[(BIAN)Co₂(μ-η⁴-P₄)₂] (2c) were obtained by recrystallizing 2a from diethyl ether and acetonitrile (and using [18]crown-6 in case of 2c). Oxidation of 2a with [Cp₂Fe]BAr₅₂ (one equivalent) and subsequent recrystallization of the product from different solvents gave [K(OEt)₂][Co(BIAN)₄(μ-η⁴-P₄)₂] (3a) and [K(dme)][(BIAN)Co₂(μ-η⁴-P₄)₂] (3b; dme = 1,2-dimethoxyethane). Neutral [(BIAN)Co₂(μ-η⁴-P₄)₂] (4) was obtained in moderate yield by oxidizing 2a with two equivalents of [Cp₂Fe]BAr₅₂. The new complexes were characterized by NMR, EPR (in the case of 3a), and UV/Vis spectroscopy, and elemental analysis. The molecular structures revealed by X-ray crystallography display planar cyclic or open-chain P₄⁺ units sandwiched between (BIAN)Co fragments.

Introduction

Transition metal-mediated transformations are a potentially attractive approach for the efficient and environmentally benign activation of white phosphorus (P₄).[1] Subsequent reactions of the resulting polyphosphido complexes may give rise to interesting new polyphosphido compounds and may contribute to the development of new, effective P₄ functionalization protocols.[2]

Traditionally, transition metal-containing polyphosphide anions have been prepared by reaction of alkali metal polyphosphides, for example, M₃P₄ (M = alkali metal), with transition metal carbonyls or transition metal halides,[3] or by reducing neutral polyphosphido complexes with electropositive metals, such as sodium, potassium, or lanthanoid complexes.[4–7] The synthesis of anionic cyclopentadienyl and β-diketiminato polyphosphorus compounds by reduction of neutral precursors has recently attracted particular attention.[8–10] The [Nb(ODipp)₂]⁻ anion (A, Dipp = 2,6-iPr₂C₆H₄; Figure 1), prepared in one step by reducing [NbCl₃(OAr)₂(thf)] with Na/Hg in the presence of P₄, is a landmark example for reactive transition metal polyphosphide anions.[8] Anion A was used as a P₄⁺– transfer agent to synthesize elusive EP₃ molecules (E = As, Sb). Low-valent transition metallic anions can be used to activate P₄ directly, forming polyphosphide anions. However, this approach has rarely been exploited to date. Ellis and coworkers prepared the intriguing sandwich complex B (Figure 1) by treating [Ti(C₆H₄Me)₃]²⁺ (C₆H₄Me = naphthalene) with P₄.[9] We investigated the reactivity of the naphthalene ferrate [Cp₂Fe(C₆H₄Me)²⁺] with P₄.[10] A mixture of several structurally diverse products was formed, including the crystallographically characterized complexes C and D (Figure 1). This result shows the potential complexity of this type of transformation.

In extension of our previous studies, we sought to prepare new complex anions that are able to activate P₄ more selectively. Herein we report that the reaction of the new cobaltate complex [K(OEt)₂][Co(BIAN)(cod)] (1, cod = 1,5-cyclooctadiene) with P₄ affords the [(BIAN)Co₂(μ-η⁴-P₄)₂]⁻ dianion, which we have isolated in the form of three potassium salts.

Figure 1. Anionic transition metal polyphosphido complexes directly obtained by P₄ activation. Cp²⁺ = C₆H₄Me, Dipp = 2,6-iPr₂C₆H₄.
A single crystal X-ray diffraction (XRD) experiment revealed the molecular structure of \( \text{1} \) (Figure 2a), which adopts a distorted planar coordination environment for cobalt with a twist angle of 17.6°. The potassium cation is \( \eta^1 \)-coordinated by the planar \( \alpha \)-diimine framework of the BIAN ligand and additionally by two THF molecules. The \( C1–N1 \) \( 1.380(3) \AA \), \( C2–N2 \) \( 1.382(3) \AA \), and \( C1–C2 \) \( 1.383(3) \AA \) bond lengths of the \( \{\text{Co(BIAN)}\} \) anion are equal within experimental error. The elongated \( C–N \) and shortened \( C–C \) bond lengths with respect to the free BIAN molecule indicate the presence of a \( \text{BIAN}^2^- \) dianion (Figure 2b).\(^{14-17} \) It is noteworthy that the iso-electronic complex \( \{\text{Ni(BIAN)}\} \), synthesized by Stephan and co-workers, features a monoanionic \( \text{BIAN}^- \) framework (\( C–N \) 1.324–1.336 \AA; \( C–C \) 1.426–1.428 \AA)\(^{17} \). The observation of a \( \text{BIAN}^- \) dianion in \( \text{1} \) is likely attributed to the low effective nuclear charge and lower reduction potential of cobalt.

DFT optimization (B3LYP/def2-TZVP level, see the supporting information for details) of the closed-shell singlet state gave a close agreement between the computed structure and the crystallographically determined one. Optimizations of the open-shell singlet using the broken symmetry formalism converged at the closed-shell structure, indicating that this represents the ground state.

One set of \(^1\text{H} \) NMR signals is observed for \( \text{1} \) in \( \text{D}_2\text{THF} \) for the BIAN fragment and coordinated cod. The latter gives rise to two multiplets at \( \delta = 1.12 \) and 2.33 ppm for the diastereotopic methylene protons and another multiplet at \( \delta = 2.91 \) ppm for the methine protons. Signals at \( \delta = 32.6 \) and 64.1 ppm are observed in the \(^{13}\text{C} / (\text{H}) \) NMR spectrum. \( \{\text{Co(cod)}\}^+ \) gives rise to similar NMR shifts.\(^{12} \) A cyclic voltammogram recorded in THF/\( n\text{Bu}_{4}\text{N} \)(PF\(_6\)) revealed a quasi-reversible one-electron oxidation process at a fairly negative potential of \( E_{1/2} = −1.72 \) V vs. \( \text{Fc/Fc}^+ \) (see the Supporting Information, Figure S59), which presumably corresponds to the oxidation of \( \text{1} \) to give neutral \( \{\text{Co(BIAN)}\} \).\(^{16} \) The UV/Vis spectrum of \( \text{1} \) in THF shows one intense absorption at \( \lambda = 289 \) nm, as well as two bands in the visible region at \( \lambda = 441 \) and 663 nm (see the Supporting Information, Figure S10). The absorption maximum of the latter band is shifted to \( \lambda = 485 \) nm in diethyl ether. This substantial change may indicate positive solvatochromism, a phenomenon that is typically observed for unsymmetrical ligand-to-ligand charge transfer (LLCT) complexes.\(^{16} \)

The reaction of \( \text{1} \) with white phosphorus gives \( \{\text{K(thf)}\}_2\{\text{BIAN} \text{Co} \} \{\mu-\eta^1\text{P}\} \) (2a, Scheme 2) in 61% yield (isolated product). Monitoring by \(^1\text{H} \) and \(^31\text{P} / (\text{H}) \) NMR spectroscopy showed that the reaction is highly selective in THF at room temperature and proceeds to completion within several hours. Crystals of \( \{\text{K(OEt)}_3\}_2\{\text{BIAN} \text{Co} \} \{\mu-\eta^1\text{P}\} \) (2b) suitable for single-crystal XRD were obtained by recrystallization from diethyl ether. The structure shows a centrosymmetric \( \{\text{BIAN} \text{Co} \} \{\mu-\eta^1\text{P}\} \) dianion with an inverted sandwich structure (Figure 3, top). The two potassium cations are each connected to two \( P \) atoms, one diethyl ether molecule, and the Dipp sub-
stituents. The salient feature of the structure is the rectangular $P_4$ unit located on the crystallographic inversion center. The $P1–P2$ bond length [2.161(1) Å] lies in the known range for aromatic $P^{n-}$ anions, for example, that in Korber’s tetraphosphide $Cs_2P_4$ [2.146(1) and 2.1484(9) Å].[20–22] $P1–P2$ [2.500(1) Å] is much longer than a typical $P–P$ single bond, but shorter than a van der Waals contact.[4b, 22, 23]

According to these structural parameters, a superposition of two resonance structures (see below, Figure 9a), comprising two $P^{n-}$ dianions (I) and a $P_4^{n-}$ unit (II), appears to be an apt description of the structural and electronic situation. Assuming the presence of monoanionic BIAN$^-$ ligands, as indicated by the structural parameters $[C1–N1 1.348(2), C2–N2 1.343(4), C1–C2 1.404(4)]$,[14–17] this would result in the two cobalt atoms having the $+II$ oxidation state.

To probe whether the potassium ions influence the shape of the Co$_4P_4$ core,[20] $[K([18]crown-6)[MeCN]_2][\{BIAN\}Co_2\mu-\eta^2:\eta^4-P_4]_2$ (2c) with an ion-separated structure was synthesized by recrystallizing 2a from acetonitrile in the presence of two equivalents of [18]crown-6. The potassium cations do not interact with the anion in the crystal structure (see the Supporting Information, Figure S7). The anion of 2c is similar to 2b, but shows slightly shorter $P–P$ bond lengths in the $P_4^{n-}$ units $[P1–P2 2.0862(6) Å], that is, 0.075 Å shorter than in 2b,$ and a slightly longer separation between these units $[P1–P2$ $2.5523(6) Å], elongated by 0.052 Å compared to 2b.

The cyclic voltammogram of 2a recorded in THF/[$nBu_4N$][PF$_6$] features two reversible one-electron oxidation processes at $E_{1/2} = −1.98$ V and $−1.26$ V vs. $Fc/Fc^+$, and an irreversible two-electron oxidation wave at $E_{pa} = −0.43$ V vs. $Fc/$
Additional weak irreversible waves at $E_{pa} = -0.66$ V and $E_{pc} = -1.58$ V presumably arise from secondary redox processes of the products formed by the irreversible oxidation event.

Stimulated by these promising CV data, we synthesized the monopotassium salt $\text{[K(Oct)}_2(\text{B{IAN})Co}]_2(\mu-\eta^1-\eta^1-\eta^1-\eta^1-P)]$ (3a) and the neutral complex $\text{[([B{IAN})Co]}_2(\mu-\eta^1-\eta^1-\eta^1-P)]$ (4) on a preparative scale by treating 2a with $[\text{Cp}_2\text{Fe}]\text{[BAr}^2]$ (eight equivalents) afforded free $P_a$ as the only species detected in the $^{31\text{P}}$ resonance structure II, Figure 9a, a framework that was previously only observed for some Zr, Nb, and Ta complexes.\(^{23,24}\) Inspection of the C–N and C–C distances [CI–N1 1.32(1), C2–N2 1.32(1), C1–C2 1.44(1) Å] indicates that mononionic BIAN–anions are present with little back-bonding of the metal.\(^{17}\)

Compared to 2b, the Co–Co distance increases by 0.2 Å [Co1–Co1′ 3.469(3) Å, cf. 3.2733(9) Å in 2b]. The potassium ion is disordered over two positions and has the same ligand environment as in 2b.

Complex 3a is paramagnetic. The solution effective magnetic moment [2.01(1) μμ] determined in DMSO indicates the presence of one unpaired electron per molecule. As a consequence of its paramagnetic nature, broad $^1\text{H}$ NMR signals are observed in the range of –0.9 to 19.3 ppm. The X-band EPR spectrum of 3a (Figure 6) recorded in THF (ca. 0.1 m nBu4N[Pf6] added to obtain a better glass) reveals a rhombic signal with cobalt hyperfine interactions characteristic for a $S = 1/2$ system. A decent simulation of the experimental spectrum was obtained assuming a hyperfine interaction (HFI) with two equivalent cobalt nuclei ($g_x = 2.127, g_y = 2.081, g_z = 2.008; A_{Co}^{xy} = 50$ MHz, $A_{Co}^{zz} = 200$ MHz, $A_{Co}^{yy} = 240$ MHz). Other HFIs are not resolved, indicating that the unpaired electron is primarily delocalized over the two cobalt atoms.

The ion-separated structure 3b was obtained by recrystallizing a sample of 3a from 1,2-dimethoxyethane (DME). The single-crystal XRD analysis (see the Supporting Information, Figure S8) shows that, in contrast to 3a, the Co4P4 core of 3b (Figure 5) features an open-chain tetraphosphabutadiene fragment (II, Figure 9a) with double bonds between the terminal phosphorus atoms [P1–P2 2.0631(5) Å] and an elongated single bond between the internal P atoms [P2–P2′ 2.3912(8) Å]. The large distance between the terminal P atoms [P1–P1′ 3.4182(2) Å] indicates the absence of a P–P bond.
The neutral compound [(BIAN)Co]_2(μ-η^4-η^4-P_4)] (4) was obtained in 49% yield by oxidizing 2a with two equivalents of [Cp_2Fe]BAr^+. The solid-state molecular structure is disordered (Figure 3 and 5) and consists of two components, a major component 4a (91% occupancy) and a minor one 4b (9% occupancy). 4a includes a rectangular, almost square-like, cyclo-P_4^- ligand [P1-P2-P3 89.7(1), P2-P3-P4 90.17(8)°] with P–P bond lengths [2.202(3)–2.274(2) Å] similar to those in monoanionic 3a. The C–N and C–C distances [C1–N1 1.344(5), C2–N2 1.336(5), C1–C2 1.444(6) Å] indicate the presence of BIAN- monoanions. 3b gives the same spectrum as 2a = 2c = 3b gives rise to one set of overlapped signals. Both res-
sonances are characterized by fast relaxation and a large line-
width. The major signal at δ = 253.9 and 249.7 ppm in a 10:1 ratio is plausible that these signals correspond to the major and minor components 4a and 4b observed in the single-crystal X-ray structure (vide supra). A variable temperature 31P^1^H NMR experiment showed only minor changes in the temperature range of –80 to 100 °C (see the Supporting Information, Figure S6); coalescence of the two signals was not observed. Similarly, 31P–31P EXSY spectra did not reveal any cross peaks between the two signals. These observations support the notion that 4a and 4b do not exchange in solution. 2a gives the same spectrum as 3a, despite the compounds having an ion-contact structure vs. an ion-separa-
rate structure in the solid state. 2a and 2c give rise to singlets at δ = –45.9 ppm for 2a and δ = –44.0 ppm for 2c in the 31P^1^H NMR spectra recorded in [D_8]DMF. The similar electronic spectra and chemical shifts indicate similar structures for these compounds in solution.

The electronic spectra of 2–4 in THF (see the Supporting Informa-
tion, Figure S11) show medium intense bands in the NIR range at λ = 795 and 1135 nm (for 2a), 777 and 1319 nm (for 3a), and 884 nm (for 4). These low-energy bands presumably arise from LLCT transitions. The spectra feature additional in-
tense absorptions in the UV and visible regions [2a and 2c: 345 and 585 nm; 3a and 3b: 342 and 575 nm; 4: 336, 427, 547, and 693 nm]. The UV/Vis spectrum of 2c is identical to that of 2a, while 3b gives the same spectrum as 3a, despite the compounds having an ion-contact structure vs. an ion-separated structure in the solid state. 2a and 2c give rise to single-
gets at δ = –45.9 ppm for 2a and δ = –44.0 ppm for 2c in the 31P^1^H NMR spectra recorded in [D_8]DMF. The similar electronic spectra and chemical shifts indicate similar structures for these compounds in solution.

Comparing the molecular structures of 2–4 (Figure 9), we can conclude that an oxidation or reduction of the whole complex apparently hardly affects the oxidation state of the P_4^- fragment. Thus, according to the structural data, the electronic structure of 2b and 2c may be described as a superposition of two mesomeric forms II–II. Resonance form I comprises two separated P_2^- units (I, Figure 9a,b), whereas II represents a P_4^- ring. The solid-state structures of mixed-valence 3a and 3b feature a rhombic cyclo-P_4^- and a chain-like catena-P_4^- fragment, respectively. The oxidation 2a–3a/b thus appears to be a metal-centered redox process; the oxidation state of the tetraphosphorus fragment remains the same. Remarkably, even neutral 4, obtained by two-electron oxidation of 2a features a cyclo-P_4^- unit for the major component 4a of the dis-
ordered structure. The oxidation state of the catena-P_4^- unit of the minor species 4b is uncertain. To summarize, the P_4^- ligand undergoes remarkable structural transformations, but retains its highly reduced tetraanionic character in the neutral, anionic, and dianionic forms of the complex. Nonetheless, its structure appears to be very sensitive to subtle changes in the
oxidation state of the cobalt atoms and the presence of differently solvated potassium counterions. Similar observations were previously made for cyclopentadienyl complexes \([\text{Cp}^3\text{M},\text{M} = \text{Fe} \text{ and Co}]\), where the substitution pattern on the cyclopentadienyl ligand has a profound effect on the structures of the \(\text{P}_4^+\) fragment.\(^{23b,28}\)

Furthermore, the structures of 2–4 can be distinguished from related \(\beta\)-diketiminate iron and cobalt complexes E–L (Figure 9) recently reported by the groups of Driess and Scheer.\(^{27,28}\) Driess and co-workers prepared \([(\text{nacnac})\text{Co}_2(\mu-\eta^1:\eta^1-\text{P}_4)\text{]}\) (G, nacnac = \(\text{CH}[\text{CMeN}(2,6-\text{Et}_2\text{C}_6\text{H}_3)]\)), \([(\text{nacnac})\text{Co}_2(\mu-\eta^1:\eta^1-\text{P}_4)\text{]}\) (H, nacnac = \(\text{CH}[\text{C}(2,6-\text{Pr}_2\text{C}_6\text{H}_4)]\)), and \([(\text{nacnac})\text{Fe}_2(\mu-\eta^1:\eta^1-\text{P}_4)\text{]}\) (K) by reducing the neutral precursors E, F, and J (Figure 9c).\(^{27}\) Scheer and co-workers compared the steric influence of different nacnac ligands in related neutral species \([(\text{nacnac})\text{Fe}_2(\mu-\eta^1:\eta^1-\text{P}_4)\text{]}\) (L, Figure 9c, nacnac = \(\text{CH}[\text{C}(2,6-\text{MeC}_6\text{H}_4)]\)) , \([(\text{nacnac})\text{Fe}_2(\mu-\eta^1:\eta^1:\eta^1-\text{P}_4)\text{]}\) (M, nacnac = \(\text{CH}[\text{CMeN}(2,6-\text{MeC}_6\text{H}_4)]\)), and \([(\text{nacnac})\text{Fe}_2(\mu-\eta^1:\eta^1:\eta^1-\text{P}_4)\text{]}\) (N, nacnac = \(\text{CH}[\text{CH}_2(2,6-\text{MeC}_6\text{H}_4)]\)).\(^{29}\) The \(\text{Co}_2\text{P}_4\) complexes E and F feature an unusual neutral cyclo-P\(_4\) ligand (Figure 9c, V), which transforms into a cyclo-P\(_4^+\) dianion (IV) upon one-electron reduction to afford G and H, respectively. Notably, 3a and 3b are isoelectronic with the \(\text{Co}_2\text{P}_4\) complexes G and H. Whereas the latter feature a dianionic P\(_4^+\) framework, the more strongly electron-donating (\(\text{BiAN}\)) units apparently induce the presence of a tetranionic P\(_4^+\) moiety in 3a as well as 3b and even in 4a (see above). The Fe\(_2\)P\(_4\) species J and K include non-interacting P\(_4^+\) units (l, Figure 9a), whereas closely related L, with more sterically encumbering Dipp substituents, features a cyclo-P\(_4^+\) dianion (III) very similar to that in the cobalt compounds G and H. In contrast to E–L, the Fe\(_2\)P\(_4\) complexes M and N (not shown in Figure 9) bear smaller 2,6-dimethylphenyl substituents. As a result, they have a tetrancular structure where a P\(_4^+\) ligand with a realgar-like structure coordinates to four (\(\text{nacnac}\))Fe fragments.\(^{28}\)

Subtle differences in the steric interaction of the ligand substituents thus appear to strongly affect the oxidation state of the central P\(_4\) unit and the structure of the Fe\(_2\)P\(_4\) core.

**Conclusion**

New dinuclear cobalt tetraphosphido complexes \([(\text{BIAN})\text{Co}_2(\mu-\eta^1-\text{P}_4)\text{]}\) (k = 0, 1, \(-1\), \(-2\)) were obtained in three different oxidation states by treating the complex anion [K(OEt\(_2\))\(_2\)](\(\text{Co(BIAN)(cod)}\)) (I) with P\(_4\) and subsequent preparative oxidation of the reaction product [K(thf)](\(\text{[BIAN]Co}(\mu-\eta^1-\text{P}_4)\text{]}\) (2a). The molecular structures of the resulting complexes feature a P\(_4^+\) framework.\(^{23}\) Its structure is significantly influenced by oxidation and reduction, as well as by coordination by the potassium cation. Thus, a cyclic P\(_4^+\) moiety is found in the molecular structures of 3a and 4a, whereas an open-chain P\(_4^+\) unit is observed in 3b. The use of the redox-active BIAN ligand appears crucial for achieving a high degree of P\(_4\) reduction.\(^{25,29}\) This observation underlines the exceptional electron-releasing and -accepting properties of the Co(BIAN) moiety. The subsequent reactivity of tetraphosphido complexes 2–4 is currently under investigation. Beyond P\(_4\) activation, the reactivity of 1 and related complexes is being pursued, including potential catalytic applications.

**Figure 9.** a) Schematic representation of possible structures for a planar P\(_4\) framework; b) summary of structural data of structural data of \(\beta\)-diketiminate complexes E–M prepared by the groups of Driess and Scheer.\(^{27,28}\)
Experimental Section

General procedures and starting materials

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques or an MBrän UniLab glovebox. Solvents were dried and degassed with an MBrän SPS800 solvent-purification system. Tetrahydrofuran and toluene were stored over molecular sieves (3 Å). Diethyl ether and n-hexane were stored over a potassium mirror. NMR spectra in solutions were recorded on Bruker Avance 300 and Avance 400 spectrometers at 300 K, if not stated otherwise, and internally referenced to residual solvent resonances. The solid-state 13C NMR measurement was performed on an Infinityplus spectrometer (Agilent) operated at 7 Tesla, equipped with a 6 mm pencil CPMAS probe. The spectrum was indirectly referenced to H2PO4 (85% in H2O). The experimental X-band EPR spectrum of 3a was recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a He temperature-control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g-values and linewidths by using the EPR simulation program WISEPR, available on request from Prof. F. Neese (MPI CEC Mülheim a/d Ruhr). Melting points were measured on samples in sealed capillaries on a Stuart SMP10 melting-point apparatus. UV/Vis spectra were recorded on a Varian Cary 50 spectrophotometer. NMR spectra were recorded on a Bruins Instruments Omega 20 spectrometer. Elemental analyses were carried out by the analytical department of Regensburg University. The starting materials [K(thf)6][Co(1,5-cod)2]43 and BIAN44 were prepared according to previously reported procedures.

Synthesis

1: A solution of BIAN (1.005 g, 2.01 mmol, 1.0 equiv) in THF (70 mL) was added to a solution of [K(thf)6][Co(1,5-cod)2]43 (660 mg, 2.01 mmol, 1.0 equiv) in THF (10 mL). An immediate color change to dark green was observed. After stirring the reaction mixture for two hours, the solvent was removed and the residue was taken up in diethyl ether (200 mL). Insoluble material was removed by filtration and the filtrate was concentrated to 3 mL and stored at room temperature. Dark green microcrystals of 1 formed upon storing for one day. Crystals suitable for X-ray diffraction were obtained by diffusion of n-hexane into a concentrated THF solution of 1. The compound contained a variable amount of THF molecules after drying in high vacuum, which could be determined by 1H NMR spectroscopy and elemental analysis. Yield 1.166 g (71%); m.p. > 230 °C (decomp. to a black oil): 1H NMR ([D8]THF, 300 K, 400.13 MHz): δ = 0.96 (br m, 12H, CH2(CH3)2), 1.12 (br m, 10H, Et4O, cod-CH3), 1.38 (br m, 12H, CH2(CH3)2), 2.33 (br m, 4H, cod-CH3), 4.50 (br m, 4H, CH2(CH3)2), 4.89 (br m, 2H, CH2(CH3)2), 6.20 (br m, 2H, CH2(CH3)2), 6.28 (br m, 2H, CH2(CH3)2), 7.00–7.09 ppm (br m, 6H, m-/p-CH2); 13C NMR ([D8]THF, 333 K, 400.13 MHz) δ = 0.96–0.99 (br m, 16H, CH2(CH3)2/cod-CH3), 1.41 (d, 3J(H,H) = 6.6 Hz, 12H, CH2(CH3)2), 2.34 (br m, 4H, cod-CH3), 2.90 (br m, 4H, cod-CH3), 4.48 (sept, 3J(H,H) = 6.6 Hz, 4H, CH2(CH3)2), 5.01 (d, 3J(H,H) = 6.3 Hz, 2H, CH2(CH3)2), 6.28 (br m, 12H, CH2(CH3)2), 6.34 (t, 3J(H,H) = 7.7 Hz, 2H, CH2(CH3)2), 7.01–7.08 ppm (br m, 6H, m-/p-CH2); 13C NMR ([D8]THF, 300 K, 100.61 MHz) δ = 24.9 (CH2(CH3)2), 25.4 (CH2(CH3)2), 28.1 (CH2(CH3)2), 32.6 (cod-CH3), 64.1 (cod-CH3), 114.3 (CH2(CH3)2), 118.6 (CH2(CH3)2), 122.7 (CH2(CH3)2), 122.9 (CH2(CH3)2), 127.3 (CH2(CH3)2), 127.5 (Cu), 135.8 (Cu), 137.8 (Cu), 143.5 (Cu), 145.2 (Cu), 154.8 ppm (iso-CH2); UV/Vis (THF): λmax (ε) = 289 (26000), 441 (12000), 663 nm (8550 Lmol⁻¹ cm⁻¹); UV/Vis (EtOH): λmax (ε) = 284 (24000), 436 (8500), 485 nm (9000 Lmol⁻¹ cm⁻¹); elemental analysis calcd for C34H44N6CoK2O12: C 63.84, H 7.10, N 9.30, found: C 63.64, H 7.21, N 8.94.

2a, 2b, and 2c: A solution of [Co(CO)2Cl2]4 (55 mg, 0.053 mmol, 1.0 equiv) in THF (3 mL) was added dropwise to a suspension of 2a (77 mg, 0.053 mmol, 1.0 equiv) in THF (3 mL). An immediate color change to dark blue was observed. After stirring the reaction mixture for 24 h, the solvent was removed and the residue was washed with n-hexane (7 mL). After extracting the residue with diethyl ether (8 mL), the filtrate was concentrated to 3 mL and stored at room temperature. Dark blue X-ray-quality crystals of 3a formed upon storing for five days. Yield: 29 mg (41%); effective magnetic moment ([D8]THF): μeff = 4.0(1) μB. 1H NMR ([D8]THF, 300 K, 400.13 MHz) δ = −0.9 (br s, 8H, Ar-H), 1.2 (br s, overlap with Et4O), 3.4 (br s, overlap with EtO), 7.3 (br s), 17.4 (br s), 19.3 (ppm s); UV/Vis (THF): λmax (ε) = 342 (44000), 575 nm (66500 Lmol⁻¹ cm⁻¹); NIR (THF): λmax (ε) = 777 (25000), 1319 nm (20000 Lmol⁻¹ cm⁻¹); elemental analysis calcd for C63H54N6CoK4P12 (135644): C 67.30, H 6.69, N 4.11, found: C 66.89, H 6.73, N 4.01. Crystals of [K(dme)2]...
A solution of [Cp₂Fe]BF₄ (157 mg, 0.149 mmol, 2.2 equiv) in THF (3.5 mL) was added dropwise to a suspension of 2 (100 mg, 0.068 mmol, 1 equiv) in THF (3 mL). A color change to dark red was observed after stirring. The reaction mixture for 24 h, the solvent was removed. The residue was extracted with diethyl ether (10 mL) and subsequently with toluene (8 mL). The resulting toluene extract was concentrated to 3 mL and stored at room temperature. Dark red X-ray-quality crystals of 4 formed upon layering the solution with n-hexane (6 mL) and storing for seven days. Yield 48 mg (49%): 1H NMR (CD₂Cl₂, 300 K, 0.403 MHz) δ = 0.93 (d, J(H,H) = 6.8 Hz, 24H, CH₂(C₆H₅)), 1.28 (d, J(H,H) = 6.8 Hz, 24H, CH₂(C₆H₅)), 4.17 (sept., J(H,H) = 6.8 Hz, 24H, CH₂(C₆H₅)), 6.54 (br, 21H, CHDipp), 6.60 (t, J(H,H) = 7.6 Hz, 8H, meta-CH₂), 7.34 (t, J(H,H) = 7.6 Hz, 4H, para-CH₂), 7.48 ppm (d, J(H,H) = 8.0 Hz, 4H, CH₃); 13C NMR (CD₂Cl₂, 300 K, 10.16 MHz) δ = 24.5 (CH₂(C₆H₅)), 25.0 (CH₂(C₆H₅)), 29.0 (C₆H₅), 120.3 (C(Dipp)), 123.8 (meta-CDipp), 125.7 (CH₂Dipp), 127.2 (para-CDipp), 129.6 (CH₂Dipp), 133.4 (C(Dipp)), 134.6 (C(Dipp)) 139.8 (o-CDipp), 154.2 (ipso-CDipp), 161.1 ppm (C(Dipp)), one 13C NMR signal of a quartet.

Full Paper


[18] A very broad, irreversible oxidation wave was detected at $E_{\text{pa}} = -0.1\text{ V}$ vs. Fc/Fc’ and secondary processes at $E_{\text{pc}} = -2.0\text{ V}$ vs. Fc/Fc’ were also observed. See the Supporting Information for further details.


[25] The half-wave potential for the reduction of 4 (E_{\text{pa}}(4-3a) = -1.26\text{ V vs. Fc/Fc}’) is more positive than that for the complexes E and F (E_{\text{pa}}(E-G) = -1.5\text{ V vs. Fc/Fc}’ (E_{\text{pa}}(F-H) = -1.4\text{ V vs. Fc/Fc}’), indicating that the BIAN complexes are more easily reduced than the the corresponding nacnac compounds."

[26] A possible explanation for the presence of two species 4a and 4b is that they are electromers. (23) In this case, the cobalt atoms and the P$_{2}$ unit might have different oxidation states, for example, P$_{2}^{+}$ + 2x Co(II) for 4a vs. P$_{2}^{2-}$ + 2x Co(II) for 4b. The interconversion of electromeric 4a and 4b might have a substantial kinetic barrier, which might explain the two species do not show exchange phenomena in solution. Further investigations must reveal the physical oxidation state of the metal atoms in these complexes. Preliminary attempts to model 4a and 4b by broken-symmetry DFT calculations failed presumably due to the poor ability of standard DFT methods to properly describe the wavefunction of this type of molecule.


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