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Synthesis and Structure of the Cobaltatetraphosphatricycloalkanes $[(\eta^5\text{-}C_5Me_5)(CO)CoP_4]$ and $[(\eta^5\text{-}C_5Me_5)_2(CO)_2Co_2P_4]$

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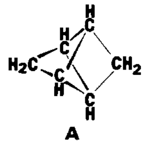
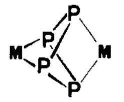
Summary: The cothermolysis of white phosphorus, P_4, and $[Cp^*Co(\mu\text{-}CO)]_2$ (**1**) affords as oxidative addition products the cobaltatetraphosphatricyclopentane, $[Cp^*(CO)CoP_4]$ (**2**), and the dicobaltatetraphosphatricyclohexane, $[Cp^*_2(CO)_2Co_2P_4]$ (**3**) ($Cp^* = \eta^5\text{-}C_5Me_5$). The X-ray crystal structures of **2** and **3** show rather short P···P distances for the PCoP bridges.

The concepts of diagonal relationship, isoelectronic families and isolobal fragments point to interesting analogies between carbon and phosphorus compounds,[1] on the one hand, and transition-metal complexes,[2] on the other hand. For example, the dimetallatetraphosphatricyclohexane B may formally be derived from the tricyclo[2.2.0.0^{2,6}]hexane A[3] by replacing its CH groups through isoelectronic P atoms and its CH_2 groups through the isolobal[2] 16-electron fragment Cp*(CO)Co (M in B).



A



B

The interaction of P_4 with $[Cp^*Co(\mu\text{-}CO)]_2$ (**1**) according to Scheme I gives the cobaltatetraphosphatricycloalkanes **2** and **3**. **3** also may be obtained in moderate yield from a combination of **1** and **2**. Complex **2** forms air-stable, dark red crystals, and **3** produces air-sensitive black crystals. Both are moderately soluble in pentane and readily soluble in toluene and dichloromethane (partial decomposition with **3**).[4]

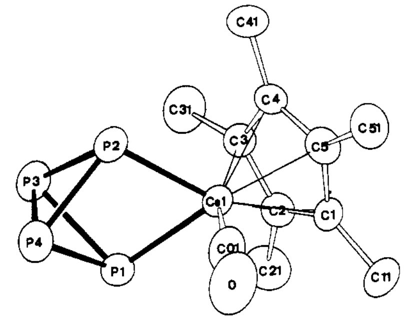
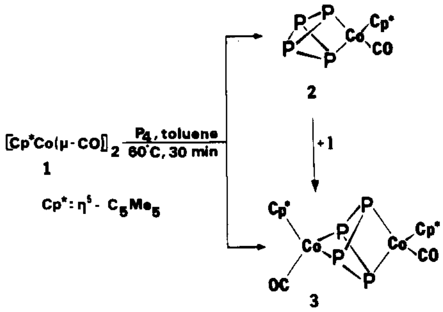


Figure 1. ORTEP drawing of complex **2** (50% probability ellipsoids are shown). Selected bond distances (Å) and bond angles (deg): Co1–P1 = 2.261 (1), Co1–P2 = 2.255 (1), P1···P2 = 2.606 (1), P1–P3 = 2.217 (2), P1–P4 = 2.214 (1), P2–P3 = 2.206 (2), P2–P4 = 2.204 (1), P3–P4 = 2.158 (2), Co1–Cp*(centr) = 1.735; P1–Co1–P2 = 70.5 (1), Co1–P1–P3 = 100.5 (1), Co1–P1–P4 = 100.3 (1), Co1–P2–P3 = 101.0 (1), Co1–P2–P4 = 100.8 (1), P1–P3–P2 = 72.2 (1), P1–P4–P2 = 72.3 (1), P3–P1–P4 = 58.3 (1), P3–P2–P4 = 58.6 (1), P1–P3–P4 = 60.8 (1), P2–P3–P4 = 60.7 (1), P1–P4–P3 = 60.9 (1), P2–P4–P3 = 60.7 (1), P1P3P4|P2P3P4 = 95°.

Scheme I



The X-ray crystal structure determinations[5] confirm the P_4 framework of white phosphorus, in which one (complex **2**, Figure 1) or two (complex **3**, Figure 2) edges are opened and bridged by a Cp*Co(CO) moiety. Formally the P_4 ligand in **2** and **3** can be regarded as P_4^{2-} (cf. Cp'_2MP_4, M = Zr, Hf,[6] single oxidative addition of P_4) and P_4^{4-} (double oxidative addition of P_4, d^6 cobalt in each case), respectively. The structural alternatives of the η^2 metal-bonded P_4 edge, verified in $[(Ph_3P)_2ClRh(\eta^2\text{-}P_4)]$ (**4**)[7] or the hitherto unknown di-η^2-coordinated P_4 edges are less probable because of the following facts: (i) In **2** and **3** the long PP distances for **2**, d(P···P) = 2.606 (1), and for **3**, 2.560 (2)|2.597 (2) Å, are distinctly longer than that of **4** (2.462 (2) Å).[7] Similar short P···P contacts of 2.57 Å (mean value) have been found with four of the six pairs of phosphorus atoms in the distorted Co_4P_4 core of the cubane-like $[CpCo(\mu_3\text{-}P)]_4$ (**5**).[8] The corresponding P–Co–P angles in

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† X-ray structure analysis.

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[3] For MINDO|3 calculations, see: Minyaev, R. M.; Minkin, V. I. *J. Org. Chem. USSR* (*Engl. Transl.*) **1985**, *21*, 2055.

[4] Preparation of **2** and **3**. All manipulations were carried out under dry Ar by using standard Schlenk techniques. A solution of $[Cp^*Co(\mu\text{-}CO)]_2$ (**1**)[15] (1.20 g, 2.69 mmol) and P_4 (1.00 g, 8.07 mmol) in 50 mL of toluene was stirred at 60 °C for 30 min until the CO band of **1** completely disappeared (IR monitored). The reaction solution was evaporated to ca. 10 mL under oil-pump vacuum, then treated with 5 g of Al_2O_3 (basic, activity II), and dried under oil-pump vacuum until freely flowing. In the chromatographic workup (column 25 × 2.5 cm), excess P_4, $Cp^*Co(CO)_2$, and some of **2** were eluted with pentane as brown yellow fraction. Pentane/toluene (10:1) elutes further **2** as a yellow fraction. After removal of the solvents the residue from the first fraction was heated to 60–70 °C for 6 h under oil-pump vacuum. This eliminates excess P_4 and $Cp^*Co(CO)_2$. The remaining residue and the residue from the second fraction were recrystallized from hexane (−18 °C) with formation of **2** (120 mg, 6%) as dark red crystals. Pentane/toluene (1:1) elutes a green fraction, which after recrystallization from toluene/hexane (5:1; −18 °C) afforded black crystals of **3** (464 mg, 30%). Anal. Calcd for $C_{11}H_{15}CoOP_4$: C, 38.18; H, 4.37. Found: C, 38.00; H, 4.35. Calcd for $C_{22}H_{30}Co_2O_2P_4$: C, 46.49; H, 5.32. Found: C, 46.50; H, 5.25.

[5] Crystal data of **2** [**3**]: triclinic, $P\bar{1}$ [monoclinic, $P2_1/c$], a = 8.6460 (5), b = 10.7005 (10), c = 8.1614 (6) Å; α = 101.249 (15), β = 99.592 (9), γ = 88.080 (10)° [a = 17.325 (2), b = 8.803 (2), c = 17.232 (3) Å; β = 106.97 (2)°], V = 730.2 [2513.5 Å^3], Z = 2 [4], d_{calcd} = 1.574 [1.502 g·cm^{-3}], Mo Kα (λ = 0.71073 Å), 21 °C, 3° < 2θ < 50°; Enraf-Nonius CAD4; total number of reflections 2676 [4821], 2360 [3614] unique reflections of which 2043 [2655] were observed ($I > 2\,\sigma(I)$); R = 0.034 [0.044], R_w = 0.041 [0.048]. Structure solution: SHELX-76, SHELXS-86. All of the nonhydrogen atoms were refined anisotropically. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG, on quoting the depository number CSD 53307, the names of the authors, and the journal citation.

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0276-7333/89/2308-0841$01.50/0

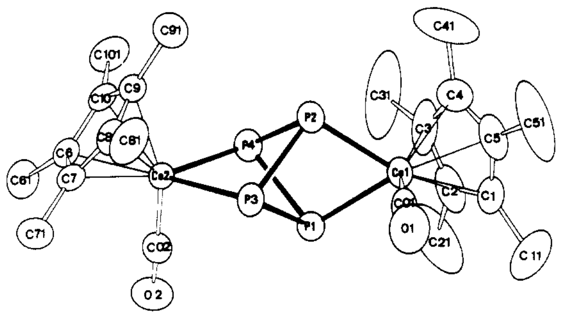

Figure 2. ORTEP drawing of complex 3 (50% probability ellipsoids are shown). Selected bond distances (Å) and bond angles (deg): Co1–P1 = 2.256 (2), Co1–P2 = 2.262 (2), Co2–P3 = 2.254 (2), Co2–P4 = 2.254 (2), P1···P2 = 2.560 (2), P3···P4 = 2.597 (2), P1–P3 = 2.221 (2), P2–P3 = 2.234 (2), P1–P4 = 2.227 (2), P2–P4 = 2.236 (2), Co1–Cp*(centr) = 1.738, Co2–Cp*(centr) = 1.737; P1–Co1–P2 = 69.0 (1), P3–Co2–P4 = 70.4 (1), P3–P1–P4 = 71.4 (1), P3–P2–P4 = 71.0 (1), P1–P3–P2 = 70.1 (1), P1–P4–P2 = 70.0 (1), Co1–P1–P3 = 97.9 (1), Co1–P1–P4 = 99.7 (1), Co1–P2–P3 = 97.3 (1), Co1–P2–P4 = 99.3 (1), Co2–P3–P1 = 96.9 (1), Co2–P3–P2 = 98.7 (1), Co2–P4–P1 = 96.7 (1), Co2–P4–P2 = 98.7 (1), P1P3P4|P2P3P4 = 89.8, P1P3P2|P1P4P2 = 90.6°.

5 (71.1° (average)) are nearly the same as in 2 (70.5°) and 3 (69.0|70.4°). The same holds for the Co–P distances ($\bar{d}$(Co–P) = 2.22|2.26 Å in 5[8] and 2.26 Å in 2 and 3). (ii) The $^{31}P\{^1H\}$NMR data[9] of 2 show a much stronger chemical shift difference (Δ = ca. 120 ppm) for the A_2XY system with respect to η^2-coordinated P_4 in 4 (A_2B_2 part, δ = −279.4|−284.0 ppm, Δ = ca. 5 ppm[7]). As with 4[7] (2.188 (2) Å) the shortest P–P distance in 2 (P3–P4 = 2.158 (2) Å, Figure 1) is opposite to the longest one (P1···P2). The distance in 2 is comparable with that of the phosphabicyclobutane derivatives $P_2(PR)_2$ (6) (6a,[10a] R = $N(SiMe_3)_2$, 2.129 Å; 6b,[10b] R = $(tBu)_3C_6H_2$, 2.166 (2) Å; 6c,[10c] $P_2(PR)(CR'_2)$, R = $(tBu)_3C_6H_2$, R′ = $SiMe_3$, 2.136 (1) Å) and $P_2(CR)_2ZrCp_2$ (7)[11] (R = tBu, 2.147 (1) Å). The folding angle between the two P_3 "wings" of the "butterfly" is 95° in 2, 95.2° in 6a,[10a] 95.5° in 6b,[10b] 105° in 6c[10c] ($P_3|P_2C$ "wings") and 110° in 7[11] (two P_2C "wings" with a Cp_2Zr bridge). In both complexes the planes $P_2Co|Cp^*$(centr.)-CoC(O) are approximately orthogonally oriented to each other [2, 88.7°; 3, 88.8 (Co1), 87.4° (Co2)].

The P atoms of the formal P_4^{4-} ligand in 3 form a bent four-membered ring with $\bar{d}$(P–P) = 2.23 Å while the corresponding $\bar{d}$(P–P) is 2.21 Å for the formal P_4^{2-} ligand in 2. In the solid-state chemistry of polyphosphides[12] a rectangular formal P_4^{4-} was found in CoP_3[13] with $\bar{d}$(Co–P) = 2.22 Å and d(P–P) = 2.24|2.34 Å.

The P_4 unit of 3 completes the series of P_4^{n-} ligands (n = 2, this work and Cp'_2MP_4 (M = Zr, Hf, Cp′ = η^5-1,3-$C_5H_3(tBu)_2$);[6] n = 4, this work and n = 6, $Cp^*_3Ni_3P_5$[14]) in organometallic chemistry.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Tables of bond distances and angles, crystal data, non-hydrogen atom coordinates, thermal parameters, and hydrogen atom coordinates for 2 and 3 (13 pages); listings of structure factor amplitudes for 2 and 3 (22 pages). Ordering information is given on any current masthead page.

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(9) $^{31}P\{^1H\}$ NMR (80.82 MHz, toluene-d_8, 85% H_3PO_4 external standard): 2, A_2XY system, $\delta(P_A)$ = −258.2 (t), $\delta(P_X)$ = −335.9 (q), $\delta(P_Y)$ = −376.9 (q), ^1J(P–P) = 156 Hz; 3, AA′XX′ system, $\delta(P_{AA'})$ = −125.1, $\delta(P_{XX'})$ = −165.4, $^1J(P_A–P_X)$ = $^1J(P_A–P_{X'})$ = ±97 Hz, $^1J(P_A–P_{A'})$ = ±56 Hz, $^1J(P_X–P_{X'})$ = ±28 Hz, $^2J(P_A–P_{X'})$ = ±44 Hz. ^1H NMR (200 MHz, C_6D_6, TMS internal standard): 2, δ = 1.31 (s, CH_3); 3, δ = 1.55 (s, CH_3). IR (pentane, ν_{CO}): 2, 2000 (vs) cm^{-1}; 3, 1990 (vs) cm^{-1}.

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Reactivity of $Ph_2PC{\equiv}CCMe_3$ toward $[PPh_4][HFe_3(CO)_{11}]$: Synthesis and X-ray Structure of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ and $[PPh_4][Fe_2(CO)_6(\mu\text{-}PPh_2CH{=}C(CMe_3)C(O))]\cdot CH_2Cl_2$

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Summary: The reaction of $Ph_2PC{\equiv}CCM_3$ with $[PPh_4][HFe_3(CO)_{11}]$ in boiling ethyl acetate leads to the formation of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ as the main product in which phosphorus–alkynyl bond cleavage has occurred and migration of hydrogen onto the β-carbon has led to a vinylidene ligand. The second product, $[PPh_4][Fe_2(CO)_6(\mu\text{-}Ph_2PCH{=}C(CMe_3)C(O))]$, contains a bridging ligand that results from hydrogen migration on the α-carbon of the alkynyl group and CO insertion between the β-carbon and one iron atom.

The reactivity of (diphenylphosphino)alkynes, $Ph_2PC{\equiv}CR$, toward polynuclear complexes has been extensively investigated by Carty et al.[1] during the last decade and has led to interesting rearrangement reactions implying generally the breaking of the phosphorus–alkynyl bond.[1,2] Considering the great reactivity of $[PPh_4][HFe_3(CO)_{11}]$ (1), toward alkynes which we have recently pointed out,[3] we thought it of interest to check the behavior of these ligands toward this cluster anion. Indeed, in this case, the presence of an hydrido ligand could extend the type of reactivity observed by the possible insertion of the carbon–carbon triple bond into the iron–hydrogen

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[†] Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique.

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