[Cp″Co(P_4){(Cp″Co)$_2$(μ-CO)}] (Cp″ = η^5-$C_5H_3t Bu_2$): A Complex with a P_4 Unit on the Way to a P_1 and a P_3 Ligand

**Manfred Scheer,*,[1a] Uta Becker,[1a]
Malcolm H. Chisholm,*,[1b] John C. Huffman,[1b]
Frédéric Lemoigno,[1c] and Odile Eisenstein,*,[1c]**

Institute of Inorganic Chemistry, University of Karlsruhe,
Engesserstrasse, D-76128 Karlsruhe, Germany,
Department of Chemistry, Indiana University,
Bloomington, Indiana 47405, and Laboratore
de Chimie Théorique, Université de Paris-Sud,
Bâtiment 490, 91405 Orsay, France

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Introduction

Reactions of P_4 phosphorus with several Cp^{x}Co-containing complexes (Cp^x = η^5-C_5Me_5, η^5-C_5Me_4Et)[2,3] have been investigated in the past few years. The thermolysis of P_4 and [Cp*Co(μ-CO)]$_2$ (Cp* = η^5-C_5Me_5) at 60 °C is known to generate [Cp*Co(CO)(η^2-P_4)] (**1**) and [{Cp*Co(CO)}$_2$(μ,η^2,η^2-P_4)] (**2**), respectively.[2] When the reaction is carried out under UV conditions at ambient temperature, the double-P_2-ligand-containing complex [(Cp*Co)$_2$(μ,η^2-P_2)$_2$] (**3**) is formed as shown by Dahl et al.[3]

Our interest in this field concerns the study of the transformation of tetrahedral P_4 into the corresponding P_x ligands. In order to trap intermediates along the reaction pathway, we have developed the simple concept of binding the lone pairs of the phosphorus atoms by addition of [Cr(CO)$_5$THF] to the reaction mixture of P_4 and the coordination compound (three-component reaction). So e.g. the reaction of [Cp″Co(CO)$_2$] (Cp″ = η^5-$C_5H_3tBu_2$) with P_4 in the presence of [Cr(CO)$_5$THF] leads to the bicyclotetraphosphine derivative [Cp″Co(CO){η^2-P_4(Cr(CO)$_5$)$_4$}] (**4**) and the *cyclo*-P_4 ligand complex [Cp″Co{η^4-P_4(Cr(CO)$_5$)$_3$}] (**5**) under UV as well as under thermal conditions.[4] Both compounds are stabilized by the chromium pentacarbonyl moieties. To compare these results with those in the absence of [Cr(CO)$_5$THF], we studied the corresponding two-component reaction under UV conditions. The results are reported herein.

Experimental Section

General Considerations. All manipulations were performed under an atmosphere of dry nitrogen using a glovebox or Schlenk techniques. Solvents were purified and degassed by standard procedures. ^{1}H-NMR spectra were recorded on a Bruker AM 500 (500.136 MHz), and ^{31}P-{^{1}H}-NMR spectra were obtained on a Nicolet NC 360 (146.186 MHz). IR spectra were recorded in CH_2Cl_2 solutions on a Nicolet 510 P FT-IR spectrometer. Elemental analysis was performed by the elemental analytical laboratory of the Department of Chemistry of the University of Halle, Germany. [Cp″Co(CO)$_2$] was prepared by a literature method.[5]

Safety Note. Elemental (white) phosphorus is flammable in air and must be handled under inert-atmosphere conditions.

Chart 1

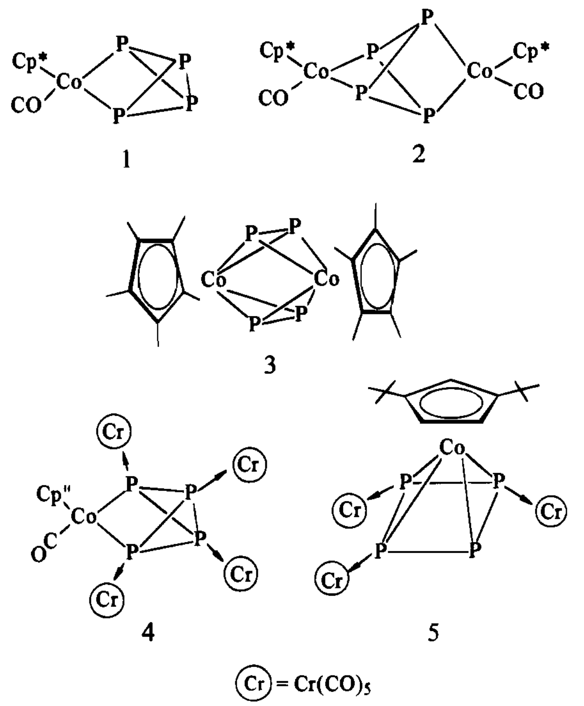

Table 1. Experimental Crystallographic Data for **7**

chem formula	$C_{40}H_{63}OP_4Co_3$	T (°C)	−90
fw	860.63	D_c (g cm^{-3})	1.371
space group	*Pnam*	λ (Å)	0.710 69
a (Å)	11.665(5)	μ(Mo Kα) (cm^{-1})	13.585
b (Å)	16.528(8)	$R(F)^a$	0.047
c (Å)	21.623(10)	$R_w(F)^b$	0.043
V (Å^3)	4168.83	min/max $\Delta\varrho$ (e/Å^3)	−0.90/0.67
Z	4		

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w = [\sigma^2(F)]^{-1}$.

Synthesis of [Cp″Co(P_4){(Cp″Co)$_2$(μ-CO)}] (7). A 0.292 g (1 mmol) sample of [Cp″Co(CO)$_2$] and 0.124 g (1 mmol) of elemental P_4 in 150 mL THF were irradiated in a UV apparatus (150 W mercury high-pressure lamp) at ambient temperature for 2 h. After the solvent was removed under reduced pressure, unreacted P_4 was removed by sublimation using a high vacuum. The mixture was separated by chromatography on a silica gel column (Merck 60, 230–400 mesh) packed with *n*-hexane. Elution with *n*-hexane revealed a small amount of the starting material [Cp″Co(CO)$_2$]. **6** was eluted using a mixture of *n*-hexane/CH_2Cl_2 (3:1) followed by **7** (eluted with CH_2Cl_2). Yields: 40 mg (13%) of **6** and 100 mg (35%) of **7** were obtained after recrystallization of the crude products of the single fractions from hexane (**6**) and CH_2Cl_2 (**7**), respectively. **6:** ^{1}H NMR (C_6D_6) δ 1.34 (s, 18H, $(CH_3)_3C$), 4.22 (s, br, 3H, Cp″). ^{31}P NMR (CD_2Cl_2) δ −50.2 (s, 4P); MS *m/z* 596.5 (M^+, 18%), 581.5 ($M^+ - CH_3$, 68%), 565.8 ($M^+ - 2CH_3$, 100%), 414.1 (Cp''_2Co^+, 42%). Anal. Calcd for $C_{26}H_{42}P_4Co_2$: C, 52.36; H, 7.10. Found: C, 52.08; H, 6.98. **7:** IR (CH_2Cl_2) 1934 cm^{-1} (ν_{CO}, br); ^{1}H NMR (in C_6D_6) δ 1.28 (s, 36 H, $(CH_3)_3C$), 1.69 (s, 18H, $(CH_3)_3C$), 4.21 (br, 2H, Cp″), 4.31 (br, 4H, Cp″), 4.72 (br, 1H, Cp″), 5.31 (br, 2H, Cp″). Anal. Calcd for $C_{40}H_{63}OP_4Co_3$: C, 55.82; H, 7.38. Found: C, 55.51; H, 7.04.

X-ray Crystal Structure of 7. Crystallographic data for **7** are collected in Table 1. A dark brown single crystal of approximate dimensions 0.50 × 0.26 × 0.06 mm was mounted on a glass fiber using silicone grease, and the mounted sample was then transferred to the goniostat where it was cooled to −90 °C. A systematic search limited to a hemisphere of reciprocal space located a set of reflections with orthorhombic symmetry, following the complete data collection (6° ≤ θ ≤ 50°).[6] The structure was solved by a combination of direct methods (MULTAN78) and standard Fourier techniques (in space group

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[1] (a) University of Karlsruhe. (b) Indiana University. (c) Université de Paris-Sud. Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

[2] Scherer, O. J.; Swarowsky, M.; Wolmershäuser, G. *Organometallics* **1989**, *8*, 841.

[3] Barr, M. E.; Dahl, L. F. *Organometallics* **1991**, *10*, 3991.

[4] Scheer, M.; Becker, U.; Huffman, J. C.; Chisholm, M. H. *J. Organomet. Chem.* **1993**, *461*, C1. Under thermal conditions, the more reactive [Cp″Co(μ-CO)]$_2$ has to be used as starting material.

[5] Scheer, M.; Schuster, K.; Becker, U.; Krug, A.; Hartung, H. *J. Organomet. Chem.* **1993**, *460*, 105.

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Table 2. Atomic Positional Parameters ($\times 10^4$)

atom	x	y	z^a
Co(1)	6847(1)	424(1)	7500*
Co(2)	4662(1)	−1084.7(4)	6931.3(3)
P(3)	6426(1)	−547(1)	8237(1)
P(4)	4982(2)	23(1)	7500*
P(5)	7609(2)	−838(1)	7500*
C(6)	5358(7)	−1798(5)	7500*
O(7)	5892(5)	−2409(4)	7500*
C(8)	2889(5)	−1109(4)	6700(3)
C(9)	3377(5)	−1889(4)	6660(3)
C(10)	4236(5)	−1898(3)	6199(3)
C(11)	4279(5)	−1094(4)	5977(3)
C(12)	3449(5)	−609(4)	6269(3)
C(13)	3111(6)	250(4)	6068(3)
C(14)	2425(8)	667(6)	6569(5)
C(15)	2377(10)	150(6)	5488(5)
C(16)	4162(8)	751(5)	5909(4)
C(17)	4855(5)	−2624(4)	5919(3)
C(18)	4745(8)	−3375(4)	6317(4)
C(19)	6126(6)	−2429(4)	5811(3)
C(20)	4279(7)	−2793(5)	5291(3)
C(21)	6688(5)	1604(3)	7827(3)
C(22)	7762(5)	1292(3)	8035(3)
C(23)	8392(7)	1086(5)	7500*
C(24)	8251(7)	1319(4)	8686(3)
C(25)	7334(10)	1472(7)	9153(4)
C(26)	8897(7)	550(5)	8852(4)
C(27)	9143(14)	2023(7)	8668(6)

[a] Parameters marked with an asterisk were not varied.

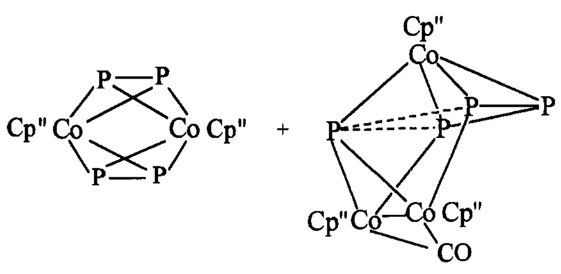
Pnam). A difference Fourier phase on the non-hydrogen atoms clearly located all hydrogen atoms, and these were included in the subsequent least-squares refinement. From the 4144 measured reflections, 2481 having [$F > 2.33\sigma(F)$] were used in the full least-squares refinement. The final residuals are $R(F) = 0.047$ and $R_w(F) = 0.043$; GOF = 1.352. Atomic coordinates, selected bond lengths and angles, and thermal parameters are listed in Tables 2 and 3.

Results and Discussion

The reaction of white phosphorus and [Cp″Co(CO)$_2$] under UV irradiation provides the purple complex [(Cp″Co)$_2$(μ,η^2-P$_2$)$_2$] (**6**) and the brown product [Cp″Co(P$_4$){(Cp″Co)$_2$(μ-CO)}] (**7**) upon column chromatography of the reaction mixture.[7]

$$[\mathrm{Cp''Co(CO)_2}] + \mathrm{P_4} \xrightarrow{\mathrm{UV}}$$

Cp″ = η^5-C$_5$H$_3$tBu$_2$



6 **7**

6 is a violet crystalline compound, and **7** forms dark brown crystals. They are readily soluble in CH$_2$Cl$_2$ and THF and slightly soluble in *n*-pentane and benzene. The analytical as well as the spectroscopic data for **6** (δ(^{31}P) = −50.2 ppm; *m/z* = 596 [M$^{\bullet+}$]) show it to be structurally analogous to **3**. The ^{31}P{H}-NMR spectrum of **7** reveals three groups of signals according to an A$_2$MX spin system (P$_A$ = P(3), P$_M$ = P(5), P$_X$ = P(4); Figure 1). The P$_A$ nuclei correspond to the P atoms lying out of the mirror plane of the molecule and appear as a doublet of doublets (δ = 227.8 ppm, J(P$_A$P$_M$) = 360 Hz, J(P$_A$P$_X$) = 44 Hz). The small P$_A$−P$_X$ coupling reflects the long distances between the atoms P$_A$ and P$_X$, observed in the X-ray structure (Figure 1). The P$_X$ signal reveals a remarkable high-field shift at −398.6 ppm (triplet); that of the P$_M$ atom is observed at much lower field, also as a triplet at 9.9 ppm.

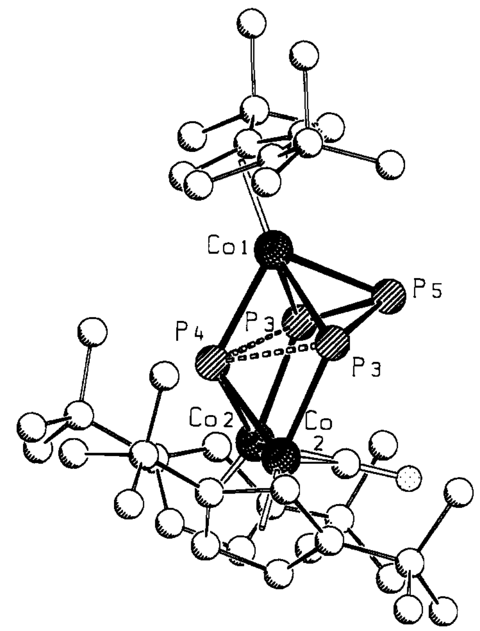


Figure 1. Molecular structure of [Cp″Co(P$_4$){(Cp″Co)$_2$(μ-CO)}] (**7**).

Table 3. Selected Bond Distances (Å) and Bond Angles (°)

Co(1)−P(3)	2.315(2)	Co(2)−P(4)	2.237(2)
Co(1)−P(4)	2.274(3)	P(3)−P(4)	2.503(2)
Co(1)−P(5)	2.267(3)	P(3)−P(5)	2.161(2)
Co(2)−P(3)	2.271(2)	Co(2)−Co(2)	2.459(2)
P(4)−P(3)−P(5)	92.52(8)	P(3)−P(5)−P(3)	94.98(12)
P(3)−P(4)−P(3)	79.07(10)	Co(1)−P(4)−Co(2)	113.47(9)

The X-ray structure of **7** (Figure 1) reveals a planar *cyclo*-P$_4$ ligand η^4-capped by a Cp″Co moiety. A CO-bridged Co dimer with d(CoCo) = 2.459(2) Å corresponding to a single bond (Co$_2$(CO)$_8$: 2.52 Å[8]) coordinates to three of the phosphorus atoms from the bottom of the P$_4$ ligand. This leads to a distortion of the P$_4$ ligand in a kite-like manner. Consequently this unit shows two short (2.161(2) Å, shorter than a P−P single bond (2.21 Å)) and two long P−P distances (2.503(2) Å). The longer distances are intermediate between a bonding P−P length and a van der Waals contact. In [(Ph$_3$P)$_2$Rh(Cl)(η^2-P$_4$)][9] the P−P distance of the side-on-coordinated edge of the P$_4$ molecule is 2.462(2) Å. In consideration of SCF−Xα calculations and spectroscopic data (^{31}P-NMR, IR) a weak P−P bonding is

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(6) For a general discussion of the X-ray diffraction facilities and operating procedures and a listing of programs employed at the IUMSC, see: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatric, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(7) To compare our results with those of Dahl et al.,[3] we carried out the reaction of [Cp*Co(CO)$_2$] and P$_4$ at ambient temperature under UV irradiation. Besides [(Cp*Co)$_2$(μ,η^2-P$_2$)$_2$] (**3**), the bicyclotetraphosphine complex [Cp*Co(CO)(η^2-P$_4$)] (**1**) was formed as the main product of this reaction. Obviously the reaction pathway is very sensitive to the used Cp^x ligand at the Co complex.

(8) Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

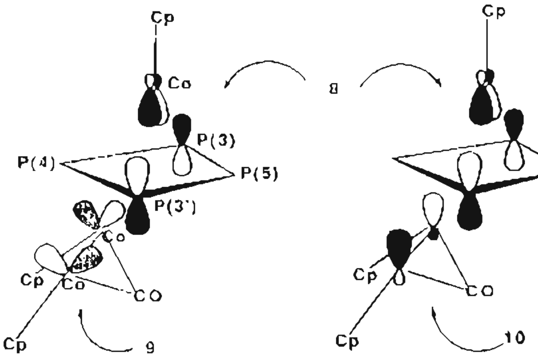
(9) Ginsberg, A. P.; Lindsell, W. E.; Mc Cullough, K. J.; Sprinkle, L. R.; Welch, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 403.

suggested. In $[\{Cp^*Co(CO)\}_2(\mu,\eta^2,\eta^2\text{-}P_4)]^2$ (**2**) the distances of the neighboring P atoms which are coordinated to the Co atoms are 2.597 and 2.606 Å, respectively. They are considered to be nonbonding.

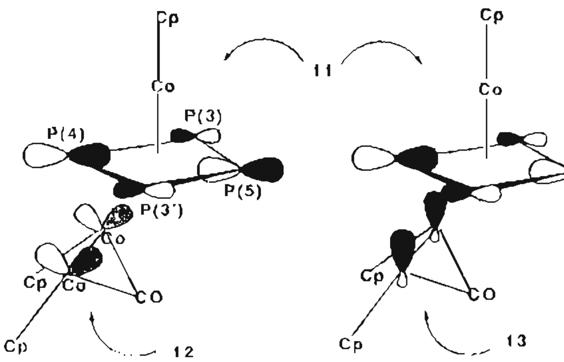
The structure of the complex **7** indicates a possible reaction pathway of the tetrahedral P_4 in the coordination sphere of transition metal complex fragments with an odd number of valence electrons. In these reactions P_1 and *cyclo*-P_3 ligand complexes are usually obtained.[10,11] So, in a first step, there could be the transformation of the P_4 tetrahedron to a square planar P_4 unit which is followed by a kite-like distortion. Finally the P_1 and the *cyclo*-P_3 ligand complexes are formed.

EHT Calculations

The factors controlling the structure of **7** have been studied by EHT calculations.[12] The structure was analyzed by looking for the preferred mode of bonding of $CpCo(P_4)$, $[P_4]$, to $Co_2Cp_2(CO)$, $[Co_2]$. The calculated system has a symmetry plane containing P(4), P(5), and the CO ligand. It is found that $[Co_2]$ coordinates $[P_4]$ in a position which is an intermediate between an η^2 (coordination below P(3),P(3′)) and an η^1 mode (coordination below P(4)). In this manner the HOMO of $[Co_2]$ (**9**) can overlap with the LUMO of $[P_4]$ (**8**). If $[Co_2]$ was to coordinate $[P_4]$ in an η^2 manner, the atomic orbitals of P(3),P(3′) in **8** would have been situated in the nodal plane of **9**. The favorable interaction between **8** and **9** in the experimental geometry is further strengthened by the participation of the empty orbital **10** which is very close in energy to **9**.



The structure of **7** raises the question as to whether the long P−P distances can still be viewed as a bonding situation. Calculation of **7** with the experimental geometry gives a very small positive overlap population between P(4) and P(3),P(3′). Although the Mulliken overlap population is not an accurate measure of the existence of a bond, the low calculated values indicate, in our opinion, a weak P−P bonding at best. In order to understand the origin of this P−P bond weakening, it is important to know how $[Co_2]$ bonds to P(4)−P(3),P(3′). One of the highest occupied orbitals of $[P_4]$ is **11**; it is located in the σ framework of $[P_4]$, bonding between P(4) and P(3),P(3′) and interacting strongly with two empty orbitals of $[Co_2]$, **12** and **13**. Removal of electrons from **11** weakens the P−P bonds. Because of mixing with other orbitals on $[P_4]$, the weakening is mostly limited to the P(4)−P(3),P(3′) bonds.



The previous results suggest that a P_4 ligand does not easily maintain a square geometry and that P−P cleavage is occurring with associated coordination of the phosphorus fragments to available metallic fragments. However a square geometry for a P_4 unit cannot be excluded and has been observed in $[W(CO)_4(\eta^4\text{-}P_4\{WCO)_5\}_4)]$.[13] In this case the lone pair of each phosphorus is coordinated to a $W(CO)_5$ fragment. A detailed study of this complex with high-level calculations would be of great interest. At present, a simple rationale for the absence of P−P cleavage in the P_4 unit is the following. The high-lying occupied orbitals describing phosphorus lone pairs are antibonding within the P−P σ framework. Electron transfer of the lone pairs into $W(CO)_5$ could thus diminish the tendency for P−P cleavage.[14]

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Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, and complete bond distances and angles and figures showing six stereoviews and an ORTEP diagram (14 pages). Ordering information is given on any current masthead page.

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(10) Vizi-Orosz, A.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1973**, *60*, C25. Vizi-Orosz, A. *J. Organomet. Chem.* **1976**, *111*, 61.

(11) Scherer, O. J.; Sitzmann, H.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351.

(12) Ammeter, J. J.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686. Parameters for Co and P: Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

(13) Scheer, M.; Herrmann, E.; Oehme, M.; Sieler, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 969. Barr, M. E.; Smith, S. K.; Spencer, B.; Dahl, L. F. *Organometallics* **1991**, *10*, 3983.

(14) The Nb complex $[Cp^*Nb(CO)_2(\eta^4\text{-}P_4)]$ seems to be an exception to this tendency although it is also slightly distorted in a kite-like way. See: Scherer, O. J.; Vondung, J.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1355.