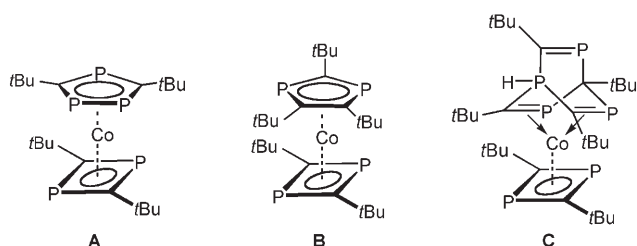


Sandwich Complexes

The Homoleptic Sandwich Anion $[\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2]^-$: A Versatile Building Block for Phosphaorganometallic Chemistry**

Robert Wolf, Andreas W. Ehlers, J. Chris Slootweg, Martin Lutz, Dietrich Gudat, Michael Hunger, Anthony L. Spek, and Koop Lammertsma*

Phosphaalkynes ($\text{RC}\equiv\text{P}$) are valuable starting materials for a wide range of low-coordinate phosphorus compounds.^[1] Similar to alkynes,^[2] these reactive, triply-bonded molecules oligomerize in the coordination sphere of transition metals to give diphosphacyclobutadienes, triphosphabenzenes, or higher oligomers.^[1,3] The reactions of phosphaalkynes with “vaporized” metal atoms are particularly intriguing, as illustrated by the reaction of cobalt atoms with $\text{tBuC}\equiv\text{P}$, which affords a mixture of three complexes (**A–C**) that are



difficult to prepare by conventional synthetic methods.^[4] Although fascinating compounds can be obtained by metal vapor (MV) synthesis,^[5,6] its applicability is limited due to the low product yields and the need for a special experimental setup.

Ellis has shown that low-valent polyarene transition metalates are efficient alternative synthons for “naked”

transition metal anions.^[7] Thus, readily accessible and well-characterized metalates such as the anthracene complex $[\text{Co}(\eta^4\text{-C}_{14}\text{H}_{10})_2]^-$ (**D**) undergo substitutions with π -acids such as carbon monoxide and olefins.^[8] We reasoned that the reaction of metalates with phosphaalkynes might therefore give access to novel anionic phosphaorganometallic sandwich complexes and thereby serve as an alternative to the MV method. Herein we present the synthesis, characterization, and three reactions of the first diphosphacyclobutadiene complex anion, $[\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2]^-$ (**1**).

Orange, crystalline $[\text{K}([\text{18}]\text{crown-6})(\text{thf})_2][\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2]^-$ (**K-1**) was prepared in 48% yield by the addition of four equivalents of $\text{tBuC}\equiv\text{P}$ to a solution of $[\text{K}([\text{18}]\text{crown-6})(\text{thf})_2][\text{Co}(\eta^4\text{-C}_{14}\text{H}_{10})_2]$ (**K-D**). This compound exists as an ion pair containing the homoleptic complex anion $[\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2]^-$ (Figure 1) and the unremarkable $[\text{K}([\text{18}]\text{crown-6})(\text{thf})_2]^+$ ion

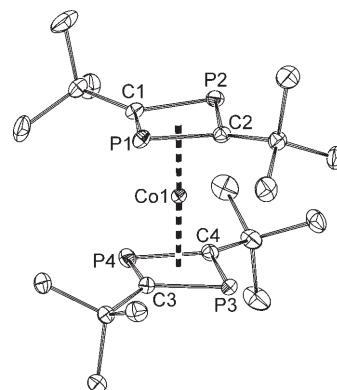


Figure 1. Solid-state structure of the anion **1** with displacement ellipsoids at the 30% probability level. H atoms and the cation have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Co1–P1, P2, P3, P4 2.2537(6)–2.2598(6), Co1–C1, C2, C3, C4 2.0649(19)–2.0724(19), P1–C1 1.791(2), P1–C2 1.798(2), P2–C1 1.797(2), P2–C2 1.794(2), P3–C3 1.795(2), P3–C4 1.799(2), P4–C3 1.801(2), P4–C4 1.793(2); P1–C1–P2 98.79(10), P1–C2–P2 98.66(10), C1–P1–C2 81.02(9), C1–P2–C2 80.95(9), P3–C3–P4 98.87(10), P3–C4–P4 99.02(10), C3–P3–C4 80.80(9), C3–P4–C4 80.79(9).

in the solid state.^[8,9] Anion **1** does not reside on a crystallographic symmetry element but displays near D_{2d} symmetry. The coordination geometry of the 1,3-diphosphacyclobutadiene ligands in **1** is similar to that of the related isoelectronic, neutral complexes **A**, **B**, $[\text{CpCo}(\text{P}_2\text{C}_2\text{tBu}_2)]$,^[10] and $[\text{Ni}(\text{P}_2\text{C}_2\text{tBu}_2)_2]$.^[11] In agreement with its symmetrical structure, the ^1H NMR spectrum of **1** shows a single tBu resonance and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows only a singlet (at $\delta = +2.4$ ppm), which is shielded by about 40 ppm relative to that of

[*] Dr. R. Wolf, Dr. A. W. Ehlers, Dr. J. C. Slootweg, Prof. Dr. K. Lammertsma
Department of Chemistry and Pharmaceutical Sciences
Vrije Universiteit Amsterdam
1081 HV Amsterdam (The Netherlands)
Fax: (+31) 20-598-7488
E-mail: k.lammertsma@few.vu.nl

Prof. Dr. D. Gudat, Prof. Dr. M. Hunger
Institut für Anorganische Chemie
Institut für Technische Chemie
Universität Stuttgart, Pfaffenwaldring 55
70569 Stuttgart (Germany)

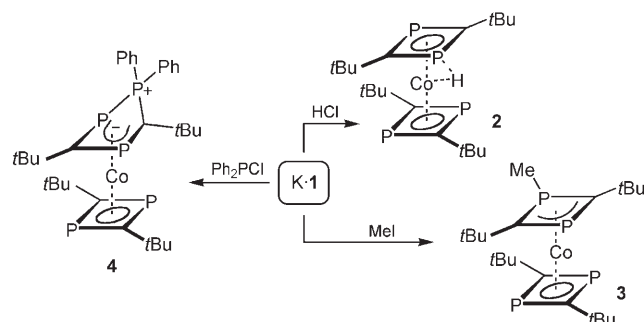
Dr. M. Lutz, Prof. Dr. A. L. Spek
Bijvoet Center for Biomolecular Research
Crystal and Structural Chemistry
Utrecht University, Padualaan 8
3584 CH Utrecht (The Netherlands)

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[CpCo(P₂C₂tBu₂)]. The UV/Vis spectrum of **1** in hexanes shows an intense charge-transfer band at 329 nm.

To assess its reactivity profile, we treated anion **1** with sources for three different electrophiles, namely a proton (H⁺), a methyl cation (Me⁺), and a phosphonium cation (Ph₂P⁺; see Scheme 1).



Scheme 1. Reactions of K-1 with electrophiles.

[Co(P₂C₂tBu₂)₂H] (**2**) was obtained as an orange, crystalline solid on protonating K-1 with HCl·OEt₂. Whereas the position of the hydrogen atom could not be ascertained by X-ray crystallography due to disorder (see the Supporting Information), the ¹H NMR spectrum of a toluene solution of **2** shows a remarkably shielded quintet at δ = −4.5 ppm (*J*_{H,P} = 16.0 Hz). The ³¹P NMR spectrum at −80 °C shows three signals at δ = −181.3, 18.2, and 118.3 ppm (1:2:1 ratio), which coalesce at temperatures above −40 °C to a very broad singlet at around δ = −5 ppm. No P–H coupling was observed due to strong line broadening even at −80 °C. The solid-state ³¹P MAS NMR spectrum shows a single spinning sideband manifold at δ = −5 ppm at room temperature and three different manifolds with isotropic chemical shifts of δ = −181.5, 18.6, and 117.5 ppm at −100 °C. These observations indicate that **2** exhibits dynamic behavior both in solution and in the solid state and that the hydrogen atom interacts with all four phosphorus atoms. The fact that no characteristic P–H, C–H, or Co–H vibration could be assigned in the IR spectrum of **2** is in agreement with this fluxional behavior.^[12]

An insight into the structure of **2** was obtained from density functional calculations at the PBE level of theory^[13] by exploring all possible isomers with the hydrogen atom bound to either cobalt, phosphorus, or carbon. The C_s-symmetrical structure **2a** (Figure 2), which has the hydrogen atom bridging the metal center and one phosphorus atom, is the global minimum and is likely to be the predominant isomer at −100 °C.^[14] Isomer **2b**, which has the hydrogen atom connected to the metal center and to a carbon atom, is 2.2 kcal mol^{−1} less stable; *exo* isomers with the hydrogen atom bound on the outer face of a P₂C₂ ring are far less stable (>11.5 kcal mol^{−1}) than **2a**.^[13] Two pathways for hydrogen exchange between the ligands were found (Figure 2). The conversion of isomer **2a** into **2b**, that is, H-shuttling from a P atom of one ring to a C atom of the other, requires a modest 4.5 kcal mol^{−1} (**TS2a-b**; C_s symmetry), whereas the degenerate process for **2a**, that is, H-shuttling between two P atoms, which relates to the observed coalescence of the ³¹P NMR spectrum at low temperature, has a barrier of 8.0 kcal mol^{−1}

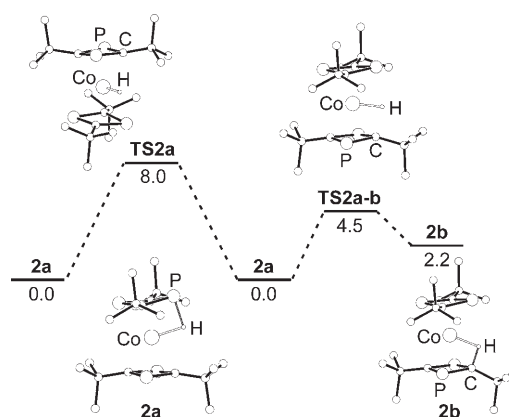


Figure 2. Relative PBE/6-311G(d,p) (SDD for Co) energies (in kcal mol^{−1}) for the interconversion of **2a** and **2b** via the transition structures **TS2a** and **TS2a-b**. Selected bond lengths [Å] and angles [°] for **2a** (C_s): Co–H 1.671, P–H 1.590; Co–H–P 90.4; **2b** (C_s): Co–H 1.656, C–H 1.232; Co–H–C 91.5; **TS2a** (C₂): Co–H 1.466, P–H 2.287, C–H 2.193; Co–H–P 71.0, Co–H–C 65.5; **TS2a-b** (C_s): Co–H 1.533, P–H 2.062, C–H 1.589; Co–H–P 76.9, Co–H–C 81.9.

(**TS2a**; C₂ symmetry). The interaction of the hydrogen atom with the cobalt center of **2a** and **2b** concurs with the highly shielded ¹H NMR resonance (δ = −4.5 ppm)^[14] and with the very small *J*_{H,P} coupling constant, even considering the averaging over four phosphorus nuclei (16.0 vs. 200 Hz for typical ¹*J*_{H,P} values).

An entirely different result was obtained for the reaction of K-1 with methyl iodide, which gives [Co(P₂C₂tBu₂Me)(P₂C₂tBu₂)] (**3**) (Scheme 1). Multinuclear NMR spectroscopic studies and a single-crystal X-ray structure^[9] revealed **3** to be the first transition metal complex of a 1,3-diphosphacyclobuten-4-yl ligand (P₂C₂tBu₂Me). Interestingly, a free 1,3-diphosphacyclobuten-4-yl radical has been isolated only recently.^[15] The formation of **3** is reminiscent of the well-documented ambiphilic behavior of diphosphacyclobutadiene ligands.^[3a] The methyl group in **3** is bound to one of the phosphorus atoms of a slightly pyramidalized η⁴-coordinated P₂C₂tBu₂ ring (sum of angles around P1: 346.41°). The Co–P distance and the intra-ring P–C distances of the methylated phosphorus atom P1 are shorter than those of the remaining P atoms (Co1–P1 = 2.1089(8), Co1–P2,P3,P4 = 2.2519(8)–2.2647(8), P1–C1,C2 = 1.747(3) and 1.746(3), P2–C1,C2 = 1.793(3) and 1.798(3) Å) and those of the precursor K-1.

A product similar to **3** might be expected from the reaction of K-1 with Ph₂PCl, but this is not the case (Scheme 1). Density functional calculations on model complexes indicated that PPh₂ insertion into a P–C bond of a diphosphabutadiene ring is favored over substitution (cf. **3**) by 24 kcal mol^{−1}.^[13] An X-ray crystal structure analysis^[9] of the reaction product [Co(P₃C₂tBu₂Ph₂)(P₂C₂tBu₂)] (**4**) confirmed the presence of an unusual triphosphacyclopentadienyl ligand (P₃C₂tBu₂Ph₂)⁺ that coordinates to cobalt through two phosphorus and two carbon atoms (Figure 3). Similar cationic ligands have been reported in [CpMoCl(CO)(η³-P₂C₂tBu₂H(OR))] (R = H, Me)^[16] and [Fe(η⁴-P₃C₂tBu₂nBuMe)(C₅R₅)] (R = H, Me),^[17] which were prepared by addition of water or methanol to [CpMoCl(CO)(η⁴-P₂C₂tBu₂)] and by lithiation/alkylation of [Fe(η⁵-P₃C₂tBu₂)-

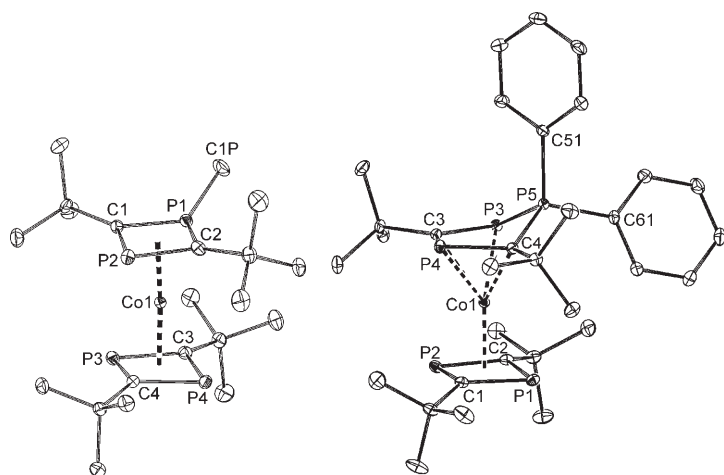


Figure 3. Solid-state structures of **3** and **4** with displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **3**: Co1–P1 2.1089(8), Co1–P2 2.2647(8), Co1–P3 2.2519(8), Co1–P4 2.2528(8), Co1–C1 2.152(3), Co1–C2 2.155(3), Co1–C3 2.059(3), Co1–C4 2.079(3), P1–C1 1.747(3), P1–C1P 1.805(3), P1–C2 1.746(3), P2–C1 1.798(3), P2–C2 1.793(3), P3–C3, P3–C4, P4–C3, P4–C4 1.789(3)–1.796(3); C1P–P1–C2 130.40(15), C1P–P1–C1 128.95(15); **4**: Co1–P1, P2, P3, P4 2.2646(4)–2.3089(4), Co1–P5 2.8704(4), Co1–C1, C2, C3 2.0791(13)–2.1166(13), Co1–C4 2.1907(13), P3–P5 2.1364(5), P3–C3 1.7894(14), P4–C4 1.7986(14), P3–C4 2.955(2), P4–C3, 1.7654(14), P5–C4 1.7759(14), P5–C51 1.8449(14), P5–C61 1.8213(14), P1–C1, P1–C2, P2–C1, P2–C2 1.7853(14)–1.8039(15); P3–C3–P4 120.58(8), P3–P5–C4 97.66(5), P4–C4–P5 110.85(7), P5–P3–C3 93.03(5).

(C₅R₅), respectively.^[16,18] The distances between the atoms P3, C3, P4, and C4 in **4** (1.776(2)–1.799(2) Å) indicate delocalized π -bonding within the P₃C₂tBu₂Ph₂ ligand. The P5–C4 distance of 1.776(2) Å is also short, while the remaining bonds within the P₃C₂ ring are in the usual range for single bonds (P3–P5 = 2.1364(5), P5–C51, C61 = 1.845(2) and 1.821(2) Å).

An insight into the charge distribution in **4** was gained from a comparison of the Mulliken charges for the model complexes [Co(P₂C₂Me₂)₂][−] (**1'**), [Co(P₂C₂Me₃)(P₂C₂Me₂)] (**3'**), and [Co(P₃C₂Me₂Ph₂)(P₂C₂Me₂)] (**4'**), in which the *tert*-butyl groups of **1**, **3**, and **4** have been replaced by methyl groups.^[12] The substituted phosphorus atom (P5) in **4'** is much more electropositive (+0.84) than the other phosphorus atoms (+0.23 to +0.47), which suggests that P5 is the cationic center. Indeed, the deshielded ³¹P{¹H} NMR multiplet of P5 (**4**) at $\delta = +68.8$ ppm is in the typical range for a phosphonium ion, while the most shielded resonance at $\delta = -121.5$ ppm is assigned to the adjacent phosphorus atom P3.^[19] The methylated phosphorus atom (P1) of **3'** (+0.63) is also more electropositive than the remaining phosphorus atoms (+0.37 to +0.43) while the Mulliken charges on Co for both **3'** and **4'** (**3'**: −0.30; **4'**: −0.33) are more negative than for **1'** (−0.09).

In conclusion, the reaction of *t*BuC≡P and [Co(η^4 -C₁₄H₁₀)₂][−] (**D**) is an efficient route to the first diphosphacyclobutadiene cobaltate [Co(P₂C₂tBu₂)₂][−] (**1**). This new approach paves the way for similar reactions with other phosphalkynes and transition metals. Three structurally distinct neutral derivatives (**2–4**) have been obtained upon treatment of **1** with three different electrophiles. An inter-

action with the metal center is observed with the smallest of these (H⁺), while the bulkier electrophiles Me⁺ and Ph₂P⁺ attack the diphosphacyclobutadiene ring. This study demonstrates that anions such as **1** are versatile building blocks for new phosphoorganometallic complexes with potential as metalloligands in catalysis or supramolecular chemistry.

Experimental Section

K-1: *t*BuC≡P (1.05 mL, 2.1 mmol; 2 M solution in hexanes) was added dropwise to a deep red-brown solution of **K-D** (0.46 g, 0.53 mmol) in about 8 mL THF at −78 °C. The mixture was allowed to warm to room temperature over several hours, whereupon the color changed to green and finally to dark orange. The solution was filtered, concentrated to about 8 mL, and about 30 mL of toluene was added. **K-1** was isolated as an orange crystalline solid after storage at −20 °C overnight, washed thoroughly with toluene (3 × 10 mL), and dried in vacuo. Yield 0.23 g (48%); slow decomp. > 250 °C; ¹H NMR (250.13 MHz, [D₈]THF): $\delta = 1.04$ (br s, 36H; *t*Bu), 1.71 (br s, 8H; THF), 3.5 (br, [18]crown-6), 3.59 ppm (br s, 8H; THF); ³¹P{¹H} NMR (101.23 MHz, [D₈]THF): $\delta = 2.4$ ppm.

2: A solution of HCl·OEt₂ (0.5 mL, 0.5 mmol; 1 M solution in OEt₂) was added to a deep-orange solution of **K-1** (0.45 g, 0.5 mmol) in THF (6 mL) at −78 °C and the mixture allowed to warm to room temperature overnight. The solvent was then evaporated to dryness and the dark-orange residue extracted with *n*-pentane (10 mL). Concentrating the orange extract to about 2 mL and storage at 5 °C for several days gave orange crystals of **2**. Yield: 0.095 g (41%); m.p.: 185–186 °C (dark oil); ¹H NMR (400.13 MHz, C₇D₈): $\delta = -4.50$ (quintet, *J*_{H,P} = 16.0 Hz, 1H), 1.12 ppm (s, 36H; *t*Bu); ³¹P{¹H} NMR (101.23 MHz, C₇D₈, +25 °C): $\delta = -5.0$ ppm (br); ³¹P{¹H} NMR (101.23 MHz, C₇D₈, −80 °C): $\delta = -181.3$ (br s, 1P), 18.2 (br s, 2P), 118.3 ppm (br s, 1P).

3: Complex **3** was prepared by a similar procedure to **2** by adding MeI (16 μ L, 0.036 g, 0.25 mmol) to a THF solution of **K-1** (0.24 g, 0.25 mmol). Yield: 0.021 g (18%); m.p.: 196–197 °C (dark oil); ¹H NMR (250.13 MHz, C₆D₆): $\delta = 1.15$ (s, 18H; *t*Bu), 1.23 (s, 9H; *t*Bu), 1.31 (s, 9H; *t*Bu), 1.53 ppm (d, *J*_{H,P} = 12.5 Hz, 3H; Me); ³¹P NMR (101.25 MHz, C₆D₆): $\delta = -50.5$ (br d, *J*_{H,P} ≈ 10 Hz, 1P), 25.5 (s, 2P), 41.7 ppm (s, 1P).

4: Complex **4** was prepared by a similar procedure to **2** by adding Ph₂PCl (0.1 mL, 0.13 g, 0.5 mmol, excess) to a THF solution of **K-1** (0.14 g, 0.15 mmol). Yield: 0.059 g (61%); decomp. > 150 °C; ¹H NMR (400.13 MHz, C₆D₆): $\delta = 1.24$ (br s, 9H; *t*Bu), 1.26 (s, 9H; *t*Bu), 1.31 (br s, 9H; *t*Bu), 1.66 (s, 9H; *t*Bu), 6.97 (m, 3H; *p,m*-Ph), 7.08 (m, 3H; *p,m*-Ph), 7.49 (m, 2H; *o*-Ph), 8.65 ppm (m, 2H; *o*-Ph); ³¹P{¹H} NMR (101.23 MHz, C₆D₆, ABCDX spin system): $\delta_A = +68.8$, $\delta_B = +43.6$, $\delta_C = +39.1$, $\delta_D = +28.0$, $\delta_X = -121.5$ (¹*J*_{A,X} = ± 310.0(1), ²*J*_{A,C} = ± 24.8(1), ²*J*_{C,X} = ± 25.6(1), ³*J*_{D,X} = 5.0(4) Hz).

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