Synthesis and Crystal Structure of Tris(4-nitrophenyl isocyanide)bis(diethyl phenylphosphonite)cobalt(I) Perchlorate

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The syntheses of five-coordinate cobalt(I) complexes of the type $[Co(4\text{-}NO_2C_6H_4NC)_{5-x}(PhP(OEt)_2)_x]ClO_4$ ($x = 2$ or 3) obtained by reaction at room temperature of 4-nitrophenyl isocyanide with cobalt(II) chloride and diethyl phenylphosphonite is reported. The compounds were characterized on the basis of their chemical and physical properties (conductivities and infrared, electronic, and ^1H NMR spectra). The crystal and molecular structure of tris(4-nitrophenyl isocyanide)bis(diethyl phenylphosphonite)cobalt(I) perchlorate, $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$, has been determined by single-crystal x-ray analysis and refined, with full-matrix least squares using anisotropic temperature parameters for all atoms, to $R = 0.072$ on F^2. The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^5), with $a = 13.085$ (5) Å, $b = 10.826$ (4) Å, $c = 33.019$ (8) Å, $\beta = 91.92$ (3)°, and $Z = 4$. The coordinated polyhedron around the cobalt atom has the shape of a slightly distorted trigonal bipyramid with isocyanide ligands in the equatorial positions. The average Co–C and Co–P distances (1.80 and 2.175 Å, respectively) clearly indicate strong double-bond character. Distortions around the phosphorus atoms are compared with those found in Ni(II) and Fe(II) complexes with the same phosphonite ligand and correlated to the M–P π interaction.

Introduction

The syntheses and characterization of five-coordinate cobalt(I) complexes of the type $[Co(CNR)_3L_2]ClO_4$ (CNR = alkyl or aryl isocyanide; L = PhP(EOt)$_2$) has been recently reported.[2] With 4-nitrophenyl isocyanide a complex is obtained in which the isocyanide:phosphine ratio is 2:3 instead of 3:2 as with the other isocyanides. This has been explained in terms of a stronger π interaction of the 4-nitrophenyl isocyanide compared to those of the other isocyanide ligands. Moreover, the low yield of this complex was found to be independent of the ratio of the starting reactants.

In order to develop a general high-yield synthetic procedure for complexes of the type $[Co(CNR)_2L_3]^+$, we have reinvestigated the preparation of $[Co(4\text{-}NO_2C_6H_4NC)_2(PhP(OEt)_2)_3]^+$. This allowed isolation also of the cation $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]^+$.

A trigonal-bipyramidal structure appears to be fairly common for cobalt(I) complexes both in solution and in the solid state.[2,3] However, the only accurate x-ray structural analysis of a five-coordinate cobalt(I) compound has been reported by Cotton[4] for the $[Co(CNCH_3)_5]ClO_4$ derivative, and therefore the structural characterization of other such complexes would certainly be desirable. In the present paper we report the crystal and molecular structure of the $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]^+$ cation to investigate the influence of the two phosphonite ligands on the molecular geometry and on the cobalt–ligand bond order.

Experimental Section

Materials. The solvents were purified and dried by standard methods. Reagent grade CoCl$_2$·6H$_2$O was dried in a vacuum oven at 110 °C in the presence of P$_2$O$_5$ or by treatment with 2,2-dimethoxypropane and used without further purification. Diethyl phenylphosphonite, PhP(OEt)$_2$, was prepared by the method of Rabinowitz and Pellon.[5] 4-Nitrophenyl isocyanide was obtained following the synthetic procedure reported elsewhere.[6]

Apparatus. Conductivities of 10^{-3} M solutions of complexes in nitrobenzene were measured at 25 °C with an LKB bridge. Infrared spectra of solids as KBr pellets and/or as dichloromethane solutions were recorded on a Perkin-Elmer 621 spectrophotometer. A Bruker HFX-10 instrument equipped with a variable-temperature probe and using TMS as internal reference was used for ^1H NMR measurements.

Syntheses of Complexes. The syntheses of complexes were carried out under nitrogen to avoid the oxidation of the phosphonite. Once isolated, the complexes were air stable and no special precautions were required for their handling.

Bis(4-nitrophenyl isocyanide)tris(diethyl phenylphosphonite)cobalt(I) Perchlorate (I) and Tris(4-nitrophenyl isocyanide)bis(diethyl phenylphosphonite)cobalt(I) Perchlorate (II). To a solution of anhydrous

cobalt(II) chloride (1.3 g, 10 mmol) in anhydrous ethanol (80 ml) under nitrogen was added diethyl phenylphosphonite (6 ml, 30 mmol). Addition of 4-nitrophenyl isocyanide (7.5 g, 50 mmol) dissolved in anhydrous ethanol (100 ml) to the stirred reaction mixture caused a color change from deep green to red-brown. A saturated solution of lithium perchlorate (1.07 g, 10 mmol) in anhydrous ethanol was then added, affording a red-brown precipitate which was recrystallized from ethanol.

The separation of the two complexes was accomplished by eluting 300 mg of crude reaction product in 3 ml of chloroform, through a silica gel column (length 60 cm, diameter 2 cm) using benzene–ethanol (50:5) as eluent. The complex $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$ was recovered by concentration of the first red eluate fraction to small volume (10 ml). Similarly, the complex $[Co(4\text{-}NO_2C_6H_4NC)_2(PhP(OEt)_2)_3]ClO_4$ precipitated out from the second brown fraction. By slowly cooling (1°/day) an ethanol solution of the crude reaction, crystals of both complexes were obtained and were mechanically separated.

The total yield was higher if a large excess of isocyanide (7:1) compared to the starting cobalt(II) salt was used. $[Co(4\text{-}NO_2C_6H_4NC)_2(PhP(OEt)_2)_3]ClO_4$ and $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$ were finally recovered in a 3:1 weight ratio.

See Table I for some properties of these complexes and Table II for spectral data.

X-Ray Analysis. Crystals suitable for x-ray analysis were obtained by cooling (3°/day) a 10^{-2} M ethanol solution of the complex $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$. A single crystal of approximate dimensions 0.13 × 0.40 × 0.26 mm was selected and mounted with the [010] direction parallel to the ϕ axis of the goniometer.

Crystal Data. For $[Co(4\text{-}NO_2C_6H_4NC)_3(PhP(OEt)_2)_2]ClO_4$, fw 998, the crystals are monoclinic, with $a = 13.085$ (5) Å, $b = 10.826$ (4) Å, $c = 33.019$ (8) Å, $\beta = 91.92$ (3)°, $V = 4402$ Å^3, $F(000) = 2016$, $d_{calcd} = 1.47$ g cm^{-3} for $Z = 4$ ($d_{obsd} = 1.48$ g cm^{-3}), and $\mu(MoK\alpha) = 6.909$ cm^{-1}.

The conditions on hkl for observed reflections are summarized as follows: hkl, no conditions (P); $h0l$, $1 = 2n$ (c); $0k0$, $k = 2n$ (2_1). On the basis of the observed extinctions the space group is $P2_1/c$ (C_{2h}^5). Approximate cell parameters were initially determined from oscillation, Weissenberg, and precession photographs. After alignment of the crystal on a Siemens four-circle automatic diffractometer, precise values of the unit cell parameters were derived by the method of least squares from angle data measured with zirconium-filtered Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å). Reflections were measured to a maximum θ value of 25° using the θ–2θ scan and the five-point measuring procedure. A total of 2358 nonzero reflections within the range $0.05 \lesssim$ (sin θ)/$\lambda \lesssim 0.60$ were recorded, including 64 symmetry-related pairs. A reflection was selected as the standard, and its intensity was recorded every 20 reflections. The fluctuations in intensity of the standard reflection were random with a maximum variation of 4%, indicating that the compound does not deteriorate under irradiation. No absorption correction was made. Atomic form factors for neutral atoms

Table I. Some Properties of [Co(4-NO$_2$C$_6$H$_4$NC)$_{5-x}$(PhP(OEt)$_2$)$_x$]ClO$_4$ (x = 2 or 3) Complexes

			Molar con- duct- ance[b]	%C		%H		%N		%Cl	
Compd	Color	Mp,[a] °C		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Co(4-NO$_2$C$_6$H$_4$NC)$_2$(PhP(OEt)$_2$)$_3$]ClO$_4$ (I)	Brown	148	23.9	50.35	50.02	5.05	4.94	5.34	5.06	3.39	3.64
[Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]ClO$_4$ (II)	Brown-red		24.0	49.32	49.45	4.21	4.22	8.42	8.25	3.56	3.78

[a] Determined in capillaries and uncorrected. [b] Molar conductances were determined in 10^{-3} M nitrobenzene solutions at 25 °C.

Table II. Spectral Data

	[Co(4-NO$_2$C$_6$H$_4$NC)$_2$(PhP(OEt)$_2$)$_3$]ClO$_4$ (I)	[Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]ClO$_4$ (II)
	ν(CN), cm^{-1}	
In CH$_2$Cl$_2$	2126 sh, 2089 s, 2072 s, 2022 sh	2125 sh, 2076 sh, 2054 s, 2010 sh
In solid	2086 s, 2061 s, 2026 sh	2124 sh, 2075 sh, 2053 s, 2010 sh
	Chemical Shifts,[a] τ	
Phenyl protons	1.77 d, 2.18 m, 2.50 m, 3.03 d	1.63 d, 2.04 m, 2.39 d
CH$_2$	5.86 m, 6.07 m	5.64 m
CH$_3$	8.66 t[b]	8.56 t[b]
	Electronic Spectra: λ mμ (ϵ)	
	4.35 (1.5 × 10^4), 310 (3.8 × 10^4), 250 sh	416 (3 × 10^4), 305 sh, 210 (6.6 × 10^4)

[a] In (CD$_3$)$_2$CO. ^{1}H NMR spectral data of complex I were recorded on a Varian HR-220 instrument. [b] J_{HH} = 7 Hz.
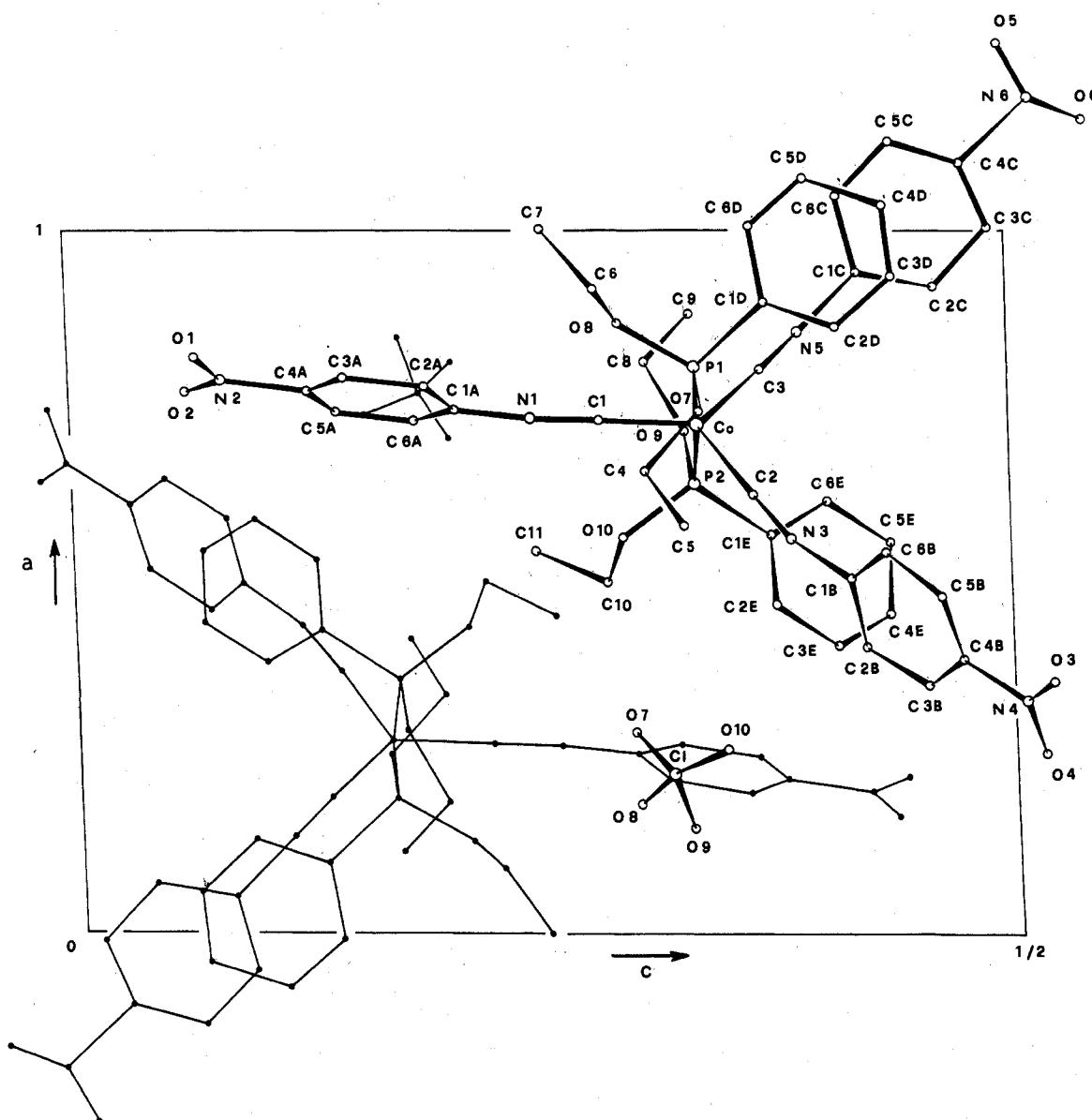
Figure 1. Projection of the structure of the [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]ClO$_4$ complex down the *b* axis, with the atom numbering.

Table III. Fractional Coordinates and Thermal Parameters with Standard Deviations[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.7235 (1)	−0.3272 (2)	0.3377 (1)	4.7 (1)	5.0 (1)	3.8 (1)	0.3 (1)	0.5 (1)	−0.2 (1)
Cl	0.2318 (5)	0.3170 (7)	0.3177 (2)	9.7 (3)	8.0 (4)	5.7 (2)	3.5 (4)	1.2 (3)	0.7 (3)
P(1)	0.8067 (3)	0.5019 (5)	0.3361 (1)	4.6 (2)	4.7 (3)	3.8 (1)	0.1 (3)	0.3 (2)	−0.4 (2)
P(2)	0.6463 (3)	0.1500 (5)	0.3340 (1)	4.2 (2)	5.1 (3)	4.0 (1)	0.5 (3)	0.4 (2)	−0.0 (2)
O(1)	0.8223 (15)	0.4346 (16)	0.0684 (4)	1.8 (16)	9.0 (11)	7.3 (9)	−2.7 (11)	7.3 (10)	0.5 (8)
O(2)	0.7700 (12)	0.2555 (16)	0.0624 (4)	13.8 (12)	12.2 (13)	4.8 (7)	−2.2 (10)	1.6 (7)	−1.9 (8)
O(3)	0.3599 (12)	0.7405 (18)	0.5247 (5)	10.8 (11)	12.8 (13)	10.2 (10)	1.2 (10)	3.4 (8)	−5.8 (10)
O(4)	0.2566 (11)	0.5919 (14)	0.5192 (4)	9.1 (8)	9.6 (11)	9.0 (8)	0.7 (8)	4.0 (7)	1.6 (8)
O(5)	1.2620 (14)	0.1964 (20)	0.5090 (6)	11.0 (11)	16.0 (16)	18.7 (16)	1.0 (13)	−6.5 (12)	0.5 (13)
O(6)	1.1591 (16)	0.1141 (22)	0.5508 (6)	16.0 (12)	16.2 (16)	10.3 (11)	3.9 (12)	−7.1 (12)	−0.1 (12)
O(7)	0.7386 (8)	0.6252 (10)	0.3395 (3)	7.3 (6)	5.1 (7)	6.5 (6)	0.6 (6)	0.6 (4)	−0.2 (6)
O(8)	0.8695 (7)	0.5183 (11)	0.2966 (3)	6.2 (6)	7.3 (7)	4.8 (6)	−1.0 (6)	1.2 (4)	−0.6 (6)
O(9)	0.7164 (7)	0.0325 (10)	0.3306 (3)	5.2 (5)	4.7 (7)	6.7 (6)	1.1 (6)	1.2 (5)	−0.2 (3)
O(10)	0.5679 (7)	0.1460 (11)	0.2959 (3)	7.0 (5)	6.3 (8)	4.4 (6)	−0.9 (6)	−0.6 (5)	0.7 (6)
O(11)	0.2907 (10)	0.2442 (12)	0.2927 (4)	11.7 (8)	8.8 (8)	12.9 (9)	1.2 (8)	5.8 (8)	−1.2 (8)
O(12)	0.1867 (17)	0.4076 (20)	0.2996 (7)	24.5 (15)	17.5 (14)	18.9 (15)	12.2 (13)	6.3 (12)	5.8 (11)
O(13)	0.1494 (22)	0.2508 (21)	0.3277 (8)	31.7 (24)	11.0 (15)	29.6 (24)	−3.0 (16)	27.4 (22)	−2.1 (14)
O(14)	0.2634 (17)	0.3291 (35)	0.3530 (7)	22.4 (14)	42.2 (38)	18.2 (14)	18.3 (21)	−13.1 (15)	−20.8 (18)
N(1)	0.7343 (9)	0.3184 (15)	0.2490 (4)	7.9 (8)	6.4 (8)	4.4 (6)	−0.1 (8)	1.6 (6)	−1.6 (8)
N(2)	0.7882 (12)	0.3456 (20)	0.0823 (4)	8.5 (9)	8.5 (15)	4.7 (10)	−1.7 (11)	1.5 (7)	−0.6 (10)
N(3)	0.5636 (10)	0.4416 (13)	0.3878 (4)	7.0 (8)	6.1 (8)	5.8 (7)	1.7 (8)	2.5 (6)	−1.0 (7)
N(4)	0.3320 (14)	0.6477 (19)	0.5092 (5)	8.0 (11)	7.9 (15)	6.4 (10)	2.1 (12)	0.3 (9)	−0.9 (9)
N(5)	0.8730 (11)	0.2286 (14)	0.4000 (5)	6.2 (8)	5.5 (9)	6.9 (8)	0.6 (8)	−0.9 (8)	−0.9 (8)
N(6)	1.1790 (2)	0.1579 (24)	0.5188 (7)	9.7 (12)	10.1 (16)	10.6 (13)	1.6 (13)	−4.2 (13)	−1.4 (15)
C(1)	0.7308 (11)	0.3240 (16)	0.2840 (4)	6.7 (8)	3.5 (8)	4.3 (8)	0.2 (8)	1.0 (7)	−0.2 (9)
C(2)	0.6238 (12)	0.3966 (15)	0.3671 (4)	6.3 (9)	4.2 (9)	4.6 (8)	−0.3 (8)	0.3 (7)	0.6 (8)
C(3)	0.8148 (12)	0.2651 (18)	0.3749 (5)	4.6 (8)	7.0 (12)	5.1 (9)	−0.7 (9)	1.0 (7)	−1.0 (9)
C(4)	0.6539 (13)	0.6508 (19)	0.3090 (5)	6.9 (10)	8.5 (14)	6.3 (10)	1.7 (11)	−2.3 (9)	0.3 (11)
C(5)	0.5768 (13)	0.7307 (18)	0.3297 (6)	6.7 (12)	7.1 (14)	11.0 (12)	2.8 (12)	1.3 (10)	0.4 (12)
C(6)	0.9194 (13)	0.6404 (18)	0.2861 (5)	8.2 (11)	7.3 (15)	7.7 (11)	−4.3 (11)	1.9 (10)	0.5 (11)
C(7)	0.9998 (14)	0.6133 (21)	0.2568 (6)	7.7 (11)	11.2 (15)	8.9 (12)	−2.8 (12)	4.3 (10)	0.1 (12)
C(8)	0.8142 (12)	0.0256 (18)	0.3102 (5)	5.3 (9)	6.9 (12)	6.8 (10)	1.5 (10)	2.1 (8)	−0.7 (10)
C(9)	0.8858 (14)	−0.0537 (20)	0.3364 (7)	7.1 (9)	7.7 (13)	13.1 (10)	1.9 (10)	0.5 (8)	0.1 (10)
C(10)	0.5014 (12)	0.0409 (18)	0.2846 (5)	5.0 (8)	5.5 (11)	7.2 (10)	−2.7 (10)	0.2 (9)	−1.3 (10)
C(11)	0.5463 (12)	−0.0216 (18)	0.2487 (5)	7.3 (10)	7.0 (13)	6.3 (9)	1.0 (10)	0.2 (8)	−2.1 (10)
C(1A)	0.7486 (11)	0.3249 (20)	0.2071 (4)	5.8 (8)	5.2 (10)	3.9 (7)	1.1 (10)	0.8 (6)	0.8 (10)
C(2A)	0.7752 (13)	0.4339 (18)	0.1911 (5)	8.2 (11)	4.3 (11)	5.4 (11)	−0.2 (10)	0.1 (8)	0.9 (9)
C(3A)	0.7924 (12)	0.4430 (16)	0.1479 (5)	7.5 (10)	3.9 (10)	4.9 (9)	−0.2 (8)	0.4 (7)	−2.0 (9)
C(4A)	0.7753 (12)	0.3391 (21)	0.1264 (5)	6.5 (8)	5.9 (12)	4.5 (9)	1.0 (10)	1.4 (7)	−0.0 (11)
C(5A)	0.7438 (12)	0.2257 (18)	0.1420 (5)	5.7 (8)	5.3 (13)	6.2 (11)	−0.2 (8)	0.7 (7)	−1.0 (10)
C(6A)	0.7295 (13)	0.2172 (16)	0.1841 (5)	9.6 (11)	5.0 (13)	4.0 (8)	−0.5 (9)	0.3 (8)	−1.3 (8)
C(1B)	0.5035 (12)	0.4941 (20)	0.4178 (5)	5.1 (8)	7.2 (13)	5.3 (8)	2.2 (9)	0.6 (7)	0.1 (9)
C(2B)	0.4118 (13)	0.4391 (18)	0.4265 (5)	6.4 (9)	8.4 (13)	5.9 (9)	2.2 (10)	1.7 (8)	−0.3 (9)
C(3B)	0.3548 (12)	0.4898 (17)	0.4572 (5)	6.6 (9)	5.3 (11)	6.1 (10)	0.2 (9)	0.7 (8)	−2.1 (9)
C(4B)	0.3926 (12)	0.5938 (18)	0.4766 (4)	5.1 (8)	6.6 (12)	4.6 (8)	2.9 (9)	0.6 (7)	−0.4 (8)
C(5B)	0.4853 (12)	0.6530 (18)	0.4689 (5)	5.1 (8)	6.9 (13)	8.2 (10)	2.0 (9)	0.6 (8)	0.3 (11)
C(6B)	0.5428 (12)	0.6020 (18)	0.4376 (5)	5.4 (8)	5.5 (11)	6.3 (10)	1.1 (9)	0.4 (8)	−0.6 (9)
C(1C)	0.9473 (12)	0.2051 (16)	0.4297 (5)	4.8 (8)	4.9 (12)	6.5 (10)	1.9 (9)	−0.8 (8)	−0.7 (10)
C(2C)	0.9200 (12)	0.1744 (18)	0.4691 (5)	6.3 (8)	5.4 (10)	5.1 (8)	0.4 (9)	0.3 (7)	0.3 (9)
C(3C)	0.9971 (14)	0.1560 (19)	0.4990 (5)	5.8 (8)	7.6 (14)	6.5 (8)	2.8 (11)	0.0 (8)	0.0 (11)
C(4C)	1.0949 (14)	0.1702 (20)	0.4873 (5)	7.3 (10)	7.5 (12)	6.0 (9)	3.7 (12)	−2.9 (9)	−0.8 (12)
C(5C)	1.1258 (12)	0.2035 (18)	0.4476 (6)	6.3 (10)	6.6 (12)	6.8 (9)	0.5 (8)	−1.6 (8)	−1.5 (9)
C(6C)	1.0491 (14)	0.2148 (16)	0.4179 (5)	6.8 (8)	5.8 (11)	6.6 (10)	1.1 (9)	0.1 (7)	−1.9 (8)
C(1D)	0.8976 (10)	0.5315 (15)	0.3777 (4)	4.7 (7)	5.8 (9)	4.8 (7)	−0.6 (8)	−0.2 (6)	−0.1 (8)
C(2D)	0.8625 (11)	0.5620 (16)	0.4150 (4)	7.5 (9)	7.8 (12)	4.1 (7)	0.7 (9)	−0.6 (7)	−1.7 (8)
C(3D)	0.9344 (15)	0.5760 (17)	0.4478 (5)	8.4 (11)	7.5 (12)	6.7 (10)	−1.1 (11)	−0.4 (9)	−0.8 (9)
C(4D)	1.0374 (15)	0.5550 (18)	0.4424 (6)	8.1 (11)	6.5 (12)	8.4 (12)	−0.8 (11)	−1.3 (10)	−0.7 (11)
C(5D)	1.0721 (12)	0.5185 (19)	0.4042 (6)	6.8 (9)	7.8 (13)	8.9 (12)	−0.2 (11)	−0.9 (9)	−1.2 (12)
C(6D)	1.0009 (12)	0.5032 (16)	0.3711 (5)	6.5 (8)	5.5 (8)	7.7 (10)	−0.8 (10)	−0.9 (8)	0.4 (8)
C(1E)	0.5710 (11)	0.0991 (14)	0.3761 (4)	5.6 (8)	3.8 (8)	4.7 (7)	0.3 (7)	0.7 (6)	0.1 (7)
C(2E)	0.4704 (11)	0.1409 (15)	0.3771 (4)	5.1 (7)	6.5 (9)	6.8 (8)	−0.9 (8)	1.1 (7)	−1.7 (8)
C(3E)	0.4130 (12)	0.0996 (18)	0.4110 (6)	6.6 (9)	7.4 (12)	8.8 (11)	−1.3 (10)	2.4 (9)	−1.0 (11)
C(4E)	0.4557 (16)	0.0211 (19)	0.4399 (5)	9.8 (12)	7.5 (13)	6.2 (10)	−2.5 (12)	1.6 (9)	0.2 (9)
C(5E)	0.5582 (15)	−0.0121 (18)	0.4396 (5)	8.2 (10)	9.3 (13)	5.9 (9)	−2.3 (12)	0.9 (8)	0.5 (9)
C(6E)	0.6146 (11)	0.0238 (15)	0.4070 (5)	6.2 (8)	5.1 (9)	5.2 (8)	−0.1 (8)	−0.5 (7)	0.8 (8)

[a] The anisotropic parameters are in the form $\exp[-0.25(h^2 a^{*2} B_{11} + \ldots + 2klb^* c^* B_{23})]$.

were taken from ref 7. The effects of anomalous dispersion were included in the calculation of the contribution of Co and P; numerical values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[8] Most calculations were carried out on a CDC 6600 computer using the "X-Ray 70" program system.[9]

Structure Determination. The structure was solved by application of the symbolic addition procedure for centrosymmetric crystals using the program of ref 10. The amplitudes $|E_A|$ for normalized structure factors were calculated according to Karle and Hauptmann.[11] The signs of 600 reflections with $|F| > 1.3$ (corresponding to about 10 reflections for nonhydrogen atom) were determined in terms of three signs for the origin-specifying reflections and four symbolic signs. For each of the system solutions the consistency index c was evaluated and from the E map corresponding to the largest value of c (0.88) the approximate atomic positions of several atoms were determined. The coordinates of the remaining nonhydrogen atoms were found from successive Fourier synthesis calculated using all data and based on the positions of these atoms. The reliability index R for the trial model

Table V. Interatomic Distances and Standard Deviations (A)

Equatorial Groups

Co–C(1)	1.78 (1)	Co–C(2)	1.81 (1)	Co–C(3)	1.81 (2)
C(1)–N(1)	1.16 (2)	C(2)–N(3)	1.16 (2)	C(3)–N(5)	1.17 (2)
N(1)–C(1A)	1.40 (2)	N(3)–C(1B)	1.40 (2)	N(5)–C(1C)	1.38 (2)
C(4A)–N(2)	1.47 (2)	C(4B)–N(4)	1.48 (2)	C(4C)–N(6)	1.49 (2)
N(2)–O(1)	1.17 (3)	N(4)–O(3)	1.18 (3)	N(6)–O(5)	1.20 (3)
N(2)–O(2)	1.20 (2)	N(4)–O(4)	1.21 (2)	N(6)–O(6)	1.23 (2)

Phenyl Groups A, B, C^{a,b}

C–C (max)	1.45	C–C (max)	1.43	C–C (max)	1.43
C–C (min)	1.35	C–C (min)	1.38	C–C (min)	1.36
C–C (mean)	1.394 ± 0.01	C–C (mean)	1.398 ± 0.01	C–C (mean)	1.397 ± 0.01

Axial Groups

Co–P(1)	2.18 (1)	Co–P(2)	2.17 (1)
P(1)–O(7)	1.61 (1)	P(2)–O(9)	1.58 (1)
P(1)–O(8)	1.58 (1)	P(2)–O(10)	1.60 (1)
P(1)–C(1D)	1.82 (1)	P(2)–C(1E)	1.82 (1)
O(7)–C(4)	1.50 (2)	O(9)–C(8)	1.47 (2)
C(4)–C(5)	1.51 (3)	C(8)–C(9)	1.52 (3)
O(8)–C(6)	1.52 (2)	O(10)–C(10)	1.47 (2)
C(6)–C(7)	1.48 (3)	C(10)–C(11)	1.50 (2)

Phenyl Groups D, E^{a,c}

C–C (max)	1.42	C–C (max)	1.44
C–C (min)	1.37	C–C (min)	1.38
C–C (mean)	1.401 ± 0.01	C–C (mean)	1.398 ± 0.01

Perchlorate Ion

Cl–O(7)	1.39 (3)	Cl–O(9)	1.35 (2)
Cl–O(8)	1.28 (1)	Cl–O(10)	1.23 (1)

^{a} The standard deviation of the mean is calculated from $[\Sigma_i\Delta_i{}^2/m(m-1)]^{1/2}$. ^{b} The esd's of the C–C distances are 0.02–0.03 A. ^{c} The esd's of the C–C distances are about 0.02 A.

was 21%, where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. Refinement of the coordinates of the atoms with isotropic vibration parameters and of the overall scale factor reduced the R factor to 10.2%. A three-dimensional difference map was then computed which showed no interpretable features about the positions of the hydrogen atoms but showed characteristic dumbbell-formed peaks, indicating anisotropy. Therefore, in the final steps all atoms, including the carbon atoms in phenyl rings, were treated as having anisotropic thermal vibrations. Positional and thermal parameters for all atoms, except hydrogen, and one scale factor were variables in the refinement. It converged with $R = 7.2\%$ when the shifts were less than about 0.1 of the estimated standard deviations. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$. A final difference Fourier map revealed around the chlorine atom two peaks with approximately 15–20% the height of an oxygen atom in previous maps. These small amounts of electron densities are probably associated with disorder in the perchlorate ion and have been ignored in the final structural model.

Atom positions, thermal parameters, and estimated standard deviations obtained from the refinement appear in Table III. Structure factors are listed in Table IV (supplementary material). Bond lengths and bond angles are reported in Tables V and VI. The equations of some relevant planes in the molecule are reported in Table VII.

Results and Discussion

Syntheses and Characterizations. [Co(4-NO$_2$C$_6$H$_4$NC)$_2$(PhP(OEt)$_2$)$_3$]$^+$ and [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]$^+$ are obtained simultaneously by reaction of the isocyanide with cobalt(I) chloride in the presence of the phosphonite ligand. They are air stable in the solid state and in solution of polar organic solvents and are somewhat inert to substitution; e.g., neither the forward nor the reverse reaction of equilibrium 1 can be detected (CNR

$$[\text{Co(CNR)}_2\text{L}_3]^+ + \text{CNR} \rightleftharpoons [\text{Co(CNR)}_3\text{L}_2]^+ + \text{L} \tag{1}$$

= 4-NO$_2$C$_6$H$_4$NC; L = PhP(OEt)$_2$) spectroscopically within 1 week for a 10^{-2} M dichloromethane solution of the complex in the presence of a large excess (>10^{-1} M) of entering ligand at room temperature.

The elemental analyses and conductivities (Table I) are in good agreement with the formulas proposed for the complexes.

Assuming a trigonal-bypyramidal geometry with the isocyanide ligands in equatorial positions one would expect, from group theory predictions, two v(CN) frequencies for complex I and only one for II. The number of bands observed for both complexes is higher than required from C_{2v} or D_{3h} symmetry, respectively (Table II). This is commonly found for isocyanide complexes and several reasons have been proposed to account for such a feature.[2,3,12] A deviation from the idealized geometry seems to be the principal reason in this case as shown by structural analysis of complex II (vide infra). The strong absorptions at 2089 and 2072 cm^{-1} for the complex [Co(4-NO$_2$C$_6$H$_4$NC)$_2$(PhP(OEt)$_2$)$_3$]$^+$ can be tentatively assigned to the A$_1$ and B$_2$ stretching modes, while the 2054-cm^{-1} band for the complex [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]$^+$ can be attributed to the E$'$ stretching mode.

That the CN bond order in complex I is higher than in complex II may indicate that the diethyl phenylphosphonite is a better π acceptor (or poorer σ donor or both) than the 4-nitrophenyl isocyanide ligand.

The ^{1}H NMR resonance of methyl protons of II appears as a triplet at τ 8.56 suggesting that the phosphonite ligands are in equivalent apical positions as previously observed for [Co(CNR)$_3$(PhP(OEt)$_2$)$_2$]$^+$ (R = substituted phenyl or cyclohexyl radicals).[2] A triplet at τ 8.66 is also observed for complex I. On the basis of previous data[2] and the structure reported here (vide infra) one would predict a structure having two apical and one equatorial phosphonite ligands for I so that two triplets are expected (1:2 intensity ratio) for the methyl protons. An observation of only one triplet could be attributed to one of the following possibilities: (a) a fast dissociative equilibrium, which can be ruled out because of the inertness of the compound to ligand exchange as mentioned for equilibrium 1; (b) poor sensitivity of the methyl proton as a structural probe, which can be ruled out because the methyl proton triplet of the free ligand in acetone is at τ 8.77,[13] 0.11 τ unit upfield compared to the same signal of the coordinated ligand; moreover, for [FeCl(CNR)$_2$(PhP(OEt)$_2$)$_3$]$^+$ complexes differences in the range τ 0.7–0.14 were observed between apical and equatorial phosphonite ligands;[13] (c) a distorted geometry in which the three phosphonite ligands are equivalent, which cannot be completely excluded since a distorted geometry is shown by x-ray analysis for the less hindered [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]$^+$ cation (this paper) and is suggested by NMR spectra for the [Co(CO)(PhP(OEt)$_2$)$_4$]$^+$ cation;[14] (d) a fast intramolecular exchange of the phosphonite ligands (nonrigidity), which seems to be the most probable possibility, even if the ^{1}H NMR spectrum does not change by lowering the temperature to −80 °C, on the basis of the fact that a limiting slow-exchange NMR spectrum was undetectable even at ca. −140 °C for the analogous five-coordinate cobalt(I) complexes HCo[P(OR)$_3$]$_4$ (R = CH$_3$, C$_2$H$_5$, i-C$_3$H$_7$, and C$_6$H$_5$).[15]

Structure Description. The crystal structure of the compound [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]ClO$_4$ consists of discrete ions. As shown in Figure 1, there is a trigonal-bipyramidal arrangement of the ligands around the cobalt atom. Deviations from the expected values are observed (Figures 2 and 3) in the axial P–Co–P angle [174.8 ± 0.2°] and in the equatorial plane angles, two of which are comparable [127.3 ± 0.7°] but significantly larger than the third [105.0 ± 0.7°]. This reduces the symmetry of the coordination polyhedron from D_{3h} to approximately C_{2v}. The nature of the equatorial ligands does not justify the observed deviations of the bond angles from 180 and 120°, respectively, which seem to be due to the asymmetry of the axial ligands. However, small changes due to the presence of intermolecular repulsion forces cannot be completely excluded. Presumably the difference in energy between a trigonal-bipyramidal structure and a distorted

Table VI. Bond Angles and Standard Deviations (deg)

Coordination Polyhedron

Atoms	Angle	σ	Atoms	Angle	σ
P(1)–Co–P(2)	174.8	0.2	P(2)–Co–C(2)	93.1	0.5
P(1)–Co–C(1)	87.1	0.6	P(2)–Co–C(3)	90.3	0.6
P(1)–Co–C(2)	91.3	0.5	C(1)–Co–C(2)	127.3	0.7
P(1)–Co–C(3)	91.1	0.6	C(1)–Co–C(3)	127.7	0.7
P(2)–Co–C(1)	88.1	0.6	C(2)–Co–C(3)	105.0	0.7

Axial Groups

Atoms	Angle	σ	Atoms	Angle	σ
Co–P(1)–O(7)	116.0	0.4	Co–P(2)–O(9)	116.6	0.4
Co–P(1)–O(8)	113.1	0.5	Co–P(2)–O(10)	110.7	0.5
Co–P(1)–C(1D)	116.7	0.6	Co–P(2)–C(1B)	119.2	0.5
O(7)–P(1)–O(8)	105.6	0.6	O(9)–P(2)–O(10)	106.4	0.6
O(7)–P(1)–C(1D)	98.7	0.7	O(9)–P(2)–C(1E)	98.2	0.7
O(8)–P(1)–C(1D)	105.1	0.6	O(10)–P(2)–C(1E)	104.1	0.6
P(1)–O(7)–C(4)	120	1	P(2)–O(9)–C(8)	126	1
O(7)–C(4)–C(5)	107	1	O(9)–C(8)–C(9)	107	1
P(1)–O(8)–C(6)	122	1	P(2)–O(10)–C(10)	125	2
O(8)–C(6)–C(7)	107	1	O(10)–C(10)–C(11)	107	1
P(1)–C(1D)–C(2D)	120	1	P(2)–C(1E)–C(2E)	117	1
P(1)–C(1D)–C(6D)	117	1	P(2)–C(1E)–C(6E)	121	1

Perchlorate Ion

The mean value of the six O–Cl–O angle is 108.5°

The esd's for the angles are between 1 and 2°

Phenyl Groups D, E[a]

Max angle	122.9		Max angle	122.0
Min angle	117.6		Min angle	115.8
Mean	119.9 ± 0.7		Mean	119.9 ± 0.7

Equatorial Groups

Atoms	Angle	σ	Atoms	Angle	σ	Atoms	Angle	σ
Co–C(1)–N(1)	178	1	Co–C(2)–N(3)	176	1	Co–C(3)–N(5)	177	1.5
C(1)–N(1)–C(1A)	172	2	C(2)–N(3)–C(1B)	171	1	C(3)–N(5)–C(1C)	171	2
N(1)–C(1A)–C(2A)	118	2	N(3)–C(1B)–C(2B)	119	2	N(5)–C(1C)–C(2C)	120	1.5
N(1)–C(1A)–C(6A)	118	2	N(3)–C(1B)–C(6B)	117	1	N(5)–C(1C)–C(6C)	116	1.5
C(2A)–C(1A)–C(6A)	124	1	C(2B)–C(1B)–C(6B)	124	1.5	C(2C)–C(1C)–C(6C)	123	1.5
C(1A)–C(2A)–C(3A)	120	2	C(1B)–C(2B)–C(3B)	118	2	C(1C)–C(2C)–C(3C)	119	1.5
C(2A)–C(3A)–C(4A)	116	2	C(2B)–C(3B)–C(4B)	118	1.5	C(2C)–C(3C)–C(4C)	117	1.5
C(3A)–C(4A)–C(5A)	126	1.5	C(3B)–C(4B)–C(5B)	126	1.5	C(3C)–C(4C)–C(5C)	126	1.5
C(4A)–C(5A)–C(6A)	118	2	C(4B)–C(5B)–C(6B)	116	1.5	C(4C)–C(5C)–C(6C)	117	1.5
C(5A)–C(6A)–C(1A)	117	1.5	C(5B)–C(6B)–C(1B)	118	1.5	C(5C)–C(6C)–C(1C)	118	1.5
N(2)–C(4A)–C(3A)	117	2	N(4)–C(4B)–C(3B)	118	1.5	N(6)–C(4C)–C(3C)	118	1.5
N(2)–C(4A)–C(5A)	117	2	N(4)–C(4B)–C(5B)	116	1.5	N(6)–C(4C)–C(5C)	116	1.5
C(4A)–N(2)–O(1)	119	2	C(4B)–N(4)–O(3)	119	2	C(4C)–N(6)–O(5)	118	1
C(4A)–N(2)–O(2)	119	2	C(4B)–N(4)–O(4)	118	2	C(4C)–N(6)–O(6)	116	2
O(1)–N(2)–O(2)	122	1.5	O(3)–N(4)–O(4)	123	2	O(5)–N(6)–O(6)	126	2

[a] The standard deviation of the mean is calculated from $[\Sigma_i \Delta_i^2 / m(m - 1)]^{1/2}$. The esd's for the angles in the two phenyl groups are about 1.5°.

trigonal-bipyramidal structure is small enough that packing considerations predominate in the crystal.

The phenylene rings A, B, and C (Figure 1) are not coplanar with the equatorial plane Co–C(1)–C(2)–C(3), but they are considerably twisted with respect to this plane (see Table VII). The nitro groups are in turn tilted ca. 6° about the C(phenylene)–N(nitro) axis.

The mean value of 1.80 Å for the three independent Co–C bond distances, which are equal within the experimental errors, is significantly shorter than that expected for a Co–C single-bond distance (2.16 Å, Pauling's estimate;[16] 2.15 Å, Cotton et al.[17]). This supports the existence of a strong metal-to-ligand π back-donation with a resulting increase of the Co–C bond order. Comparison of 1.80 Å with 1.87 ± 0.015 Å, which is the mean of the corresponding distances for the [Co-(CH$_3$NC)$_5$]$^+$ cation,[4] indicates that the back-donation effects are stronger in the [Co(4-NO$_2$C$_6$H$_4$NC)$_3$(PhP(OEt)$_2$)$_2$]$^+$ complex than in the pentakis(methyl isocyanide)cobalt(I) derivative. This is not surprising if one considers that the presence of a strong electron-withdrawing nitro group in the

para position of the phenyl ring makes these isocyanides weaker σ donors and stronger π acceptors than the methyl isocyanide.

The bend of 8–9° in the three CoCNC chains is a further indication of the relatively high π character in the Co–C bonds and is consistent with a resonance structure between the two forms

$$M-C\equiv N-C \leftrightarrow M=C=\bar{N}\diagdown_C$$
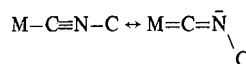
with a very large predominance of the first. The Co–C π interaction has apparently little effect on the C–N bond lengths (mean 1.163 Å), which are in good agreement with the value normally accepted for a CN triple bond and particularly with 1.166 Å found for free CH$_3$—N≡C.[18]
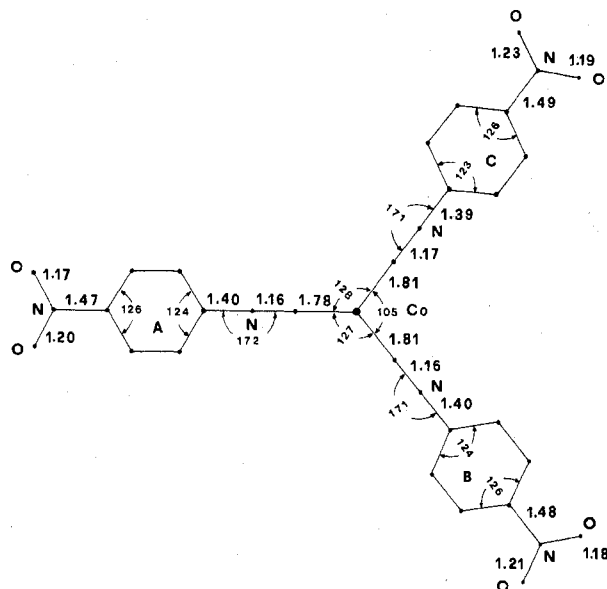
The mean value of 1.396 Å for the N–C(sp^2) bonds indicates that there is some double-bond character, the shortening being due to the fact that this formal single bond is between a multiple bond and an aromatic ring; therefore a

Table VII. Equations of Least-Squares Planes, Deviations (Å) of the Relevant Atoms from the Planes,^{a} and Dihedral Angles between the Planes
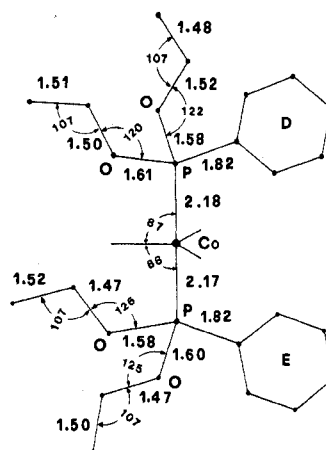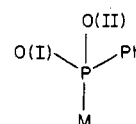
Plane	Equations and deviations			
1	$6.472X + 9.407Y + 0.108Z = 7.805$			
	Co	−0.008	C(2)	0.002
	C(1)	0.003	C(3)	0.002
2	$12.485X − 2.827Y + 3.775Z = 9.192$			
	C(1A)	0.017	C(4A)	0.006
	C(3A)	0.007	C(6A)	−0.003
3	$5.963X − 6.300Y + 21.722Z = 8.958$			
	C(1B)	0.007	C(4B)	−0.005
	C(2B)	−0.004	C(5B)	0.007
	C(3B)	0.003	C(6B)	−0.008
4	$−0.597X + 10.533Y + 7.525Z = 4.812$			
	C(1C)	0.015	C(4C)	−0.006
	C(2C)	0.005	C(5C)	0.026
	C(3C)	−0.009	C(6C)	−0.031
5	$1.834X + 10.402Y − 8.044Z = 4.107$			
	C(1D)	0.030	C(4D)	0.010
	C(2D)	−0.017	C(5D)	0.002
	C(3D)	−0.003	C(6D)	−0.022
6	$3.539X + 8.779Y + 16.825Z = 9.235$			
	C(1E)	−0.017	C(4E)	−0.036
	C(2E)	0.011	C(5E)	0.030
	C(3E)	0.015	C(6E)	−0.003

Planes	Dihedral angle, deg	Planes	Dihedral angle, deg	Planes	Dihedral angle, deg
1–2	75.6	2–3	46.7	5–4	29.0
1–3	74.5	2–4	74.7	5–6	46.1
1–4	34.2	3–4	64.2	6–3	90.0
1–5	25.9	5–3	49.0	6–4	26.6
1–6	31.9				

^{a} The equations are in the form $AX + BY + CZ = D$, where X, Y, and Z represent fractional coordinates in the crystal system.

Figure 3. Schematic drawing of the arrangment of the apical diethyl phosphonite ligands.

Figure 4. Schematic arrangment at the phosphorus atom in the coordinated diethyl phenylphosphonite.

C–C bond length is in good agreement with the mean value of 1.394 Å tabulated by Sutton.[23]

Average C–C–C angles in the phosphonite phenyl rings D and E are normal (mean value 119.9°), but for the internal angles in the phenylenes, there appear to be deviations from the ideal value. The internal angles at the N-bonded carbon atoms are significantly larger than 120°, with values of 124° at C(1A) and C(1B), 123° at C(1C), and 126° at C(4A), C(4A), C(4B), and C(4C), respectively. This is not surprising if one takes into account that these carbon atoms are bonded to more electronegative nitrogen atoms. The higher electronegativity forces the C–N bonding pair to take up a smaller space in the valency shell of the central carbon atom so that there is a weaker interaction with the neighboring C–C bonding pairs.[24] The resulting effect is the enlargement of the C–C–C bond angles, and one can expect this effect to be more pronounced for the carbon atoms bonded to the strong electron-withdrawing nitro groups.

The axial metal–phosphonito Co–P bonds (Figure 3) are shorter than expected for normal covalent bonds and this can be due to the good π-acceptor ability of the phosphonite ligands.[25,26]

Bonding about the phosphorus atoms is roughly tetrahedral with the Co–P–X (X = O, C) angles larger than 109.5° and X–P–X angles less than 109.5°. This is consistent with the fact that in the tetrahedral arrangement of four orbitals, one of which has a double-bond strong character, the angles involving the double bond are always larger than the tetrahedral angle, leaving the angles between the single bonds less than the tetrahedral angle, as a consequence of the greater repulsion expected for a double bond than for a single bond. On this basis it is reasonable to assume that the tetrahedral distortion at the phosphorus atom is correlated to the extent of the MP double-bond character (Figure 4). The valency angles reported in Table VIII show that while the distortion is quite similar for the cobalt(I) and nickel(II) complexes, it is more pronounced in the iron(II) derivative, indicating a stronger M–P π interaction in the latter compound than in the former two complexes. This suggests that the presence of the good π-acceptor isocyanide or cyanide ligands on the d^8 cobalt(I) and nickel(II) metals makes these atoms less effective M–P π donors than the d^6 iron(II) atom.

Figure 2. Schematic drawing of the arrangment of the equatorial isocyanide ligands.

greater binding energy is provided by electron delocalization. On the contrary, the three N(nitro)–C(sp^2) distances agree with a paraffinic N–C covalent bond (1.42 and 1.48 Å in NH2CH3[19,20] and 1.47 Å in N(CH3)3[20]) and also with the corresponding value in nitrobenzene (1.48 Å[22]). The three phenylene rings A, B, and C and the two phenyl rings D and E are planar, within the experimental errors, and the average

Table VIII. Valency Angles (deg) at the Phosphorus Atoms in Some Diethyl Phenylphosphonite (L) Complexes

Angles[a]	[Co(CNR)$_3$-L$_2$]$^+$ [b]	[Ni(CN)$_2$-L$_3$][c]	[H$_2$-FeL$_4$][d]
O(I)-P-Ph	98.4	97.2	94.6
O(II)-P-Ph	104.6	106.2	100.3
O(I)-P-O(II)	106.0	105.6	101.1
M-P-Ph	118.4	117.3	119.4
M-P-O(I)	116.3	119.8	123.4
M-P-O(II)	111.9	109.2	113.7

[a] The symbols are in accordance with Figure 4. [b] This work. [c] From J. K. Stalick and J. A. Ibers, *Inorg. Chem.,* 8, 1085 (1969). [d] L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Am. Chem. Soc.,* 94, 1135 (1972).

σ orbitals used by the oxygen atoms can best be described as sp^2 hybrids, as shown by the close approach of the P–O–C bond angles to 120°. All O–C–C angles are 107°. Some of the CH$_2$–CH$_3$ distances, which average 1.50 Å, are somewhat shorter than expected, but this shortening is probably due to vibrational effects. The geometry of the perchlorate anion is essentially tetrahedral. The generally high thermal parameters of the oxygen atoms presumably indicate some disorder, an effect which is also reflected in the wide variation of chlorine–oxygen bond lengths and bond angles. For this reason the atomic sites of the oxygen atoms [particularly O(9) and O(10)] are approximate. No other model was sought for this group.

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Supplementary Material Available: Table IV, listing structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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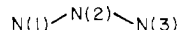(26) J. D. Verkade, *Coord. Chem. Rev.,* 9, 1 (1972).

Crystal Structure of Bis(triphenylphosphine)chloro-1,3-di-*p*-tolyltriazenidopalladium(II)

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The title compound has square-planar coordination with the phosphine groups trans to each other and the triazenido group acting as monodentate ligand. The

$$N(1)^{\diagup N(2)\diagdown}N(3)$$

plane contains the metal atom; thus interactions of the N=N π electrons seem to be absent. This and the short Pd⋯N(3) distance suggest that the fluxional behavior of the compound could be explained as occurring via a σ,σ-chelating intermediate according to the mechanism (L = phosphine)
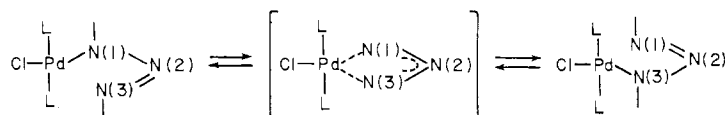
Introduction

1,3-Diaryl- (or dialkyl-) triazenido ligands R—N—N=N—R (dpt for R = C$_6$H$_5$, dtt for R = C$_6$H$_4$CH$_3$, dmt for R = CH$_3$) can form coordination metal complexes in which they act as monodentate or bidentate (chelate or bridging) ligands.

A chelate structure with square-planar coordination about the metal was proposed for Ni(dpt)$_2$ and a mixed-chelate-bridged structure was proposed for Ni$_2$(dpt)$_4$[2] on the basis of magnetic susceptibility and molecular weight measurements.

Subsequently x-ray diffraction studies proved that in Ni$_2$(dpt)$_4$ the nickel atoms are bridged by four ligand groups through the terminal nitrogen atoms.[3] Bridged structures were also shown by x-ray diffraction for Cu$_2$(dpt)$_2$[4] and assigned by spectroscopic and magnetic methods for Cu$_2$(dpt)$_4$ and Pd$_2$(dpt)$_4$.[5]

Recently, [(π-methallyl)Pd(dmt)]$_2$[6] and [(1,3-π-allyl)-Pd(dtt)]$_2$[7] were shown to have the bridged structure by x-ray diffraction. An example of a complex containing the chelate