of hemerythrin and related proteins will require ligands that stabilize the bridged binuclear structure in the reduced, diiron(II) state and permit coordination of exogenous ligands at a nonbridging coordination site. Studies to produce such compounds are in progress.

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Registry No. 1, 86177-70-0; **2**, 89908-14-5; **3**, 89890-13-1.

Supplementary Material Available: Tables S1–S6 reporting observed and calculated structure factor amplitudes and thermal parameters for all atoms and fixed hydrogen atom positional parameters (38 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Opening of the P_4 Molecule: Preparation and Crystal Structure of a Cobalt Complex of a η^4-Tetraphosphabutadiene Ligand

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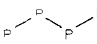
Investigations of the reactivity of white phosphorus toward various organometallic compounds have so far provided rather sparse results, most likely because of the well-known "high reactivity" of the P_4 species. Only recently it has been found that P_4 is capable of coordinating to metallic centers as a η^1 or η^2 ligand.[1,2] More frequently the P_4 molecule has been observed to break apart with subsequent formation of complexes containing the *cyclo*-P_3[3] and -P_2[4] fragments or unsubstituted phosphorus atoms[5] coordinated to the metal.

In this communication we present evidence for the preparation and the crystal structure of a unique complex, [Co($Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2$)]$BF_4$, which contains an unusual zigzag type tetraphosphorus fragment  This complex apparently arises from a P_4 molecule which has been induced to rearrange to a linear P_4 chain by two bis(diphenylphosphino)methane (dppm) ligands.

The preparation of the compound was accomplished by reacting white phosphorus with $Co(BF_4)_2 \cdot 6H_2O$ and dppm in a THF-1-butanol mixture under N_2.[6] The complex was a moderately air-stable, diamagnetic solid that behaves as an 1:1 electrolyte in methylene chloride solution.

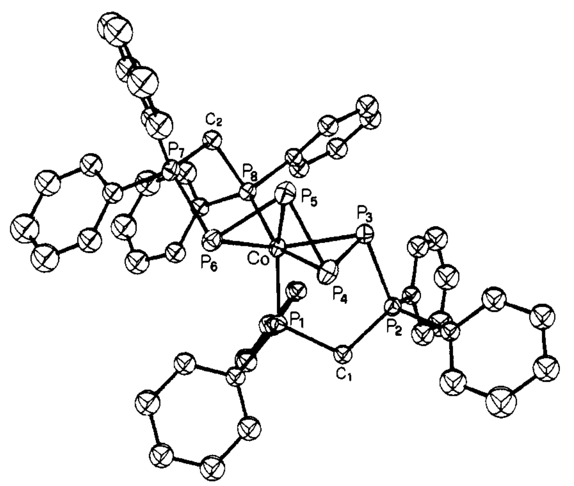


Figure 1. Perspective view of the complex cation [Co($Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2$)]$^+$. ORTEP drawing with 30% probability ellipsoids.

Table I. Selected Bond Distances (Å) and Angles (deg)

Co–P1	2.203 (2)	P2–P3	2.183 (3)
Co–P3	2.281 (2)	P3–P4	2.173 (3)
Co–P4	2.285 (2)	P4–P5	2.197 (3)
Co–P5	2.305 (2)	P5–P6	2.171 (3)
Co–P6	2.281 (2)	P6–P7	2.196 (3)
Co–P8	2.196 (2)		
P1–Co–P3	98.8 (1)	P6–Co–P8	98.1 (1)
P1–Co–P4	95.2 (1)	P2–P3–Co	100.8 (1)
P1–Co–P5	149.9 (1)	P4–P3–Co	61.7 (1)
P1–Co–P6	112.1 (1)	P2–P3–P4	93.4 (1)
P1–Co–P8	109.8 (1)	P3–P4–Co	61.5 (1)
P3–Co–P4	56.8 (1)	P5–P4–Co	61.9 (1)
P3–Co–P5	77.1 (1)	P3–P4–P5	81.6 (1)
P3–Co–P6	130.3 (1)	P4–P5–Co	60.9 (1)
P3–Co–P8	107.1 (1)	P6–P5–Co	61.2 (1)
P4–Co–P5	57.2 (1)	P4–P5–P6	86.2 (1)
P4–Co–P6	81.6 (1)	P5–P6–Co	62.3 (1)
P4–Co–P8	152.7 (1)	P7–P6–Co	100.0 (1)
P5–Co–P6	56.5 (1)	P5–P6–P7	91.8 (1)
P5–Co–P8	99.8 (1)		

The molecular structure of the title compound has been established by a single-crystal X-ray diffraction study.[7] The solution

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[6] A solution of white phosphorus (1.5 mmol) dissolved in THF was added, under a nitrogen atmosphere, to a mixture of $Co(BF_4)_2 \cdot 6H_2O$ (1 mmol) dissolved in 1-butanol and bis(diphenylphosphino)methane (dppm) (2 mmol) dissolved in THF; the resulting solution was heated to the boiling temperature; the solvents were distilled off until the solution turned deep red and then red crystals of analytical formula $C_{50}H_{44}BCoF_4P_8$ precipitated. The yield amounts to 75% based on $Co(BF_4)_2 \cdot 6H_2O$. The complex was recrystallized from methylene chloride/1-butanol.

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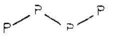
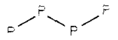
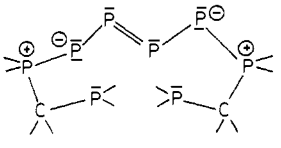
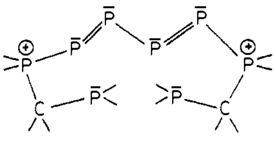
of the structure revealed that a novel ligand $Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2$, resulting from the opening of the P_4 molecule by the attack of two dppm ligands, was formed. Figure 1 shows a perspective view of the complex cation, and Table I reports selected bond distances and angles.

The metal atom has a very distorted octahedral geometry in which the new ligand coordinates through all the phosphorus atoms of the P_4 fragment and two of the four phosphorus atoms belonging to the dppm moieties. Two phosphorus atoms of the dppm remain uncoordinated. Due to the steric requirements of the P_4 fragment which acts as a η^4 ligand, there are significant distortions from octahedral geometry as shown by the values of the axial angles (130.3 (1)°, 149.9 (1)°, 152.7 (1)°). The Co–P bond lengths, involving the phosphorus atoms of the zigzag fragment, have comparable values ranging from 2.281 (2) to 2.305 (2) Å, and, as previously found for *cyclo*-triphosphorus derivatives,[8] are larger than those (2.196 (2) and 2.203 (2) Å) involving the terminal tertiary phosphorus atoms. Of the P–P bond distances within the  chain, the central bond is somewhat larger, 2.197 (3) Å, than the external ones, 2.171 (3) and 2.173 (3) Å. The latter values are significantly larger than those reported for the covalent P=P double bond in noncoordinated bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (2.034 (2) Å)[9] but are somewhat shorter than the values of 2.21 and 2.217 (6) Å, respectively, found in the P_4[10] and $(PhP)_5$[11] molecules, containing covalent P–P single bonds. Although the overall electronic structure must be considered as essentially delocalized, considering that a lengthening of the multiple bonds always occurs upon coordination,[12] we can still assign a partial double bond character to the external P–P bonds of the P_4 chain.

From an electron count point of view, the central atom can reach an 18 outer electron configuration by considering the ligand as either uncharged, 10e$^-$ donor (cobalt(I)) (I), or bipositive, 8e$^-$ donor (cobalt(–I)) (II).[13] The different P–P bond distances, together with the practically identical values of the Co–P distances, seem to be in agreement with the formal resonance structure II. Thus the complex cation may be described as a cobalt(–I) species having a pesudotetrahedral coordination sphere which would involve two double P=P bonds and two ligating phosphines. It is noteworthy that the value of the sole P–Co–P unconstrainted angle, P_1–Co–P_8, is 109.8 (1)°. This approach is further supported by an X-ray structure determination of the $Zr(\eta^5\text{-}C_5H_5)_2$(*s-trans*-PhCH=CH—CH=CHPh) complex,[14] where the diphenylbutadiene exhibits a ligating mode fully comparable to that of the  fragment in the title compound.

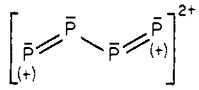


I

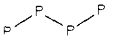


II

On the basis of the structural results presented here we assume that the reaction involves an oxidation of the P_4 molecule to the species III which is then nucleophilically attacked by the dppm phosphorus atoms at the positively charged phosphorus sites of this tetraphosphorus chain.



III

Preliminary results of the studies on reactivity of this compound can be summarized as follows: (i) the phosphorus atoms of the  fragment are coordinatively unsaturated, the present complex reacting with $W(CO)_6$ to form the derivative $[Co(PhPCH_2PPh_2PPPPPh_2PCH_2PPh_2)W(CO)_5]BPh_4$,[15] and (ii) the complex can be used instead of white phosphorus to obtain *cyclo*-P_3 derivatives.

Registry No. dppm, 2071-20-7; $[Co(Ph_2PCH_2PPh_2PPPPPh_2PCH_2PPh_2)]BF_4$, 90149-67-0; $Co(BF_4)_2$, 26490-63-1; $W(CO)_6$, 14040-11-0; phosphorus, 7723-14-0.

Supplementary Material Available: Listing of observed and calculated structure factors and tables of positional and thermal parameters (30 pages). Ordering information is given on any current masthead page.

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(7) Space group $P2_1/n$, $a = 19.071$ (7) Å, $b = 26.712$ (9) Å, $c = 9.709$ (4) Å, $\beta = 93.92$ (5)°, $Z = 4$, $V = 4934.4$ Å^3, $d_c = 1.397$ g cm^{-3}. Intensity data were collected on a Philips PW 1100 automatic diffractometer by using the ω–2θ scan technique and monochromatized Mo Kα radiation. The structure was solved by the heavy-atom method and, after correction for absorption, refined by full-matrix least-squares using isotropic thermal parameters for the carbon atoms and anisotropic for the heavier ones. The phenyl rings were treated as rigid groups and the hydrogen atoms were introduced in calculated positions but not refined. The final values of the R and R_w factors for 4703 reflections having $I \geq 3\sigma(I)$ are 0.063 and 0.064, respectively.

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A Chiral Primary Alcohol Equivalent: Silyl-Assisted Asymmetric Induction in the Ester Enolate Claisen Rearrangement[1]

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In an earlier publication[2] from these laboratories, a scheme for the total synthesis of the prostanoids was presented, and the construction of a racemic derivative of PGA_1 was delineated. This work was an initial example of the power of the ester enolate Claisen rearrangement for the convergent synthesis of complex molecules. The observation[2] that ester enolate geometry could be controlled by choice of reaction conditions led to the use of this Claisen variant for selective production of diastereomeric disubstituted γ,δ-unsaturated acids. When the allylic system is enantiomerically pure, the use of this feature for stereochemical control in the synthesis of acyclic systems with large numbers of contiguous asymmetric centers has led to the construction of ionophores,[3] macrolides,[4] terepenoids,[5] and other natural products.[6]

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(1) Contribution No. 6980. Grateful acknowledgement for the support of this investigation through National Science Foundation Grant CHE-78-21066. No reprints available.

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