Di-tert-butyldiphosphatetrahedrane as a Source of 1,2-Diphosphacyclobutadiene Ligands

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Abstract: Reactions of di-tert-butyldiphosphatetrahedrane (1) with cycloocta-1,5-diene- or anthracene-stabilised metalate anions of iron and cobalt consistently afford complexes of the rarely encountered 1,2-diphosphacyclobutadiene ligand, which have previously been very challenging synthetic targets. The subsequent reactivity of 1,2-diphosphacyclobutadiene cobaltates toward various electrophiles has also been investigated and is compared to reactions of related 1,3-diphosphacyclobutadiene complexes. The results highlight the distinct reactivity of such isomeric species, showing that the 1,2-isomers can act as precursors for previously unknown triphospholium ligands. The electronic structures of the new complexes were investigated by several methods, including NMR, EPR and Mößbauer spectroscopies as well as quantum chemical calculations.

Introduction

Tetrahedranes are highly strained derivatives of the simplest platonic hydrocarbon C_4H_4. [1] The first isolated tetrahedrane was undoubtedly white phosphorus, P_4, first prepared in the 17th century. Much more recently (1978), the group of Maier showed that the carbon-based tetrahedrane tBu_4C_4 can be accessed as well. [2] Even though heavier group 14 tetrahedranes with various substituents have been prepared, mixed neutral tetrahedranes have remained scarce. [3] This is especially conspicuous considering the great number of mixed anionic tetrahedranes containing group 13, 14 or 15 elements. [4] Our group recently showed that mixed group 14 / group 15 tetrahedranes are indeed accessible. [5] A simple nickel-catalysed dimerisation reaction of tBuCP affords the phosphaalkyne dimer di-tert-butyldiphosphatetrahedrane (tBuCP)_2 (1, Figure 1A), which can be considered a ‘hybrid’ between P_4 and (tBuC)_4. The related tri-tert-butyldiphosphatetrahedrane was reported shortly thereafter by Cummins and co-workers. [6]

Having been synthetically inaccessible until recently, the reactivity of these phosphatetrahedranes is still largely unexplored, although preliminary results suggest that 1 possesses a versatile coordination chemistry. For example, 1 reacts with...
various Ni(0) and Ni(I) complexes to form (tBuCP)$_n$ ($n = 2, 4$) frameworks with novel coordination modes.\cite{31} Moreover, it coordinates in an η$_3$-fashion via its lone pairs to silver(I) (Figure 1B)\cite{32}. Significantly, in this latter case the behaviour of 1 is noticeably different from that of either P$_4$ or the monomeric tert-butylphosphaalkyne, both of which react with Ag$^+$ cations to give homoleptic complexes [AgL$_2$]$^+$ (L = η$_3$-P$_4$, η$_2$-tBuCP).\cite{33}

Furthermore, in one of our most recent contributions, the reactivity of 1 towards carbones was investigated.\cite{9} This study highlighted that, while 1 appears to be reactive towards similar substrates as P$_4$ and tBuCP, these reactions furnish distinctly different and otherwise inaccessible products.

Based on the above results, we were highly motivated to investigate the reactivity of 1 towards low-valent 3d metalates. The reactions of these species with P$_4$ have been extensively studied: for example, Ellis and Urněžus were able to synthesise the first completely inorganic sandwich complex [(η$_3$-P$_4$)$_2$Ti]$^+$ by reaction of a titanate with P$_4$.\cite{10} Our group has also contributed to this area by reaction of alkenes- or arene-stabilised cobaltates and ferrates with P$_4$.\cite{11,12} Many of the same metalates are also known to react with tBuCP to give 1,3-diphosphacyclobutadiene complexes of the type [M(1,3-R,C$_2$P$_2$)$_2$]$^+$ (M = Fe, Co; R = tBu, tPent, Ad) by head-to-tail cyclodimerisation of the phosphaalkyne.\cite{13,14}

These 1,3-tBu$_2$C$_2$P$_2$ complexes possess versatile coordination behaviour and display much other onward reactivity, and can be used to access a variety of other coordination compounds.\cite{15} By analogy with our previous studies, it was anticipated that related reactions of metalates with 1 could provide access to similarly interesting and synthetically useful coordination complexes, that would not be accessible using established precursors.

**Results and Discussion**

**Syntheses and molecular structures**

To begin, the reaction of two equivalents of 1 with one equivalent of the anthracene ferrate [K([18]crown-6)][Fe(anthracene)] in THF was studied. Addition of 1 to a dark red solution of [K([18]crown-6)][Fe(anthracene)] in THF at −80 °C afforded an intense green solution after stirring the reaction overnight, while allowing it to warm to room temperature. X-ray diffraction analysis on single crystals grown from benzene/n-hexane revealed the formation of the heteroleptic complex [K([18]crown-6)][Fe(1,2-tBu$_2$C$_2$P$_2$)(anthracene)] (2) in the solid state (anion shown only).\cite{21} Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and the [K([18]crown-6)]$^+$ cation are omitted for clarity. Selected bond lengths (Å) and angles [°]: P1–P2 2.1738(6), P1–C1 1.8328(15), P2–C2 1.8274(14). C1–C2 1.440(2), Fe–C$_1$(C$_1$-C$_2$-P$_1$-P$_2$) 1.783(2), C1–C2 1.428(2), C1–C3 1.403(2), C1–C14 1.432(2), C3–C14 1.432(2). C1–P1 78.85(5), C2–P2 78.03(5), C2–P–P1 101.97(10), C1–C–P2 101.14(10)

![Scheme 1. Reaction of [K([18]crown-6)][Fe(anthracene)] with (tBuCP)$_2$.](image)

![Figure 2. Molecular structure of [K([18]crown-6)][Fe(1,2-tBu$_2$C$_2$P$_2$)(anthracene)].](image)

The bond lengths within the anthracene ligand (C11–C12 1.428(2) Å, C12–C13 1.403(2) Å, C13–C14 1.432(2) Å) indicate back donation from an Fe(I) to the π-system of the ligand. Notably, 1,2-diphosphacyclobutadiene ligands are very rare compared to their 1,3-isomers, which are commonly prepared by dimerisation of phosphaalkynes in the coordination sphere of transition metals.\cite{16,17} Hence, the formation of complex 2 suggested a distinct synthetic utility of 1 in the synthesis of 1,2-diphosphacyclobutadiene complexes, for which no reliable, general synthetic routes have previously been available (see below). Notably, attempts to isolate the isomer [Fe(1,3-tBu$_2$C$_2$P$_2$)(anthracene)]$^-$ from the reaction of two equivalents of tBuCP and [K([18]crown-6)][Fe(anthracene)]$^-$ have not been successful so far.

Complex 2 was characterised by UV/Vis spectroscopy, showing an intense absorption band at 650 nm, which accounts for its green colour. The complex is paramagnetic with an effective magnetic moment of $\mu_{eff} = 1.9(1)$ μB determined by the Evans NMR method. As a result of the paramagnetism, the $^1$H NMR spectrum of isolated 2 in THF-d$_8$ shows no signals except for the solvent signals in the range from −150 to 150 ppm. Further characterisation data, including the X-band EPR and zero-field 19^Fe Mössbauer spectra, are described in the section Electronic Structure Analysis (see below).
To test the generality of 1,2-diphosphacyclobutadiene formation, 1 was next reacted with the cobaltate \([\text{K(thf)}_{2.2}]\)[Co(\(\eta^4\)-cod)], \((\text{cod} = 1,5$-$cyclooctadiene). Addition of two equivalents of 1 to a THF solution at $-80^\circ\text{C}$ led to the formation of an orange-brown solution. The $^{31}$P(\(\text{H}\)) NMR spectrum of the reaction mixture showed two major singlet species with chemical shifts of $-102.3$ and $3.3$ ppm in a 5:1 ratio (integration). The latter, minor shift is close to the reported value for \([\text{K(\(\eta^4\)-crown-6)(thf)}][\text{Co(\(\eta^4\)-cod)}] \), and the new, isomeric complex \([\text{K(\(\eta^4\)-crown-6)(1,4-dioxane})][\text{Co(\(\eta^4\)-tBuCP)}] \) (3), containing a 1,2-diphosphacyclobutadiene ligand (Scheme 2). \([10]\) The ‘mixed’ isomer containing both 1,2- and 1,3-diphosphacyclobutadiene ligands is not observed, which is attributed to increased steric repulsion between the tBu groups in this isomer, as discussed in the computational details (see the Supporting Information). Again, these results highlight both the divergent reactivity of 1 and tBuCP (whose reactions with \([\text{K(thf)}_{2.2}]\)[Co(\(\eta^4\)-cod)], preferentially form the 1,2-isomer 3 and the 1,3-isomer 3’, respectively), and the ability of 1 to act as a 1,2-diphosphacyclobutadiene ligand precursor.

The solid-state molecular structure of 3 revealed a polymer built upon coordination of the 1,2-diphosphacyclobutadiene ligands to \([\text{K(1,4-dioxane)}]^{-}\) units (Figure 3). The P$–$P bond length of \(2.1798\) (6) Å and the C$–$C bond length of \(1.443(2)\) Å of the diphosphacyclobutadiene ligand compare well to 2, as well as to the Co complex \([\text{Co(\(\eta^4\)-tBuCP)}]^{-}\) mentioned above. The two \(\eta^4\)-bound tBuCP units are in a staggered conformation with the tBu groups pointing away from each other. Due to very similar solubilities, 3 could not be separated from 3’.

Moreover, heating the crude reaction mixture to $110^\circ\text{C}$ for several days did not change the integral ratio of the signals for 3 and 3’ in the $^{31}$P(\(\text{H}\)) NMR spectrum; thus, showing that the two species do not convert into each other under these conditions. The reaction of \([\text{K(thf)}_{2.2}]\)[Co(\(\eta^4\)-cod)] with just one equivalent of 1 also afforded the same mixture of homoleptic cobalt complexes in the $^{31}$P(\(\text{H}\)) NMR spectrum (signals at $-102.3$ and $3.3$ ppm) alongside unsubsumed \([\text{K(thf)}_{2.2}]\)[Co(\(\eta^4\)-cod)], as identified in the $^1$H NMR spectrum.

To establish whether 1,2-diphosphacyclobutadiene ligand formation from 1 is a general phenomenon, reactions were next performed using the BIAN cobaltate \([\text{K(thf)}_{2.2}]\)(Dipp$\text{BIAN}$)[Co(\(\eta^4\)-cod)] (BIAN = bis(aryl)acenaphthenquinodimine, Dipp = 2,6-di-iso-propylphenyl), whose reactions with species have previously been shown to proceed with particularly high selectivity.\([12]\) Addition of one equivalent of 1 to a dark green solution of \([\text{K(thf)}_{2.2}]\)(Dipp$\text{BIAN}$)[Co(\(\eta^4\)-cod)] resulted in a colour change to turquoise overnight. Reaction monitoring by $^{31}$P(\(\text{H}\)) NMR spectroscopy revealed full consumption of 1 after stirring the reaction for 3 days at ambient temperature. Gratifyingly, the selective formation of one species with a singlet resonance at a chemical shift of $-121.8$ ppm was observed. Single crystal X-ray diffraction studies on crystals grown from 1,4-dioxane/n-hexane revealed the formation of the heteroleptic 1,2-diphosphacyclobutadiene complex \([\text{K(1,4-dioxane)}][\text{Co(\(\eta^4\)-tBuCP)}]^{-}\) (4, Scheme 3, Figure 4). In the solid state, each $\text{K}^+$ counterion is coordinated by the two P atoms of one anion, the Dipp substituent of another anion, and a 1,4-dioxane molecule, resulting in a dimeric structure (see Figure S33). The bond metrical parameters of the 1,2-tBuCP ligand resemble the data obtained for 2 and 3. While the C$–$C bond length of \(1.403(3)\) Å is in good agreement with a dianionic Dipp$\text{BIAN}^-$ ligand \(1.402(4)\) Å in $\text{Na}_2$Dipp$\text{BIAN}$, the N$–$C$–$N bond length of \(1.353(3)\) Å and N$–$C$–$P \(1.347(3)\) Å bond lengths deviate slightly from the reported values of \(1.387(4)\) and \(1.386(4)\) Å.\([19]\) A more detailed analysis of the bond metric data of the BIAN ligands will be discussed below (section on Electronic Structure Analysis).

Compound 4 was isolated in $63\%$ crystalline yield and fully characterised by NMR and UV/Vis spectroscopies as well as elemental analysis. The $^1$H and $^{13}$C($^1$H) NMR spectra of 4 reveal a diamagnetic compound with one signal set for the Dipp$\text{BIAN}$ and one signal set for the tBuCP ligand. The $^{31}$P(\(\text{H}\)) NMR spectrum shows a singlet resonance at $-121.8$ ppm, which is comparable

Figure 3. Molecular structure of 3 (left: anion shown only, right: structure as coordination polymer) in the solid state.\([11]\) Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): $\text{P1}$–$\text{P2}$ 2.1798(6), $\text{P1}$–$\text{C1}$ 1.8234(17), $\text{P2}$–$\text{C2}$ 1.8136(17), $\text{C1}$–$\text{C2}$ 1.443(2), $\text{K1}$–$\text{P1}$ 3.4898(5), $\text{Co}$–$\text{C}$ (o-\text{iso-p)} 1.748(2), $\text{C1}$–$\text{P1}$ 2.78.26(6), $\text{C2}$–$\text{P2}$ 2.78.36(6), $\text{C2}$–$\text{C1}$–$\text{P1}$ 101.39(12), $\text{C1}$–$\text{C2}$–$\text{P2}$ 102.00(11).

Figure 4. Reaction of \([\text{K(thf)}_{2.2}]\)[Co(\(\eta^4\)-cod)] with (tBuCP)$_2$.
to 3 and to the complex [(CP"Co(1,2-tBuC₅P₃)₃)] (δ(P(H)) = –83.8 ppm).[16]

As noted previously, 1,3-diphosphacyclobutadiene complexes can be prepared by head-to-tail cyclodimerisation reactions. Indeed, the reaction of 2 equivalents of 4BuC=CP with the same precursor [K(thf)₅][18BAN]Co(η⁴-cod)] afforded the isomeric 1,3-diphosphacyclobutadiene complex [K(thf)₅][18BAN]Co(1,3-tBuC₅P₃)] (5) in 64% yield as turquoise crystals. The solid-state molecular structure of 5 shows chelation of the potassium cation by one P atom of the 4BuC=CP ring and the phenyl ring of the Dipp group in the same anion, resulting in a monomeric structure (in contrast to 4). The P–C bond lengths in this complex lie in the range of 1.787(4) to 1.802(4) Å and the bond metric data of the ligand will be discussed below. In the ³¹P{¹H} NMR spectrum one singlet at 1.8 ppm was observed. Compounds 4 and 5 represent rare examples of heteroleptic transition metalate anions with terminal 1,3-diphosphacyclobutadiene ligands.

The intense turquoise colouration of both 4 and 5 when dissolved in THF can be rationalised by their UV/Vis absorption spectra, with absorption bands at 630 nm (4) and 605 nm (5). When heating a solution of 5 in THF–d₄ for 5 days to 60 °C, the selective formation of 4 was observed. This is in line with a computational analysis on the stability of the truncated model complexes [18BAN]Co(1,2-tBuC₅P₃)⁻ and [18BAN]Co(1,3-tBuC₅P₃)⁻ (Dmp = 2,6-dimethylphenyl) at the RI-PWP895-D3BJ/def2-TZVP level of theory. Although single point calculations using this double hybrid functional suggest little difference in energy between the isomers, the 1,2-diphosphacyclobutadiene is thermodynamically more stable than its 1,3-isomer (see the Supporting Information). A single related thermal isomerisation of a 1,3-diphosphacyclobutadiene ligand to its 1,2-isomer has been observed by Scheer and co-workers to generate [(CP"Co(1,2-tBuC₅P₃)₃)].[16]

To probe whether these differences in reactivity could be further extended, the analogous ferrate [K[18BAN]Fe(η⁴-cod)] was reacted with 4BuCP and its dimer 1 (Scheme 3). Single crystals suitable for X-ray diffraction studies were obtained from both reactions, which confirmed the analogous formation of two isomeric products: [K[18BAN]Fe(1,4-dioxane)][18BAN]Fe(1,2-tBuC₅P₃)] (6, from 1) and [K[18BAN]Fe(1,4-dioxane)][18BAN]Fe(1,3-tBuC₅P₃)] (7, from 4BuCP, Figure 4). 6 and 7 were isolated as dark blue or violet crystals in 70% and 50% yield, respectively. The bond metrical data for both complexes are very similar to the values obtained for the related cobaltates. However, and in contrast to the cobaltates, 6 and 7 are paramagnetic and, therefore, reveal broad resonances in their ¹H NMR spectra in the region from 1.59 to 3.6 ppm (δ(C–H)).
—4 to +12 ppm (see the Supporting Information for spectra). The results of magnetic susceptibility, EPR and $^{57}$Fe Mössbauer measurements are discussed in the section Electronic Structure Analysis (see below).

Reactivity studies

Having substantial quantities of the 1,2- and 1,3-riBu$_2$C$_2$P$_2$ cobaltates 4 and 5 in hand, reactions of these complexes with different electrophiles were conducted, to examine differences in their reactivities. Reactions of the 1,3-isomer 5 with HCl, Me$_2$SiCl and Cy$_2$PCl afforded only crystals of the neutral, partially deligated complex [(DioxyBIAN)Co(μ-Cl)$_2$] (Scheme 4, Figure 5), a neutral complex featuring a μ-bridging 1,2-diphosphacyclobutadiene ligand. This compound was also identified as a product in the reaction of 5 with Me$_2$SiCl and Mel and represents another example of 1,3-riBu$_2$C$_2$P$_2$ to 1,2-riBu$_2$C$_2$P$_2$ ligand isomerisation. Bridging diphosphacyclobutadiene complexes are scarce, and this is the first example of the 1,2-isomer being isolated in such a bridging coordination mode. Dinuclear complex 8 could plausibly form from the reaction of 0.5 equivalents of the bridging chlorido complex [(DioxyBIAN)Co(μ-Cl)$_2$] (formed as an intermediate, see above) with one equivalent of 4 and concomitant elimination of KCl. Regardless, due to difficulties in isolating [(DioxyBIAN)Co(μ-Cl)$_2$], this hypothesis has not yet been confirmed experimentally.

Complex 8 was isolated in 12% yield using 4 as starting material and Me$_2$SiCl as electrophile and characterised by X-ray crystallography and elemental analysis as well as NMR and UV/Vis spectroscopy. The solid-state molecular structure of 8 reveals a long P1–P1’ bond (2.3417(8) Å), two slightly elongated P1–C1 bonds (1.8602(16) Å) and a C1–C1’ bond length (1.449(3) Å) that compares well to complexes 4 and 5. The Co1–Co1’ distance of 3.5547(5) Å signifies non-significant interaction between the metal atoms. The bond metric data of the BIAN ligand allows for a classification as monoanionic BIAN– (C6–C7 1.425(2) Å, N1–C6 1.327(2) Å, N2–C7 1.334(2) Å; cf. C–C 1.446(2) Å and C–N 1.3239(18) and 1.3326(19) Å in Na$_{10}$BIAN.[18] A detailed discussion of the oxidation state of the BIAN ligand is given in the section Electronic Structure Analysis. Complex 8 is diamagnetic and features a 31P(1H) NMR singlet at a chemical shift of 194.2 ppm. The UV/Vis spectrum shows absorption bands at 620 and 830 nm, accounting for its dark blue colour in solution.

The reaction of Cy$_2$PCl with 4 and 5 revealed the particular synthetic utility of 4. The neutral complex [(DioxyBIAN)Co(η$^4$-SiCl$_2$P$_2$Cy$_2$)] (9), featuring an expanded 1,2,3-triphospholium ligand, was obtained upon insertion of a PCy$_3$ fragment into the P–P bond of 4 (Scheme 4). In case of 5, this reaction was unselective giving rise to several signals in the 31P(1H) NMR spectrum (see Figure S19, Supporting Information). Even though substituted C$_2$P$_2$ rings are known (e.g. tri-organopenta(1,2-riBu$_2$C$_2$P$_2$)$_2$trihydrogenphospholene), the motif of diorganosubstitution of P2 of a triphospholium ligand has not been reported to date.[19]

The solid-state molecular structure of 9 reveals η$^4$-coordination of the riBu$_2$C$_2$P$_2$-ligand with P–P bond lengths (P1–P3 2.1549(6) Å, P2–P3 2.1535(6) Å) in the range commonly observed for P–P single bonds (Figure 6).[20] The structural parameters indicate the presence of a monoanionic BIAN– ligand (C1–C2 1.447(3) Å, N1–C11 1.347(2) Å, N2–C12 1.338(2) Å)[18] Complex 9 was isolated in 71% yield as dark blue crystals and is diamagnetic in solution as revealed by sharp resonances for the DioxyBIAN ligand and the riBu and Cy groups. The 31P(1H) NMR spectrum shows two signals: a doublet at −90.3 ppm (J$_{PP}$ = 349.6 Hz), corresponding to the three-coordinate P-atoms, and a coupled triplet resonance at 55.5 ppm, which can be assigned to the tetracordinate P atom. The blue
Electronic structure analysis

Several spectroscopic and quantum chemical methods were employed in order to analyse the electronic structure of the complexes described herein. We were especially interested in the physical oxidation states of the metal atoms. Therefore, the bond lengths in all BIAN-containing complexes were analysed using the recently developed protocol for diazabutadiene-based ligands. This method is based on a statistical analysis of bond metric data obtained from X-ray crystallography and can be used to determine a (non-integer) metrical oxidation state (MOS) model is expected to underestimate the bond lengths for reduced BIAN ligands and, therefore, further investigations on the complexes’ electronic structure were conducted by spectroscopic analysis and quantum chemical calculations.

First, X-band EPR spectra of paramagnetic species (2, 6 and 7) were recorded at 10 and 20 K, revealing rhombic spectra for all systems investigated without any resolved hyperfine features (see Figure 7). The spectra were simulated and the obtained g-values are given in Table 1; these g-values point towards a single metal-centred unpaired electron (\(S = \frac{1}{2}\) spin system); thus, implying low-spin Fe(I) or Fe(III) complexes. The g-tensors were also calculated at the CASSCF-NEVPT2/DKH-def2-TZVP level of theory for the anionic complexes [Fe(1,2-tBuC,P)(anthracene)]\(^{−}\) (2), [\((\text{Dmp}^{\text{Bian}})\text{Fe}(1,2\text{-tBuC,P})\)]\(^{−}\) (6) and [\((\text{Dmp}^{\text{Bian}})\text{Fe}(1,3\text{-tBuC,P})\)]\(^{−}\) (7). The values obtained from these calculations for all compounds are in good agreement with the experimental values, suggesting that the calculated electronic structure fits the experimentally observed structure.

Next, the solution magnetic moments of 2, 6 and 7 in THF-\(_d_8\) were determined using the Evans NMR method. A magnetic moment of 1.9(1) \(\mu_B\) was measured for 2, which is close to the spin-only value for a \(S = \frac{1}{2}\) ground state (\(\mu_{\text{eff}}^{\text{spin-only}} = 1.73\)). Accordingly, the magnetic moments of 6 and 7 were determined as \(\mu_{\text{eff}} = 2.0(1)\mu_B\) in both cases. These values are consistent with low-spin Fe(I) and Fe(III) systems.

The zero-field \(^{57}\)Fe Mössbauer spectra of [K[18]crown-6][Fe(1,2-tBuC,P)(anthracene)] (2), [K[18]crown-6)(1,4-dioxan-ene)][(Dmp^{Bian})Fe(1,2-tBuC,P)] (6) and [K[18]crown-6](thf)][(Dmp^{Bian})Fe(1,3-tBuC,P)] (7) are shown in Figure 8. These spectra show the presence of a single species with an

![Figure 6](image-url) Molecular structure of 9 in the solid state.

![Figure 7](image-url) Experimental and simulated X-band EPR spectrum of 2 (top left), 6 (top right) and 7 (bottom) in a 2-methyl-THF glass. 2: temperature: 10 K, Freq.: 9.646813 GHz, power: 0.2000 mW, mod. amp.: 3.000 Gauss; g-tensor parameters obtained from simulations are: \(g_1 = 2.161, g_2 = 2.081, g_3 = 2.003\); \(\mu_{\text{eff}} = 2.003\), 1.10 mT Gaussian line width, 0.029 MHz; 6: temperature: 20 K, Freq.: 9.642478 GHz, power: 0.6325 mW, mod. amp.: 1.000 Gauss; g-tensor parameters obtained from simulations are: \(g_1 = 2.617, g_2 = 2.015, g_3 = 2.007\); 7: temperature: 20 K, Freq.: 9.646713 GHz, power: 0.6325 mW, mod. amp.: 4.000 Gauss; g-tensor parameters obtained from simulations are: \(g_1 = 2.478, g_2 = 2.027, g_3 = 1.999\).

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<th>Compound</th>
<th>(g_1)</th>
<th>(g_2)</th>
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<tr>
<td>2</td>
<td>Exp.</td>
<td>2.161</td>
<td>2.081</td>
</tr>
<tr>
<td>6</td>
<td>Exp.</td>
<td>2.617</td>
<td>2.015</td>
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<tr>
<td>7</td>
<td>Exp.</td>
<td>2.478</td>
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<td></td>
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<td>2.203</td>
<td>2.107</td>
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<td>Calc.</td>
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<tr>
<td></td>
<td>Calc.</td>
<td>2.404</td>
<td>2.015</td>
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(Fe(1,2-tBuC,P)(anthracene))\(^{−}\) (2), [\((\text{Dmp}^{\text{Bian}})\text{Fe}(1,2\text{-tBuC,P})\)]\(^{−}\) (6) and [\((\text{Dmp}^{\text{Bian}})\text{Fe}(1,3\text{-tBuC,P})\)]\(^{−}\) (7).
The isomer shifts, $\delta$, range from 0.46 (7) to 0.55 mm·s\(^{-1}\) (2). The quadrupole splittings, $\Delta E_Q$, of 6 and 7 are similar (1.12 and 1.18 mm·s\(^{-1}\), respectively), while the value obtained for 2 differs (0.87 mm·s\(^{-1}\)). The isomer shifts and quadrupole splittings of the related complexes [K([18]crown-6)][Cp*Fe(anthracene)] (Cp* = C\(_5\)Me\(_5\); $\delta = 0.56$ mm·s\(^{-1}\), $\Delta E_Q = 2.56$ mm·s\(^{-1}\), $T = 78$ K), [K([18]crown-6)(thf)][Fe(1,3-tBu\(_2\)C\(_5\)P\(_2\))\(_2\)] ($\delta = 0.431$ mm·s\(^{-1}\), $\Delta E_Q = 1.16$ mm·s\(^{-1}\), $T = 85$ K)[23] and [K([18]crown-6)(thf)][(Dmp\(_{2}\)BIAN)Fe(1,5-cod)] ($\delta = 0.23$ mm·s\(^{-1}\), $\Delta E_Q = 2.26$ mm·s\(^{-1}\), $T = 80$ K) have been reported previously.[24-26] A comparison reveals that the isomer shift of the 1,2-diphosphacyclobutadiene iron complexes (2 and 6) are comparable to [K([18]crown-6)][Cp*Fe(anthracene)], whereas the 1,3-diphosphacyclobutadiene complex 7 compares best to the homolectic complex [K([18]crown-6)(thf)][Fe(1,3-tBu\(_2\)C\(_5\)P\(_2\))\(_2\)]. This comparison reveals that the iron centre in 7 has a lower electron density than in the isomeric complex 6 (Table 2), suggesting that the acceptor strength of the 1,2-diphosphacyclobutadiene ligand is higher compared to its 1,3-isomer. As shown in Table 2, the quadrupole splittings were well reproduced by CASSCF calculations. Moreover, the electron densities on the iron nuclei of all complexes were calculated, giving a similar trend as the isomer shifts. As such, the electron density at the iron atom in 2 is the lowest, which is in agreement with its rather high (positive) isomer shift.

Table 2. \(^{57}\)Fe Mössbauer spectroscopic parameters for compounds 2, 6 and 7.

<table>
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<tr>
<th>Compound</th>
<th>$\delta^{(a)}$ [mm·s(^{-1})]</th>
<th>$\Delta E_Q^{(b)}$ [mm·s(^{-1})]</th>
<th>$\Delta E_Q^{(c)}$ [mm·s(^{-1})]</th>
<th>$\Gamma_{abs}^{(d)}$ [mm·s(^{-1})]</th>
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<td>Calc.</td>
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<td>1.12</td>
<td>0.62</td>
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<tr>
<td>6 Exp.</td>
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(a) Isomer shift, (b) Calculated electron density at the nucleus (arbitrary unit, CASSCF), (c) Experimentally determined and calculated (CASSCF) quadrupole splittings, (d) Full width at half maximum.

Figure 8. Experimental and simulated zero-field \(^{57}\)Fe Mössbauer spectra of solid samples of 2 (top left), 6 (top right) and 7 (bottom) recorded at 77 K.

Figure 9. Selected localised molecular orbitals below the active space of a CASSCF calculation [RIJCOSX/TZVP-def2/JK, CP(PPP) on Co] on [(Dmp\(_{2}\)BIAN)Co(1,2-tBu\(_2\)C\(_5\)P\(_2\))\(_2\)]. The occupancy of each orbital is given in parentheses (2.0). Isosurface value for MO-22 and MO-23: 0.0075; for MO-84 and MO-85: 0.06.

MO-22 (occ. 2.0)  MO-23 (occ. 2.0)  MO-84 (occ. 2.0)  MO-85 (occ. 2.0)
butadiene complexes and makes the assignment of an oxidation state to the metal centres ambiguous. Overall, and considering the presence of BIAN—and, the bonding scenario can be described as being intermediate between two extreme cases, namely a neutral π-accepting tBuC₆P₆ ligand and a low-spin metal(II) centre or a dianionic π-donating tBuC₆P₆ ligand and a low-spin metal(III) centre.

**Conclusion**

In summary, we have shown that the recently reported mixed tetrahe drane (tBuC₆P₆) acts as a reliable source of previously
difficult-to-access 1,2-diphosphacyclobutadiene ligands in reactions with cobalt and iron metalat es. While these 1,2-isomers are available by P–C bond cleavage of the C₆P₆ tetrahe drad, the corresponding 1,3-isomers are also available by head-to-tail cyclodimerisation of tBuC₆P₆ upon reaction with the same metalates. In this manner it has been possible to rapidly prepare a family of iron and cobalt complexes, including both homoleptic and heteroleptic examples. Such convenient access to both isomers has permitted direct comparative studies of their reactivity, establishing clear differences in the behaviour of the 1,2- and 1,3-complexes. These have revealed the particular utility of 1,2-diphosphacyclobutadiene complexes for further transformations, as exemplified by unprecedented preparations of both an diorgano-substituted triphospholium ligand and a tBuC₆P₆ ligand in a μ-η²-coordination mode. Further reactivity studies on the use of the new metalates in synthesis and catalysis are ongoing.

**Experimental Section**

**General synthetic methods**

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H₂O and <0.1 ppm O₂). [K(thf)][Co(η²-cood)]₇, [K(18-crown-6)][Fe-(anthracene)]₅, [K(dime)][Co(anthracene)]₅, [K(thf)][Co(η²-cood)]₇, [K(18-crown-6)][(dppBIAN)Fe(η²-cood)]₉, (tBuC₆P₆)ₖ and BIAN₃₆ were prepared according to previously reported procedures. All other chemicals were purchased from commercial suppliers and used without further purification. Solvents were dried and degassed with a MBraun SPS800 solvent purification system. All dry solvents except n-hexane were stored under argon over 4 Å molecular sieves in gas-tight ampules. All dry solvents except toluene, acetone and degassed with a MBraun SPS800 solvent purification system. All dry solvents except water were stored under argon over 4 Å molecular sieves in gas-tight ampules.

**General Analytical Techniques**

NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers at 300 K, unless otherwise noted, and internally referenced to residual solvent resonances (¹H NMR: THF-d₈: 7.22 ppm, CDCl₃: 7.16 ppm, ¹³C(H) NMR: THF-d₈: 25.13 ppm, CDCl₃: 128.56 ppm). Chemical shifts δ are given in ppm referring to external standards of tetramethylsilane (¹H, ¹³C(H)), 85% phosphoric acid (³¹P and ³²P[¹H] spectra), ¹H and ¹³C NMR signals were assigned based on 2D NMR spectra (¹H,¹H-COSY, ¹H,¹³C-HSQC, ¹H,¹³C-HMQC).

UV/Vis electronic absorption spectra were recorded on an Ocean Optics Flame Spectrometer. Diluted solutions of the complexes in THF were prepared in the following concentrations: 5.9·10⁻² M (2), 3.8·10⁻³ M (4), 1.8·10⁻³ M (5), 3.2·10⁻³ M (6), 3.5·10⁻³ M (7), 4.5·10⁻³ M (8), 6.3·10⁻³ M (9). CHN combustion elemental analyses were performed by the central analytics department of the University of Regensburg. Details on single crystals X-ray crystallography are given in the Supporting Information.

**Synthesis of compounds**

[ ([18-crown-6])[Fe(1,2-tBuC₆P₆)(anthracene)] (2) ]

To a deep red, cold (~80 °C) solution of [K([18-crown-6])[Fe-(anthracene)]₅] (3053.4 mg, 1.23 mmol, 1.0 eq.) was added (tBuC₆P₆), (3.0 mL, c = 0.5 M in toluene, 1.47 mmol, 1.2 eq.). After stirring overnight and allowing the solution to warm to ambient temperature, a colour change to deep green was observed. Subsequently, the solvent was removed and the dark green residue was dried in vacuo. The residue was washed with n-hexane (30 mL) and benzene (30 mL) and dried in vacuo. After extraction with THF (10 mL), the deep green solution was layered with n-hexane (60 mL). Slow diffusion over 3 days at ambient temperature afforded green blocks of [K([18-crown-6])[Fe(1,2-tBuC₆P₆)(anthracene)] (2)], which were isolated by decanting the supernatant and dried in vacuo. These crystals still contain residual benzene (Figure S1), which can be removed upon grinding the sample and further drying in vacuo. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of n-hexane into a saturated solution of 2 in benzene.

![Diagram](image-url)

**[K(1,4-dioxane)][(dppBIAN)Co(1,2-tBuC₆P₆)] (4)**

To a solution of [K(thf)][(dppBIAN)Co(η²-cood)] (250 mg, 0.32 mmol, 1.0 eq) in THF (5 mL) was added (tBuC₆P₆), (1.2 mL, c = 0.4 M in toluene, 0.48 mmol, 1.5 eq.). The deep green solution was stirred at ambient temperature for three days whilst turning turquoise. Subsequently, the solvent was removed in vacuo and the residue was washed with n-hexane (15 mL) and extracted with 1,4-dioxane (20 mL). The solution was concentrated to ca. 5 mL and layered with n-hexane (30 mL). Storage at room temperature for 5 days afforded deep turquoise crystals of [K(1,4-dioxane)][(dppBIAN)Co(1,2-tBuC₆P₆)] (4). The supernatant was decanted and the crystals were dried in vacuo. Elemental analysis and the ¹H and ¹³C NMR spectra indicate that the 1,4-dioxane molecule remains in the crystalline solid after drying.
Crystals suitable for X-ray crystallography were grown by slow diffusion of n-hexane into a saturated solution of 4 in 1,4-dioxane at ambient temperature.

A solution of 

\[ \text{Crystals suitable for X-ray crystallography were grown by slow diffusion of n-hexane into a saturated solution of 4 in 1,4-dioxane at ambient temperature.} \]

C\(_{6}\)H\(_{4}\)CoKnO\(_{4}\)P\(_{2}\), MW = 887.07 g mol\(^{-1}\); yield: 180 mg (63 %). \(^{1}H\) NMR (400 MHz, 300 K, THF-d\(_{6}\)) \( \delta = 0.81 \) (d, \( J_{HH} = 6.7 \) Hz, 12H, C\(_{12}\)H\(_{2}\)), 1.10 (s, 18H, C\(_{12}\)H\(_{2}\)), 1.27 (d, \( J_{HH} = 6.8 \) Hz, C\(_{12}\)H\(_{2}\)), 3.55 (s, 8H, 1,4-dioxane), 4.71 (sept, \( J_{HH} = 6.7 \) Hz, 4H, C\(_{3}\)H\(_{2}\)), 4.99 (d, \( J_{HH} = 7.0 \) Hz, 2H, C\(_{3}\)H\(_{2}\)), 6.42 (pseudo-t, \( J_{HH} = 7.6 \) Hz, 2H, C\(_{3}\)H\(_{2}\)), 6.61 (d, \( J_{HH} = 8.2 \) Hz, 2H, C\(_{3}\)H\(_{2}\)), 7.14 (m, 6H, C\(_{8}\)H\(_{2}\)), 1.10 (s, 18H, C\(_{8}\)H\(_{2}\)), 123.3 (s, C\(_{13}\)), 123.8 (s, C\(_{13}\)), 127.7 (s, C\(_{13}\)), 129.5 (s, C\(_{13}\)), 136.1 (s, C\(_{13}\)), 137.3 (s, C\(_{13}\)), 142.5 (s, C\(_{13}\)), 161.6 (s, C\(_{13}\)) ppm. \(^{31}P\)(\(^{1}H\)) NMR (162 MHz, 300 K, THF-d\(_{6}\)) \( \delta = -121.8 \) (s ppm). Elemental Analysis calcd. C 68.62, H 8.14, N 2.76, found. C 68.63, H 7.96, N 2.07. UV/Vis (THF): \( \lambda_{max} \) (nm, \( \epsilon_{max} / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) = 294 (22800), 388 (6000), 605 (17000), 738 (7800).

\[ K[[18]-6(dioxane)]\] (dioxane)\(^{2+}\) ([Co\((\text{1,3-tBuCP})_2\)] \( \text{(dioxane)} \)) \( \text{[K(18)-6[(dioxane)]}(\text{dioxane})^{2+}\)] (dioxane))

C\(_{6}\)H\(_{4}\)FeKN\(_{4}\)O\(_{4}\)P\(_{2}\), MW = 1148.30 g mol\(^{-1}\); yield: 290 mg (70 %). \(^{1}H\) NMR (400 MHz, 300 K, THF-d\(_{6}\)) \( \delta = 3.9 \) (br s), 0.7 (br s), 2.7 (br s), 3.8 (s, 1,4-dioxane), 6.1 (br s), 7.7 (br s), 10.9 (br s) ppm. Evans NMR: \( \mu = 2.0(1) \) \( \mu_{eq} \). \(^{31}P\)(\(^{1}H\)) NMR (162 MHz, 300 K, THF-d\(_{6}\)) No signal was observed in the range \(-150-150 \) ppm. Elemental Analysis calcd. C 64.85, H 7.90, N 2.44; found C 65.24, H 7.80, N 2.07. UV/Vis (THF): \( \lambda_{max} \) (nm, \( \epsilon_{max} / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \)) = 290 (30 000s), 350 (16 000s), 430 (9 000s), 570 (14 000s), 810 (14 000s).

\[ K[[18]-6(\text{thf})]_{n}[\text{Fe}(\text{1,2-tBuCP})_2], n = 1 \text{ or 2} \] (dioxane)\(^{2+}\) ([Co\((\text{1,3-tBuCP})_2\)] \( \text{(dioxane)} \)) \( \text{[K(18)-6(\text{thf})]_{n}[\text{Fe}(\text{1,2-tBuCP})_2], n = 1 \text{ or 2} \} \))

A solution of \( f_8\text{BuCP} \) (0.18 mL, \( c = 3.2 \) M in TMSO, 0.58 mmol, 2.1 eq) was added dropwise to a cold \((-30^\circ \text{C})\) solution of \([ \text{K}(\text{thf})]_{n}[\text{Co}(\text{1,3-tBuCP})_2] \) in THF at ambient temperature.
To a solution of [K(1,4-dioxane)][(μ-(η⁴-η⁴-Dipp)] in THF (5 mL) at −80 °C was added Me_5SiCl (0.12 mL, c = 1.58 M in toluene, 0.19 mmol, 1.1 eq.). The solution was allowed to warm to room temperature within 18 h. During this time, the colour of the reaction solution changed from turquoise to dark blue. Subsequently, the solvent was removed in vacuo and the residue was extracted with n-hexane (5 mL). Storage at −30 °C for three days afforded dark blue crystals of [(μ⁴-BIAN)Co(μ-η⁴-η⁴-Dipp)](n-Bu,C_6H_5)P]. The supernatant was decanted and the crystals were dried in vacuo. Crystals suitable for X-ray crystallography were grown by storing a saturated solution of [(μ⁴-BIAN)Co(μ-η⁴-η⁴-Dipp)](n-Bu,C_6H_5)P] in n-hexane at ambient temperature overnight.

C₆H₆Co(NO)₃P = C_5H_6C_5H_4 = 1319.53 g mol⁻¹; yield: 13 mg (12 %). ¹H NMR (400 MHz, 300 K, CD₂Cl₂) δ = 0.83 (d, J₂₃ = 6.7 Hz, 24H, C⁵H₁₈), 1.15 (s, 18H, CH₃), 1.20 (d, J₂₃ = 6.7 Hz, CH₃), 3.7 (br s, 8H, CH₃), 6.55 (pseudo-t, J₄₅ = 7.4 Hz, CH₃, overlapping with signal for C⁵H₁₈), 6.58 (dd, J₃₄ = 7.4 Hz, J₃₅ = 1.2 Hz, CH₃), 7.11 (d, J₂₃ = 7.3 Hz, CH₃), 7.38 (t, J₃₄ = 7.3 Hz, C²), 7.89 (dd, J₃₄ = 7.3 Hz, J₃₅ = 1.1 Hz, C⁵H₈) ppm. ¹³C(NMR) (100 MHz, 300 K, CD₂Cl₂) δ = 24.5 (s, C⁵), 25.8 (s, C⁵), 28.7 (s, C⁵), 31.5 (s, C⁵), 37.7 (s, C⁵), 119.1 (s, C⁴), 122.9 (s, C⁴), 124.1 (s, C⁴), 126.8 (s, C⁴), 130.1 (s, C⁴), 131.2 (s, C⁴), 135.7 (s, C⁴), 136.3 (s, C⁴), 142.8 (s, C⁴), 159.3 (s, C⁴), 162.7 (s, C⁴) ppm (C⁴ could not be detected; H / ¹³C(IF) HMBC suggests a signal at ca. 113 ppm). ³¹P(¹H) NMR (162 MHz, 300 K, CD₂Cl₂) δ = 194.2 (s) ppm. Elemental Analysis calc. C 74.64, H 7.49, N 4.25; found C 74.67, H 7.68, N 3.80.

UV/Vis (THF): λ_max (nm, ε_max /L·mol⁻¹·cm⁻¹) 320 (17 000), 440 (9 300), 560 (12 000), 660 (12 500).

30 minutes at ambient temperature, the solvent was removed in vacuo. The residue was extracted with n-hexane/toluene-mixture (10:1 v/v, 5 mL). Storage at −30 °C for three days afforded dark blue crystals of [(μ⁴-BIAN)Co(μ-η⁴-η⁴-Dipp)](n-Bu,C_6H_5)P]. The supernatant was decanted and the crystals were dried in vacuo. The complex crystallises as a solvate with n-hexane and toluene according to ¹H and ¹³C(IF) NMR and elemental analysis. A solvent content of 1 toluene and 0.5 n-hexane molecules per formula unit was determined. Crystals suitable for X-ray crystallography were grown by storing a saturated solution of [(μ⁴-BIAN)Co(μ-η⁴-η⁴-Dipp)](n-Bu,C_6H_5)P] in n-hexane at ambient temperature overnight.

To a solution of K[H₂FeK₂PO₄-C₅H₅OH, MW = 1276.51 g mol⁻¹ (for 7 THF)] yields: 180 mg (50 %). ¹H NMR (400 MHz, 300 K, THF-d₈) δ = −3.5 (br s), −1.7 (br s), 2.2 (br s), 6.8 (br s), 7.9 (br s), 8.7 (br s), 10.6 (br s) ppm. Evans NMR: μ = 2.01 (μ), ¹₃P(¹H) NMR (162 MHz, 300 K, THF-d₈) No signal was observed in the range −150−150 ppm. Elemental Analysis calc. C 65.86, H 8.37, N 2.19; found C 65.92, H 8.09, N 2.09.

UV/Vis (THF): λ_max (nm, ε_max /L·mol⁻¹·cm⁻¹) 290 (29 000), 370 (14 000sh), 540 (12 000), 800 (12 000).

[(μ⁴-BIAN)Co(μ-η⁴-η⁴-Dipp)] (9)