similar to the dibenzyl complex.

Reactivity studies of **3** as a nucleophile and a reducing agent as well as addition and photolysis reactions of **1** and **2** are in progress.

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Registry No. **1**, 63630-86-4; **2**, 67350-79-2; $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Mo(CH_2C_6H_5)]_2$, 67328-64-7; $(CH_3CO_2)_4Mo_2$, 14221-06-8.

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Contribution from the Istituto di Chimica Generale ed Inorganica, Università, Laboratorio CNR, Florence, Italy

Synthesis, Characterization, and Structure of the Complex (η^3-*cyclo*-Triphosphorus)(tris(2-diphenylphosphinoethyl)amine)cobalt

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Recently we have described the first examples of metal complexes with the cyclic unit δ-P_3 acting as a η^3 ligand.[1] These compounds are obtained by direct action of white phosphorus on cobalt(II) and nickel(II) hydrated salts in the presence of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos, and have formulas $[(\text{triphos})M\text{-}\mu(\eta^3\text{-}P_3)\text{-}M(\text{triphos})]Y_2$ (M = Co, Ni; Y = BF_4, BPh_4) and $[(\eta^3\text{-}P_3)Co(\text{triphos})]$. In all these complexes each metal atom is coordinated by six phosphorus atoms, three belonging to the triphos ligand and three to the δ-P_3 unit.

With the aim of obtaining other δ-P_3 metal complexes we have tried to use another tripod ligand, the potentially tetradentate tri(tertiary phosphine) tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$, np$_3$. From the reaction of $Co(BF_4)_2{\cdot}6H_2O$ with np$_3$ and white phosphorus in tetrahydrofuran–ethanol solution, a new (*cyclo*-triphosphorus)cobalt complex was obtained. This compound, having formula $[(\eta^3\text{-}P_3)Co(np_3)]{\cdot}0.5C_4H_8O$ was characterized by the usual methods. Its structure was elucidated by means of a three-dimensional X-ray diffraction analysis.

Experimental Section

Reagents. All solvents were of reagent grade quality and were used without further purification. The ligand np$_3$ was prepared by the method previously described.[2]

Preparation of the $[(\eta^3\text{-}P_3)Co(np_3)]{\cdot}0.5C_4H_8O$ Complex. The reaction was carried out under dry nitrogen. One millimole of $Co(BF_4)_2{\cdot}6H_2O$ in 10 mL of ethanol was added to 1 mmol of np$_3$ in 15 mL of THF. Then a THF solution of white phosphorus P_4 (1 mmol in 15 mL of THF) was added slowly, with stirring, at room temperature. Gentle heating of the resulting solution (ca. 50 °C for ca. 0.5 h) precipitated bright red crystals. They were filtered off and washed with THF, ethanol, and finally petroleum ether before being dried. Anal. Calcd. for $C_{44}H_{46}CoNO_{0.5}P_6$: C, 62.79; H, 5.51; Co, 7.00; N, 1.66; P, 22.08. Found: C, 61.70; H, 6.01; Co, 6.70; N, 1.43; P, 20.80. The analytical data are slightly lower than those in agreement with the structural results. This disagreement can be attributed to the presence of impurities which we could not eliminate by recrystallization on account of the low solubility of the compound.

Physical Measurements. Magnetic and spectrophotometric measurements were carried out using methods already described.[3]

Collection of X-ray Data. The crystals, quite stable in air, are rhombohedral, space group $R\bar{3}$, with $a = 28.950$ (6) Å, $c = 26.896$ (6) Å (hexagonal cell), $Z = 18$, $D_{\text{calcd}} = 1.29$ g cm^{-3}, and $D_{\text{measd}} = 1.30$ g cm^{-3}. The crystal used for data collection was a rhombohedron having edges of about 0.3 mm. Cell parameters were determined by least-squares refinement of 20 reflections centered on a four-circle Philips PW1100 automatic diffractometer at about 22 °C, using Mo Kα radiation (λ 0.7107 Å). The intensity data were measured in the range $6° \leq 2\theta \leq 40°$ using Mo Kα radiation monochromatized by a flat graphite crystal. The method used was the θ–ω scan technique: scans of 0.7° in 10 s were taken across the peaks (background was counted for 5 s on each side of the peak). Three standard reflections were measured every 120 min: no systematic loss of intensity was noticed during the collection. The standard deviations on the intensities were calculated by the expression $\sigma(I) = [P - 0.25(B_1 + B_2)(T_p/T_b) + (0.03I)^2]^{1/2}$,[4] where P is the peak count, B_1 and B_2 are the background counts, T_p and T_b are the count times on the peak and background, respectively, and I is the intensity itself.

The 2320 reflections having $I \geq 3\sigma(I)$ were considered observed and were used in the structure analysis. An absorption correction ($\mu = 6.39$ cm^{-1}) was applied by a numerical method.[5] The intensities were corrected for Lorentz and polarization effects. The Lp factor for the graphite monochromator is 4.64. Atomic scattering factors for cobalt, phosphorus, oxygen, nitrogen, and carbon atoms were taken from ref 6 (all in the neutral state); those for hydrogen atoms were taken from ref 7 (in the neutral state).

Solution and Refinement of the Structure. The positions of the cobalt and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of all nonhydrogen atoms of the structure. The atoms of the tetrahydrofuran molecule gave peaks lower in magnitude than those of the carbon atoms of the np$_3$ ligand. A population parameter of 0.5 will be assigned to these atoms on the basis of a least-squares refinement. Refinement was performed with the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[8] The minimized function was $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were assigned only to cobalt and phosphorus atoms; isotropic temperature factors were used for the lighter atoms. The hydrogen atoms of the np$_3$ ligand were introduced in calculated positions (C–H = 0.95 Å) with temperature factors $B_H = 1 + B_{C(\text{attached})}$. The carbon atoms of the phenyl groups were refined

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Table I. Atomic[a] Parameters for the Structure of $[(\eta^3\text{-}P_3)Co(np_3)]\cdot 0.5C_4H_8O$ (All Quantities ×10^4)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	3314 (1)	1637 (1)	4129 (1)	391 (12)	303 (12)	517 (12)	172 (10)	24 (10)	13 (11)
P(1)	3478 (2)	1063 (2)	3665 (2)	624 (31)	419 (28)	677 (32)	311 (25)	114 (25)	−46 (24)
P(2)	2985 (2)	746 (2)	4308 (2)	603 (30)	285 (25)	793 (33)	198 (24)	73 (25)	64 (23)
P(3)	2686 (2)	929 (2)	3655 (2)	535 (28)	406 (27)	621 (30)	179 (23)	−65 (24)	−110 (23)
P(4)	2732 (2)	1755 (2)	4597 (1)	463 (26)	337 (24)	503 (27)	224 (21)	33 (22)	32 (21)
P(5)	3561 (2)	2275 (1)	3549 (2)	413 (26)	323 (24)	544 (26)	161 (22)	28 (22)	34 (21)
P(6)	4048 (2)	1966 (2)	4613 (1)	444 (26)	399 (26)	486 (26)	227 (22)	24 (21)	47 (21)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots))$. F(relative scale factor) = 106616.

Table II. Atomic Parameters for the Structure of $[(\eta^3\text{-}P_3)Co(np_3)]\cdot 0.5C_4H_8O$ (All Quantities ×10^4)

atom	x	y	z	U, Å^2
N	3776 (4)	2901 (4)	4573 (4)	475 (31)
C(1)	2805 (5)	2431 (5)	4611 (5)	461 (41)
C(2)	3323 (6)	2841 (6)	4836 (5)	558 (44)
C(3)	4088 (5)	2954 (5)	3713 (5)	446 (40)
C(4)	3925 (5)	3214 (6)	4126 (5)	516 (42)
C(5)	4140 (5)	2461 (5)	5092 (5)	477 (39)
C(6)	4220 (5)	2988 (5)	4870 (5)	529 (42)
O	1586 (18)	656 (18)	2473 (19)	2717 (17)
C(20)	1185 (22)	630 (24)	2875 (21)	1765 (199)
C(21)	1171 (19)	151 (21)	2889 (19)	1583 (166)
C(22)	995 (20)	−11 (21)	2368 (21)	1886 (178)
C(23)	1206 (32)	601 (33)	2181 (29)	1753 (325)

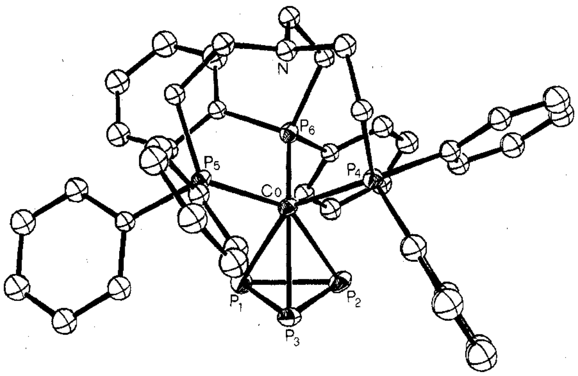

Figure 1. Perspective view of the $[(\eta^3\text{-}P_3)Co(np_3)]$ molecule.

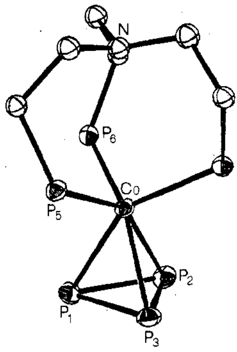

Figure 2. Perspective view of the skeleton of the $[(\eta^3\text{-}P_3)Co(np_3)]$ molecule.

as a rigid body. The final conventional R factor was 0.066, and the R_w factor, defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.078. A ΔF Fourier synthesis calculated at the end of refinement did not show remarkable features. The positional and thermal parameters of the atoms of the compound are reported in Tables I–IV.

Results and Discussion

The $[(\eta^3\text{-}P_3)Co(np_3)]\cdot 0.5C_4H_8O$ complex, which is insoluble in organic solvents such as 1,2-dichloroethane, nitroethane, benzene, and tetrahydrofuran, is diamagnetic. Its reflectance spectrum shows two shoulders at 20.4 and 24.4 μm^{-1}.

The structure consists of $[(\eta^3\text{-}P_3)Co(np_3)]$ and tetrahydrofuran molecules (Figure 1). The cobalt atom is coordinated by three phosphorus atoms of the np_3 ligand and by the three phosphorus atoms of the cyclic P_3 unit. The phosphorus atoms of the P_3 group are in staggered positions with respect to the three phosphorus atoms of the np_3 ligand (Figure 2). Distances and angles in the coordination polyhedron are reported in Table V. The Co–P (np_3 ligand) distances (av 2.25 Å) are close to the analogous distances found in other np_3 metal complexes[9] but are remarkably shorter than the Co–P (*cyclo*-triphosphorus) distances (av 2.31 Å). On the other hand the P–Co–P (np_3 ligand) angles have a mean value of 102.6° which is much larger than the value of 54.9° found for the P–Co–P (*cyclo*-triphosphorus) angles. As a consequence, the cobalt atom lies in a position which is much closer to the P(4)–P(5)–P(6) plane than to the P(1)–P(2)–P(3) plane.

The average P–P distance in the cyclic P_3 group, 2.14 Å, is equal to the average P–P distance found in the analogous $[(\eta^3\text{-}P_3)Co(triphos)]$ complex;[1] it is significantly shorter than the P–P bond lengths found in the tetrahedral P_4 molecule (2.21 Å).[10] A similar shrinking has been found also for the triangular As_3 group in the $[As_3Co(CO)_3]$ complex.[11] As has been pointed out by Dahl et al.,[11] this shortening of the As–As (or P–P) distance is rationalized through a partial delocalization of the electron charge from the As_3 (or P_3) fragment to the more electronegative CoL moiety (L = $(CO)_3$, np_3) with a consequent decrease of the Coulombic-pair repulsions among the pnicogen atoms.

The nitrogen atom of the np_3 ligand is considered not coordinated to the metal, lying at 3.42 (1) Å from the cobalt atom. The quasi-coplanarity of the nitrogen atom with the carbon atoms linked to it (C–N–C angles, av 115.6°) as well as the short N–C distances (av 1.43 Å) are consistent with the sp^2 hybridization for the nitrogen atom.[12] As observed in other np_3 metal derivatives the electronic configuration of the

Table III. Final Least-Squares Parameters for $[(\eta^3\text{-}P_3)Co(np_3)]\cdot 0.5C_4H_8O$ Groups[a]

group	x'	y'	z'	θ	ϕ	ψ
1	0.2614 (2)	0.1498 (2)	0.5711 (2)	1.758 (8)	−1.430 (7)	−2.573 (8)
2	0.1546 (3)	0.1032 (3)	0.4381 (2)	2.753 (6)	−0.518 (12)	1.979 (9)
3	0.2732 (3)	0.2521 (3)	0.3120 (2)	2.715 (5)	−1.216 (7)	2.176 (5)
4	0.3993 (3)	0.2085 (3)	0.2585 (2)	1.065 (7)	1.331 (7)	2.395 (6)
5	0.5158 (3)	0.2465 (3)	0.4146 (2)	1.235 (6)	0.441 (6)	2.573 (6)
6	0.4176 (2)	0.1149 (2)	0.5232 (2)	1.472 (7)	0.548 (6)	0.858 (7)

[a] x', y', and z' (fractional coordinates) define the origin of the working system of the group. The Goldstein definition is used for Euler angles θ, ϕ, and ψ (radians): H. Goldstein, "Classical Mechanics", Addison-Wesley, Reading, Mass., 1959.

Table IV. Thermal and Derived Positional Parameters of Group Atoms (All Quantities $\times 10^4$)

atom	*x*	*y*	*z*	*U*, Å^2
C(1) 1	2665 (3)	1604 (3)	5279 (2)	489 (39)
C(2) 1	2406 (3)	1790 (3)	5585 (2)	557 (43)
C(3) 1	2347 (3)	1667 (3)	6090 (2)	768 (49)
C(4) 1	2546 (3)	1357 (3)	6288 (2)	734 (51)
C(5) 1	2805 (3)	1171 (3)	5981 (2)	717 (48)
C(6) 1	2865 (3)	1294 (3)	5477 (2)	555 (42)
C(1) 2	2008 (3)	1324 (4)	4464 (3)	512 (40)
C(2) 2	1699 (3)	1526 (4)	4268 (3)	642 (46)
C(3) 2	1160 (3)	1184 (4)	4171 (3)	858 (54)
C(4) 2	931 (3)	641 (4)	4270 (3)	904 (60)
C(5) 2	1239 (3)	440 (4)	4466 (3)	783 (51)
C(6) 2	1778 (3)	782 (4)	4563 (3)	659 (46)
C(1) 3	3054 (4)	2424 (4)	3292 (3)	436 (37)
C(2) 3	2522 (4)	2024 (4)	3255 (3)	578 (44)
C(3) 3	2147 (4)	2137 (4)	3054 (3)	754 (50)
C(4) 3	2303 (4)	2651 (4)	2890 (3)	753 (49)
C(5) 3	2835 (4)	3051 (4)	2926 (3)	727 (50)
C(6) 3	3210 (4)	2938 (4)	3127 (3)	749 (49)
C(1) 4	3833 (4)	2172 (4)	2962 (3)	428 (37)
C(2) 4	4370 (4)	2479 (4)	2836 (3)	626 (45)
C(3) 4	4556 (4)	2377 (4)	2396 (3)	708 (48)
C(4) 4	4206 (4)	1968 (4)	2083 (3)	748 (51)
C(5) 4	3670 (4)	1661 (4)	2210 (3)	692 (50)
C(6) 4	3483 (4)	1763 (4)	2649 (3)	599 (42)
C(1) 5	4726 (3)	2290 (4)	4325 (3)	427 (37)
C(2) 5	4779 (3)	2161 (4)	3838 (3)	509 (40)
C(3) 5	5284 (3)	2365 (4)	3630 (3)	714 (46)
C(4) 5	5736 (3)	2699 (4)	3908 (3)	748 (54)
C(5) 5	5682 (3)	2828 (4)	4395 (3)	863 (48)
C(6) 5	5177 (3)	2624 (4)	4603 (3)	787 (50)
C(1) 6	4123 (3)	1472 (3)	5003 (3)	425 (37)
C(2) 6	4067 (3)	1446 (3)	5517 (3)	616 (45)
C(3) 6	4128 (3)	1069 (3)	5786 (3)	675 (46)
C(4) 6	4246 (3)	718 (3)	5539 (3)	652 (46)
C(5) 6	4302 (3)	743 (3)	5024 (3)	658 (47)
C(6) 6	4241 (3)	1121 (3)	4756 (3)	542 (42)

Table V. Distances (Å) and Angles (deg) in the Coordination Polyhedron with Estimated Standard Deviations in Parentheses

Distances

Co-P(1)	2.311 (6)	Co-P(6)	2.257 (4)
Co-P(2)	2.310 (5)	P(1)-P(2)	2.137 (6)
Co-P(3)	2.325 (4)	P(1)-P(3)	2.128 (7)
Co-P(4)	2.261 (5)	P(2)-P(3)	2.139 (7)
Co-P(5)	2.243 (4)		

Angles

P(1)-Co-P(2)	55.1 (2)	P(2)-Co-P(4)	97.4 (2)
P(1)-Co-P(3)	54.6 (2)	P(2)-Co-P(6)	97.2 (2)
P(2)-Co-P(3)	55.0 (2)	P(3)-Co-P(4)	97.1 (2)
P(1)-Co-P(4)	147.8 (1)	P(3)-Co-P(5)	97.5 (2)
P(2)-Co-P(5)	148.0 (2)	P(4)-Co-P(5)	102.6 (2)
P(3)-Co-P(6)	147.6 (2)	P(4)-Co-P(6)	103.3 (2)
P(1)-Co-P(5)	96.9 (2)	P(5)-Co-P(6)	102.1 (1)
P(1)-Co-P(6)	97.2 (2)		

metal atom plays a very important role in determining whether the central nitrogen of np$_3$ can be bound or not to the metal. In this respect the two complexes $[(\text{CO})\text{Ni}(\text{np}_3)]$ (d^{10} metal, N not bound, tetrahedral) and $[(\text{CO})\text{Co}(\text{np}_3)]^+$ (d^8 metal, N bound, TBP)[13] are a typical significant example of the effect exerted by the configuration of the metal on the ligating properties of the np$_3$ ligand. In the present $[(\eta^3\text{-P}_3)\text{Co}(\text{np}_3)]$ complex, where the *cyclo*-triphosphorus group donates three electrons to the d^9 cobalt atom, only three electron pairs from the donor atoms of np$_3$ are required by the central atom to reach the 18-outer-electron configuration. The large Co–N distance is thus attributed to the repulsion between the electron lone pair of the nitrogen atom and the 18-electron complete shell of the metal.

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Registry No. $[(\eta^3\text{-P}_3)\text{Co}(\text{np}_3)]\cdot 0.5\text{C}_4\text{H}_8\text{O}$, 67523-78-8; $\text{Co}(\text{BF}_4)_2$, 26490-63-1.

Supplementary Material Available: A listing of calculated and observed structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Refinement of the Crystal Structure of Orthorhombic Zinc Chloride[1]

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The preparation and an approximate crystal structure of an orthorhombic form of anhydrous zinc chloride were reported recently.[4] Transitions of this form to one or more of the modifications described by Brehler[5] were noted experimentally when the material was examined under conditions that excluded air in a less than stringent manner. A refinement of the approximate structure of orthorhombic zinc chloride has been carried out, and the results are summarized in this note.

Experimental Section

A single crystal with dimensions roughly 0.1 mm × 0.1 mm × 0.04 mm was isolated from crushed fragments of orthorhombic zinc chloride that had been melted and recrystallized in a temperature gradient according to the Stockbarger method.[4] All operations with this material were performed in a helium-filled drybox with <2 ppm of H_2O and <6 ppm of O_2. The selected crystal was forced into a tapered section of a cleaned, thin-walled glass capillary that was then fused shut with a Pt hot wire. After preliminary X-ray diffraction photographs disclosed reasonable mosaic spread and orientation, the crystal was transferred to an automated Picker diffractometer for collection of intensity data using Nb-filtered Mo $K\bar{\alpha}$ X radiation ($\bar{\lambda}$ 0.7107 Å).

Measurements of Bragg angles of six representative reflections showed no significant differences from those predicted with the reported unit cell parameters at 20 ± 1 °C, viz., $a = 6.443$ (2) Å, $b = 7.693$ (4) Å, and $c = 6.125$ (4) Å.[4] Intensities of 688 reflections in what was assumed to be the $+h,+k,+l$ octant of reciprocal space were recorded in an ω-scan mode. The assumption is required in view of the proposed polar space group $Pna2_1$. Since typical rocking curves for this crystal were 0.5 to 1.0° in breadth, each reflection was scanned over a 3° ω range at 0.05° steps, with a 5-s counting time at each step. Data were collected to 60° 2θ at which angle diffracted intensities had fallen to background levels for the counting parameters used.