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Contribution from the Istituto per lo Studio della Stereochimica
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A Tetraphosphorus Chain as Part of a P_8-Containing Ligand. Synthesis and Properties of the η^4-Phosphabutadiene Cobalt Complex $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$ and of Its Carbonyl Derivatives $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}BF_4$ and $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}Y$ (Y = BPh_4, BF_4). X-ray Crystal Structure of $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$

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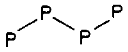
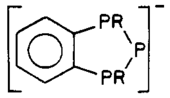
Cobalt(II) tetrafluoroborate hexahydrate in the presence of bis(diphenylphosphino)methane, dppm, reacts with white phosphorus to give the η^4-phosphabutadiene cobalt complex $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$ (**1**) containing the tetraphosphorus zigzag chain



A complete X-ray structure determination has been carried out. Crystal data for **1**: *a* = 19.071 (7) Å, *b* = 26.712 (9) Å, *c* = 9.709 (4) Å, β = 93.92 (5)°, space group $P2_1/n$, *Z* = 4. Full-matrix least-squares refinement led to a conventional *R* factor of 0.063 for 4703 observed reflections. The cobalt atom is surrounded in a distorted octahedral fashion by the novel ligand $Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2$, arising from the opening of the P_4 molecule by the attack of two dppm ligands. The cobalt is coordinated to the four phosphorus atoms of the zigzag P–P–P–P fragment and to two of the four phosphorus atoms of the dppm ligands. In the reaction of **1** with hexacarbonyl derivatives, the heterometal complexes of formula $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}BF_4$ (**2**) and $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}Y$ (Y = BPh_4 (**3**) and Y = BF_4 (**4**)) are formed. Crystals affording only a low-precision structure analysis for **3** have been obtained, the results of which are deposited in the supplementary material. This shows that one of the two central phosphorus atoms of the zigzag P–P–P–P chain is linked to the tungsten atom of a $W(CO)_5$ fragment. The coordination geometry around the cobalt atom is essentially unchanged with respect to that of the starting complex **1**.

Introduction

Recent investigations have shown that the highly reactive P_4 molecule of white phosphorus is attacked and degraded both by metal centers and by phosphinate or phosphide ions. In the first case, transition-metal complexes containing the P_4 molecule acting as a η^1 or η^2 ligand have been reported.[1,2] More frequently, metal complexes containing fragments arising from the cleavage of the P_4 molecule, such as *c*-P_3,[3] P_2,[3c,4] P,[5] and very recently *c*-P_6[3c] have been obtained. In the second case strong nucleophiles like phosphinite or phosphide ions have been found to dissociate or to disproportionate the P_4 molecule to give phosphinite or phosphide complexes of P^+ and P_2, such as triphosphinate $[OR_2PPPR_2O]^-$, tetraphosphinate $[OR_2PPPPR_2O]^{2-}$, or cyclic triphosphide[6]



In this work we have treated white phosphorus with $Co(BF_4)_2{\cdot}6H_2O$ and dppm (bis(diphenylphosphino)methane) in a THF/1-butanol mixture to give a unique cobalt complex of formula $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$ (**1**), whose structure determination reveals a ring-opened and η^4-coordinated P_4 moiety.

In order to verify the nucleophilic character of the phosphorus atoms of the P–P–P–P fragment in complex **1**, this was reacted with an excess of $Cr(CO)_6$ to yield the $Cr(CO)_5$ bisadduct $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}BF_4$ (**2**). The analogous reaction with $W(CO)_6$ leads to $W(CO)_5$ monoadducts $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}Y$, where Y = BPh_4 (**3**) and Y = BF_4 (**4**).

Complexes **1**–**4** have been characterized by appropriate physical methods. Complete X-ray structure determinations for complexes **1** and **3** have been carried out. A preliminary report has been published.[7]

Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen. Solvents were of reagent grade or better. IR data were recorded on a Perkin-Elmer 283 spectrophotometer. NMR spectra were obtained on a Varian CFT20; external standards were used for all spectra: 85% H_3PO_4 for ^{31}P NMR; $Si(CH_3)_4$ for ^1H NMR. Downfield shifts have positive values. $Ph_2PCH_2PPh_2$ (Strem Chemical Co.) and $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (Pressure Chemical Co.) were purchased from commercial sources.

Preparation of $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$ (1). A solution of $[Co(H_2O)_6](BF_4)_2$ (0.34 g, 1 mmol) in 20 mL of 1-butanol was added at room temperature to a solution of bis(diphenylphosphino)methane (0.77 g, 2 mmol) in 20 mL of THF. A solution of white phosphorus (0.19 g, 1.5 mmol) in 25 mL of THF was added to the mixture. The resulting solution was heated to the boiling point, and the solvents were distilled off until crystallization started. Upon cooling, red-brown crystals were formed, which were washed with three 25-mL portions of benzene and isolated by filtration. The crystals were next washed with petroluem ether and dried under a stream of nitrogen; yield 75%. The complex was recrystallized from methylene chloride/1-butanol. Anal. Calcd for $C_{50}H_{44}BCoF_4P_8$: C, 57.83; H, 4.27; Co, 5.67; P, 23.86. Found: C, 57.88; H, 4.34; Co, 5.61; P, 23.51. ^1H NMR (CD_2Cl_2): δ 7.3 (12), 3.3 (1).

Preparation of $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}BF_4$ (2). Complex **1** (0.20 g, 0.19 mmol) was dissolved in 30 mL of methylene chloride under nitrogen, and chromium hexacarbonyl (0.17 g, 0.76 mmol) was added. The mixture was refluxed under UV light for 1 h. The resulting red-brown mixture was filtered, and benzene (20 mL) was added to the filtrate. After concentration under a stream of nitrogen at room temperature, red-brown crystals precipitated. These were filtered

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(1) (a) Dapporto, P.; Midollini, S.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 469. (b) Dappporto, P.; Sacconi, L.; Stoppioni, P.; Zanobini, F. *Inorg. Chem.* **1981**, *20*, 3834.

(2) Lindsell, W. E.; McCullogh, K. S.; Welch, A. *J. Am. Chem. Soc.* **1983**, *105*, 4487.

(3) (a) Di Vaira, M.; Ghilardi, C. A.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1978**, *100*, 2550. (b) Vizi-Orosz, A. *J. Organomet. Chem.* **1976**, *111*, 61. (c) Sherer, O. J.; Sitzmann, K.; Wolmershäuser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351.

(4) Campana, C. F.; Vizi-Orosz, A.; Palayi, G.; Markò, L.; Dahl, L. F. *Inorg. Chem.* **1979**, *18*, 3054.

(5) Simon, G. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 2175.

(6) Schmidpeter, A.; Lochschmidt, S.; Burget, G.; Sheldrich, W. S. *Phosphorus Sulfur*, **1983**, *18*, 23.

(7) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Am. Chem. Soc.* **1984**, *106*, 3667.

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Table I. Crystal Data and Data Collection Details

	1	3
formula	$C_{50}H_{44}BCoF_4P_8$	$C_{79}H_{64}BCoO_5P_8W$
mol wt	1038.4	1594.8
space group	$P2_1/n$	$P2_1/a$
a, Å	19.071 (7)	20.403 (10)
b, Å	26.712 (9)	25.212 (13)
c, Å	9.709 (4)	14.227 (7)
β, deg	93.92 (5)	94.06 (7)
V, Å^3	4934.4	7300.0
Z	4	4
d_{calcd}, g cm^{-3}	1.397	1.451
color	red-brown	red-brown
habit	regular prism	irregularly shaped
dimens, mm	0.19 × 0.30 × 0.55	0.02 × 0.07 × 0.13
linear abs coeff, cm^{-1}	6.5	20.5
transmissn factors	0.78–0.90	
diffractometer	Philips PW 1100	Philips PW 1100
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
monochromator	graphite crystal	graphite crystal
method	ω–2θ	ω–2θ
scan speed, deg s^{-1}	0.08	0.05
scan width, deg	0.70 + 0.3 tan θ	0.80 + 0.3 tan θ
bkgd time	half the scan time	half the scan time
stds	3 every 2 h	3 every 2 h
max dev stds, %	5	20
2θ limits, deg	$5 \le 2\theta \le 50$	$5 \le 2\theta \le 40$
data collcd	$\pm h,+k,+l$	$\pm h,+k,+l$
no. of total data	9425	7415
no. of data used ($I \ge 3\sigma(I)$)	4703	1642
no. of final params	229	287
final max shift/esd	0.3	0.7
temp, °C	22	22

off, washed with benzene and petroleum ether, and dried under nitrogen; yield 69%. The complex was recrystallized from methylene chloride/benzene. Anal. Calcd for $C_{60}H_{44}BCoCr_2F_4O_{10}P_8$: C, 50.66; H, 3.12; Co, 4.14; Cr, 7.31. Found: C, 49.98; H, 3.41; Co, 3.80; Cr, 6.90.

Preparation of $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}BPh_4$ (3). The red-brown derivative $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}BF_4$ was prepared by reacting complex **1** (0.20 g, 0.19 mmol) with tungsten hexacarbonyl (0.30 g, 0.76 mmol) according to the method used for the preparation of **2**. The crude microcrystalline compound was dissolved in 20 mL of acetone, and sodium tetraphenylborate (0.05 g, 0.15 mmol) in 20 mL of 1-butanol was added. After concentration of the solution at room temperature under a stream of nitrogen, crystals were precipitated. They were filtered off and washed with 1-butanol and petroleum ether; yield 74%. Anal. Calcd for $C_{79}H_{64}BCoO_5P_8W$: C, 59.50; H, 4.05; Co, 3.70. Found: C, 58.56; H, 4.15; Co, 3.90.

Preparation of $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}BF_4$ (4). Complex **4** was prepared according to the procedure used for complex **3** but without adding sodium tetrapheylborate; yield 67%. Anal. Calcd for $C_{55}H_{44}BCoF_4O_5P_8W$: C, 48.49; H, 3.25; Co, 4.32. Found: C, 48.85; H, 3.62; Co, 4.13.

X-ray Data Collection and Reduction. The crystals used for X-ray work were mounted on a glass fiber along the b crystallographic axis for compound **1** and in a random orientation for compound **3**. Intensity data of both compounds were collected on a Philips PW 1100 automatic diffractometer. Relevant data for the crystals and data collection are reported in Table I. Cell constants were determined from a least-squares refinement of the setting angles of 22 and 20 carefully centered reflections for compounds **1** and **3**, respectively. Both crystals belong to the monoclinic system with extinction characteristics of space groups $P2_1/n$ (**1**) and $P2_1/a$ (**3**). The intensity data were processed as described elsewhere.[8] The intensities were rescaled on the basis of three standard reflections, which were checked during the data collection. While compound **1** showed no significant trend, compound **3** showed 20% decay in intensities. The intensities, I, were assigned standard deviations $\sigma(I)$, calculated with an instability factor p = 0.03 for both compounds.[9] Intensities were corrected for Lorentz–polarization effects, and an absorption correction[10] by the numerical-integration method was applied to compound **1** (faces 100, 101, 120, $\bar{1}20$, $\bar{1}00$, $\bar{1}0\bar{1}$, $\bar{1}\bar{2}0$, $1\bar{2}0$). For compound **3** the absorption correction was not applied due to its irregular shape.

Solution and Refinement of the Structures. All the calculations were performed by using the SHELX-76[10] and ORTEP[11] programs on a SEL 32/77 computer installed in our institute. Atomic scattering factors for all non-hydrogen atoms were taken from ref 12, and those for hydrogen atoms from ref 13. Corrections for anomalous dispersion effects, real and imaginary,[14] were applied to the calculated structure factor amplitudes. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, where w is $1/[\sigma^2(F_o) + gF_o^2]$ with $g = 0.0$.

$[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$. The structure was solved by the heavy-atom method from a three-dimensional Patterson synthesis. Successive Fourier maps showed all non-hydrogen atoms. Full-matrix least-squares refinements were then undertaken; some isotropic cycles were followed by mixed ones, in which anisotropic thermal parameters were assigned to cobalt, phosphorus, and fluorine atoms. During the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry (C–C = 1.395 Å). Hydrogen atoms were introduced in their calculated positions (C–H = 0.95 Å) but not refined. Refinement converged to R and R_w of 0.063 and 0.064, respectively. Final positional parameters are given in Table II.

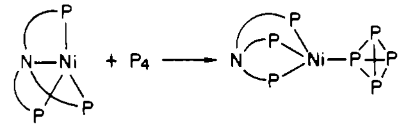
$\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}BPh_4$. Owing to unsatisfactory convergence of the data for this structure determination, we consider it useful only to determine the connectivity of the atoms. The atomic positional parameters and selected distance and angle data have been deposited in the supplementary material for future reference.

Results and Discussion

Thus far, three types of reactivity are seen for the P_4 molecule toward metal complexes:

(a) Coordination of intact P_4 on complexes containing easily displaced ligands, such as $(R_3P)_3RhCl$[2] or $(np_3)Ni$[3] (np_3 = $N(CH_2CH_2PPh_2)_3$)

$$(R_3P)_3RhCl + P_4 \longrightarrow (R_3P)_2RhClP_4 + PR_3 \qquad (1)$$


(2)

(b) reaction of P_4 with dissociation or disproportionation into P_n fragments (n = 1–3, 6), in coordination to complexes containing easily cleaved metal–metal bonds, such as $Co_2(CO)_8$[3b] or $(Me_5C_5)_2Mo_2(CO)_4$[3c]

$$Co_2(CO)_8 \xrightarrow{P_4} \left\{\begin{array}{l} P_3Co(CO)_3 \\ P_2[Co(CO)_3]_2 \\ P[Co(CO)_3]_3 \end{array}\right. \qquad (3)$$

$$[(\eta^5\text{-}Me_5C_5)Mo(CO)_2]_2 \xrightarrow{P_4} \left\{\begin{array}{l} P_6[(Me_5C_5)Mo]_2 \\ P_3[(Me_5C_5)Mo(CO)_2] \\ P_2[(Me_5C_5)Mo(CO)_2]_2 \end{array}\right. \qquad (4)$$

(c) reaction of P_4 with formation of P_n fragments, in coordination to divalent ions containing polydentate phosphines, which by themselves are unable to coordinatively saturate the metal center such as $[(triphos)ML_n]^{2+}$ (triphos = $CH_3C(CH_2PPh_2)_3$; M = Co, Ni; L = solvent, H_2O)[15]

$$[Co(H_2O)_6]^{2+} + \text{triphos} \xrightarrow{P_4} (\text{triphos})CoP_3 + \{[(\text{triphos})Co]_2P_3\}^{2+} \qquad (5)$$

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[8] Bianchi, A.; Dapporto, P.; Fallani, G.; Ghilardi, C. A.; Sacconi, L. *J. Chem. Soc., Dalton Trans.* **1973**, 641.

[9] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1976**, *6*, 197.

[10] Sheldrick, G. M. *System of Computing Programs*; University of Cambridge: Cambridge, England, 1976.

[11] Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1976**, *ORNL-5138*.

[12] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 99.

[13] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[14] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 149.

Table II. Positional Parameters ($\times 10^4$) for $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	1952 (1)	479 (1)	−3691 (1)	C63	2995 (3)	2431 (2)	−3439 (5)
P1	1880 (1)	1040 (1)	−2045 (2)	C14	1517 (2)	2175 (2)	−5538 (5)
P2	2020 (1)	1732 (1)	−4480 (2)	C24	1740 (2)	2279 (2)	−6847 (5)
P3	2094 (1)	1007 (1)	−5497 (2)	C34	1369 (2)	2621 (2)	−7704 (5)
P4	1033 (1)	791 (1)	−5063 (2)	C44	776 (2)	2859 (2)	−7252 (5)
P5	1436 (1)	46 (1)	−5548 (2)	C54	553 (2)	2755 (2)	−5943 (5)
P6	1181 (1)	−166 (1)	−3482 (2)	C64	924 (2)	2413 (2)	−5086 (5)
P7	1912 (1)	−802 (1)	−3454 (2)	C15	1609 (3)	−1317 (2)	−4553 (6)
P8	2932 (1)	51 (1)	−3350 (2)	C25	940 (3)	−1302 (2)	−5231 (6)
F1	1509 (3)	2827 (2)	−1841 (7)	C35	703 (3)	−1702 (2)	−6062 (6)
F2	911 (4)	3319 (3)	−492 (7)	C45	1135 (3)	−2117 (2)	−6215 (6)
F3	457 (4)	2651 (3)	−1476 (11)	C55	1803 (3)	−2132 (2)	−5537 (6)
F4	644 (5)	3305 (3)	−2626 (7)	C65	2040 (3)	−1733 (2)	−4706 (6)
C1	1638 (3)	1659 (2)	−2850 (7)	C16	2028 (2)	−1032 (2)	−1716 (5)
C2	2750 (3)	−595 (2)	−4017 (7)	C26	2627 (2)	−1300 (2)	−1255 (5)
C11	2679 (2)	1207 (2)	−959 (4)	C36	2696 (2)	−1479 (2)	96 (5)
C21	3303 (2)	1245 (2)	−1622 (4)	C46	2166 (2)	−1391 (2)	988 (5)
C31	3927 (2)	1372 (2)	−870 (4)	C56	1567 (2)	−1123 (2)	528 (5)
C41	3927 (2)	1461 (2)	546 (4)	C66	1498 (2)	−944 (2)	−824 (5)
C51	3303 (2)	1423 (2)	1209 (4)	C17	3321 (2)	−112 (2)	−1628 (5)
C61	2679 (2)	1296 (2)	457 (4)	C27	2935 (2)	−21 (2)	−485 (5)
C12	1223 (3)	988 (2)	−747 (5)	C37	3182 (2)	−192 (2)	817 (5)
C22	1076 (3)	510 (2)	−268 (5)	C47	3816 (2)	−453 (2)	975 (5)
C32	643 (3)	451 (2)	822 (5)	C57	4202 (2)	−544 (2)	−168 (5)
C42	357 (3)	870 (2)	1433 (5)	C67	3955 (2)	−374 (2)	−1470 (5)
C52	505 (3)	1348 (2)	954 (5)	C18	3690 (2)	262 (2)	−4274 (4)
C62	937 (3)	1407 (2)	−136 (5)	C28	3622 (2)	267 (2)	−5714 (4)
C13	2879 (3)	2000 (2)	−4233 (5)	C38	4133 (2)	499 (2)	−6454 (4)
C23	3421 (3)	1799 (2)	−4954 (5)	C48	4713 (2)	725 (2)	−5755 (4)
C33	4079 (3)	2029 (2)	−4881 (5)	C58	4781 (2)	720 (2)	−4315 (4)
C43	4195 (3)	2460 (2)	−4087 (5)	C68	4270 (2)	488 (2)	−3575 (4)
C53	3653 (3)	2661 (2)	−3366 (5)	B	886 (6)	3024 (5)	−1611 (13)

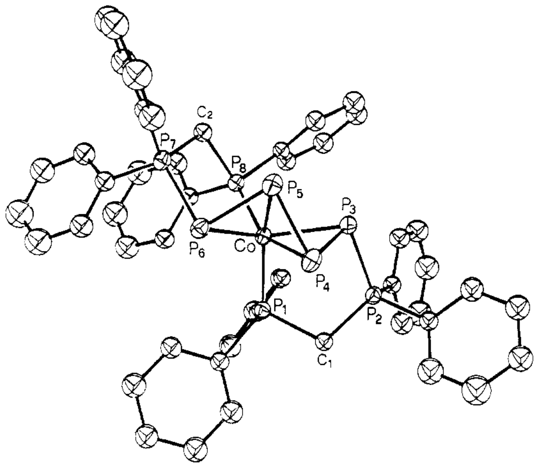

Figure 1. Perspective view of the complex cation $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]^+$; ORTEP drawing with 30% probability ellipsoids.

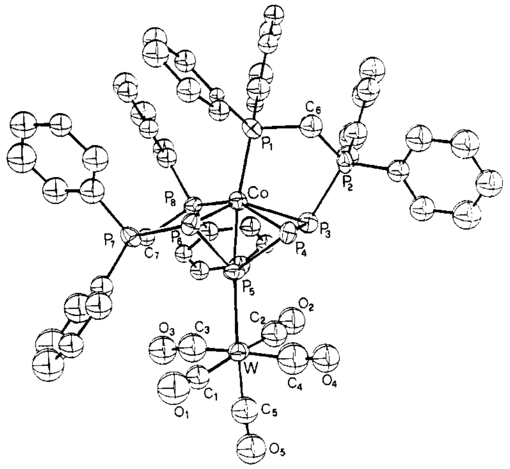

Figure 2. Perspective view of the complex cation $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}^+$; ORTEP drawing with 30% probability ellipsoids.

On this basis the system $[Co(H_2O)_6](BF_4)_2$/dppm in organic solvents seemed suitable in order to test the activation of the P_4 molecule. Indeed the required properties of the dppm ligand are illustrated by its inability to completely coordinate the Co^{2+} ions.[16] Dppm adducts are ill-defined[17] and rapidly react with other ligands to yield stable five-coordinated complexes (X^-,[18] (H_2S,[19] or CO[19]).

$$[Co(H_2O)_6]^{2+} + 2dppm \longrightarrow \begin{cases} \xrightarrow{X^-} [Co(dppm)_2X]^+ \\ \xrightarrow{H_2S} [Co(dppm)_2SH]^+ \\ \xrightarrow{CO} [Co(dppm)_2CO]^+ \end{cases} \tag{6}$$

(X = Cl, Br, I)

Thus we find that the salt $[Co(H_2O)_6](BF_4)_2$ reacts with white phosphorus in the presence of dppm at about 100 °C in THF/1-butanol solution and under nitrogen to form red-brown crystals of $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]BF_4$ (**1**).

When we tried to react $CoCl_2$ with dppm and P_4 under the same conditions, we did not obtain any P_n complexes. Clearly the five-coordinated complex $[Co(dppm)_2Cl]^+$ is stable and is not capable of reacting with the P_4 molecule; this is also true for the stable square-planar $[Ni(dppm)_2]^{2+}$[20] and $[Co(dppe)_2]^{2+}$[21] (dppe = $Ph_2PCH_2CH_2PPh_2$) complexes. These illustrate the fact that

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(15) Di Vaira, M.; Midollini, S.; Sacconi, L. *J. Am. Chem. Soc.* **1979**, *101*, 1757.

(16) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99.

(17) We are unable to isolate any complex from the solutions of $[Co(H_2O)_6](BF_4)_2$ and dppm.

(18) Chow, K. K.; McAuliffe, C. A. *Inorg. Chim. Acta* **1975**, *14*, 121.

(19) Cecconi, F.; Midollini, S. unpublished results.

(20) Levason, W.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 173.

(21) Fogleman, W. W.; Jonassen, M. B. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1536.

Table III. Selected Bond Distances (Å) and Angles (deg) for **1**

Co–P1	2.203 (2)	P1–Co–P3	98.8 (1)
Co–P3	2.281 (2)	P1–Co–P4	95.2 (1)
Co–P4	2.285 (2)	P1–Co–P5	149.9 (1)
Co–P5	2.305 (2)	P1–Co–P6	112.1 (1)
Co–P6	2.281 (2)	P1–Co–P8	109.8 (1)
Co–P8	2.196 (2)	P3–Co–P4	56.8 (1)
P2–P3	2.183 (3)	P3–Co–P5	77.1 (1)
P3–P4	2.173 (3)	P3–Co–P6	130.3 (1)
P4–P5	2.197 (3)	P3–Co–P8	107.1 (1)
P5–P6	2.171 (3)	P4–Co–P5	57.2 (1)
P6–P7	2.196 (3)	P4–Co–P6	81.6 (1)
P1–C1	1.873 (6)	P4–Co–P8	152.7 (1)
P1–C11	1.847 (4)	P5–Co–P6	56.5 (1)
P1–C12	1.842 (5)	P5–Co–P8	99.8 (1)
P2–C1	1.798 (6)	P6–Co–P8	98.1 (1)
P2–C13	1.787 (5)	P2–P3–Co	100.8 (1)
P2–C14	1.800 (5)	P4–P3–Co	61.7 (1)
P7–C2	1.809 (6)	P2–P3–P4	93.4 (1)
P7–C15	1.813 (6)	P3–P4–Co	61.5 (1)
P7–C16	1.796 (6)	P5–P4–Co	61.9 (1)
P8–C2	1.869 (6)	P3–P4–P5	81.6 (1)
P8–C17	1.835 (5)	P4–P5–Co	60.9 (1)
P8–C18	1.842 (5)	P6–P5–Co	61.2 (1)
		P6–P5–P4	86.2 (1)
		P5–P6–Co	62.3 (1)
		P7–P6–Co	100.0 (1)
		P5–P6–P7	91.8 (1)

if the organometallic system is not labile enough, the reaction with P_4 does not occur.

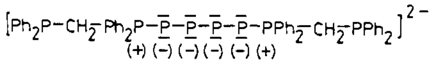
Complex **1** is diamagnetic and soluble as a 1:1 electrolyte in polar solvents such as methylene chloride, acetone, and nitroethane. The compound slowly decomposes in air both in solution and in the solid state.

The molecular structure consists of discrete complex cations $[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)]^+$ and tetrafluoroborate anions. A perspective view of the complex cation is shown in Figure 1; selected bond distances and angles are given in Table III.

The X-ray diffraction study reveals the formation of the novel ligand $Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2$, which arises from the opening of the P_4 molecule and its rearrangement, induced by two dppm molecules, to a linear tetraphosphorus zigzag chain. The metal atom displays a distorted octahedral geometry with the new ligand coordinating through all the phosphorus atoms of the zigzag P–P–P–P group and two of the four phosphorus atoms belonging to the dppm fragments. Two phosphorus atoms of the dppm remain uncoordinated. The distortion from the idealized octahedral geometry, well evidenced by the values of the axial angles (130.3 (1), 149.9 (1), and 152.7 (1)°), seems mainly due to the steric requirement of the P_4 fragment, which acts as a η^4 ligand. Indeed the P_4 molecule, undergoing the breaking of three of the six P–P bonds, opens to surround the metal, until the dihedral angle between planes $P_2P_3P_4$ and $P_3P_4P_5$ reaches the value of 121.1°. The Co–P bond distances involving the phosphorus atoms of the P_4 chain (range 2.281 (2)–2.305 (2) Å) are somewhat larger than the values related to the terminal tertiary phosphorus atoms (2.196 (2) and 2.203 (2) Å). This trend has been already noticed for *cyclo*-triphosphorus derivatives. In particular, in the cobalt complex (triphos)Co(η^3-P_3), the Co–P(η^3-P_3) and Co–P(triphos) bond distances are 2.301 (1) and 2.186 (1) Å, respectively.[3a]

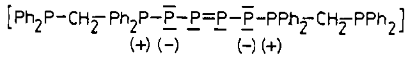
As concerns the P–P bonds within the P_4 fragment, it is noteworthy that the central distance (2.197 (3) Å) is somewhat larger than the external ones (2.171 (3) and 2.173 (3) Å); however, all these distances, although significantly larger than the values reported for the P=P covalent double bond in noncoordinated bis(2,4,6-tri-*tert*-butylphenyl)diphosphine (2.034 (2) Å),[22] are somewhat shorter than the values of 2.21 and 2.217 (6) Å, respectively, reported for the P_4[23] and $(PhP)_5$[24] molecules, in which P–P covalent single bonds are present. On this basis, even if the electronic structure should be considered essentially delocalized, we can assign a partial double-bond character to the external P–P bonds of the P_4 fragment, taking into account that a lengthening of multiple bonds occurs upon coordination.[25]

From an electron-counting viewpoint, the metal atom can reach the 18-valence-electron configuration in three ways: by considering (i) the $Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2$ ligand as binegative and a 12-electron donor (structure I) with the metal as cobalt(III),



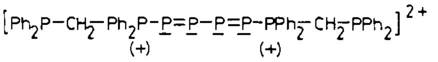
$$[\mathrm{Ph_2P{-}CH_2{-}\underset{(+)}{Ph_2P}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underset{(+)}{PPh_2}{-}CH_2{-}PPh_2}]^{2-}$$

I



$$[\mathrm{Ph_2P{-}CH_2{-}\underset{(+)}{Ph_2P}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underline{P}{=}\underline{P}{-}\underset{(-)}{\overline{\underline{P}}}{-}\underset{(+)}{PPh_2}{-}CH_2{-}PPh_2}]$$

II



$$[\mathrm{Ph_2P{-}CH_2{-}\underset{(+)}{Ph_2P}{-}\underline{P}{=}\underline{P}{-}\underline{P}{=}\underline{P}{-}\underset{(+)}{PPh_2}{-}CH_2{-}PPh_2}]^{2+}$$

III

(ii) the ligand as being uncharged and a 10-electron donor (structure II) on cobalt(I), or (iii) the ligand as bipositive and an 8-electron donor (structure III) on cobalt(−I).

On the basis of the difference noted between the P–P bond distances and the equivalence of the Co–P bond lengths, limiting-structure III seems to be preferred. In this context the cation may be considered as a cobalt(−I) species, tetrahedrally coordinated by two P=P double bonds and two ligating phosphines. The value of the unique P–Co–P unconstrainted angle of 109.8 (1)° is in agreement with this assertion. On the other hand, the Zr(η^5-C_5H_5)$_2$(*s-trans*-PhCH=CH—CH=CHPh) complex,[26] where the diphenylbutadiene shows an attachment mode fully comparable to that of the P_4 fragment in the title derivative, seems a further support.

It has been recently found by Schmidpeter et al. that P_4 can be degraded by strong nucleophilic agents such as phosphine, phosphinite, and phosphides. By termination of a singly bonded, all-octet P_n chain with a phosphino or phosphine oxide group, two series, $(R_3P)_2P_n^{\,2-n}$ and $(OR_2P)_2P_n^{\,n-}$, result formally:

	I	II
$n = 0$	$R_3P\text{-}PR_3^{\,2+}$	$O{=}R_2P\text{-}PR_2{=}O$
1	$R_3P\text{-}P\text{-}PR_3^{\,+}$ [27]	$O{=}R_2P\text{-}P\text{-}PR_2{=}O^-$ [28]
2	$R_3P\text{-}P\text{-}P\text{-}PR_3$	$O{=}R_2P\text{-}P\text{-}P\text{-}PR_2{=}O^{2-}$ [28]
3	$R_3P\text{-}P\text{-}P\text{-}P\text{-}PR_3^{\,-}$	
4	$R_3P\text{-}P\text{-}P\text{-}P\text{-}P\text{-}PR_3^{\,2-}$	

Of the first series, only the $n = 1$ representative was prepared. In this context, our complex may be regarded as containing the $n = 4$ representative, a 12-electron donor (limiting formal structure I with Co^{III}); clearly the $R_3P(P_4)PR_3$ ligand is, here, stabilized by electron withdrawal to the metal. This electron transfer can be expressed by using the oxidized forms II and III together with Co^I and Co^{-I}, respectively. These considerations well agree with the above crystallographic results.

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(22) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirutsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(23) *Spec. Publ.—Chem. Soc.* **1965**, *No. 18.*

(24) Daly, J. J. *J. Chem. Soc.* **1964**, 6147.

(25) Chatt, J.; Hitchcock, P. B.; Pidcock, A.; Warrens, C. P.; Dixon, K. R. *J. Chem. Soc., Chem. Commun.* **1982**, 932.

(26) Kay, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1982**, 191.

(27) Schmidpeter, A.; Lochschmidt, S.; Scheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226.

(28) Schmidpeter, A.; Burget, G.; Von Schnering, H. G.; Weber, D. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 816.

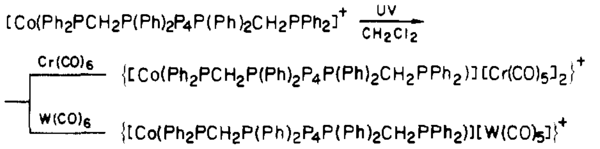
Complex **1**, containing the zigzag P–P–P–P chain as a part of an organometallic framework, can substitute for white phosphorus in reaction 5 as follows:

$$[Co(H_2O)_6]^{2+} + \text{triphos} \xrightarrow{\mathbf{1}} [(\text{triphos})CoP_3Co(\text{triphos})]^{2+} \quad (7)$$

In reaction 7, only the dimeric derivative $[(\text{triphos})CoP_3Co(\text{triphos})]^{2+}$ is formed.

In spite of this, complex **1** appears of low reactivity: e.g. no reactions are observed with S_8, CH_3I, or I_2, at 60 °C, in THF solution. The starting compound is recovered essentially unreacted in somewhat lower yield, owing to some decomposition. It is interesting to note that the complex $(\text{triphos})CoP_3$ reacts completely with I_2 or S_8 under the same conditions. Unfortunately, we were unable to identify all the reaction products.

In complex **1** each phosphorus atom of the P_4 fragment utilizes at most three of its five valence electrons (limiting structure III); therefore, electrophilic reactions at the phosphorus atoms are to be expected. Complex **1** was thus shown to react with an excess of hexacarbonyl group VI (6)[29] metal complexes to yield, under UV irradiation, $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}BF_4$ (**2**) or $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}Y$ ($Y = BPh_4$ (**3**) $Y = BF_4$ (**4**)) (reaction 8).



$$[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2]^+ \xrightarrow[CH_2Cl_2]{UV} \begin{cases} \xrightarrow{Cr(CO)_6} \{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][Cr(CO)_5]_2\}^+ \\ \xrightarrow{W(CO)_6} \{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}^+ \end{cases} \quad (8)$$

Complexes **2–4** essentially show the same general properties as those of the parent complex, **1**. The IR spectra of the complexes (Nujol mulls) show, in the CO stretching vibration region, bands at 2075 (m) and 1990 (w) cm^{-1} and a large envelope (vs) centered at 1950 cm^{-1} for **2** and bands at 2080 (m) and 1997 (w) cm^{-1} and a large envelope (vs) centered at 1950 cm^{-1} for **3** and **4**. These spectra indicate the presence of $M(CO)_5$ fragments in derivatives **2–4**.

From the reaction with molybdenum carbonyl only oily products are formed, which we were unable to crystallize. However, the IR spectrum in the CO sttretching region seems essentially analogous to those of the Cr and W derivatives.

The X-ray analysis of **3** has shown that the structure consists of complex cations $\{[Co(Ph_2PCH_2P(Ph)_2P_4P(Ph)_2CH_2PPh_2)][W(CO)_5]\}^+$ (Figure 2) and BPh_4^- anions; see supplemental material. In **3** the cobalt atom is coordinated as found in complex **1**, in a very distorted octahedral geometry, through all the phosphorus atoms of the P–P–P–P zigzag fragment and two of the four phosphorus atoms of the dppm groups. Two phosphorus atoms of the dppm groups remain uncoordinated. One of the two central phosphorus atoms of the zigzag P–P–P–P grouping is linked to the tungsten atom of the $W(CO)_5$ fragment. The coordination geometry around the cobalt atom is essentially unchanged with respect to the mononuclear donor complex **1**.

The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2, at room temperature, shows three very complicated multiplets centered at δ 74, 47, and −76 (intensity ratio (1:1:2), which may be tentatively attributed to the dppm (the first two) and to the P–P–P–P phosphorus atoms (the last). We intend to examine the spectra at higher resolution and at varying temperatures to determine the conformation of **1** in solution. Indeed the knowledge of the solution chemistry of **1** should be of great interest to verify whether a possible destruction of the complex causes the definitive fragmentation of the zigzag P–P–P–P chain or the possible recovery of the tetrahedral P_4 molecule.

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Registry No. **1**, 90149-67-0; **2**, 101376-91-4; **3**, 101376-93-6; **4**, 101469-66-3; dppm, 2071-20-7; $[Co(H_2O)_6](BF_4)_2$, 37041-75-1; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; P, 7723-14-0.

Supplementary Material Available: Tables of thermal parameters and calculated and observed structure factors for **1** and tables of atomic positional and thermal parameters, calculated and observed structure factors, and selected bond distances and angles and a description of solution and refinement of the structure for **3** (46 pages). Ordering information is given on any current masthead page.

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[29] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 and 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)