

C4—Mo—C3	36.3 (4)	C16—N1—Mo	124.2 (8)
C1—Mo—N2	99.5 (5)	C18—N1—Mo	117.9 (8)
C2—Mo—N2	167.0 (4)	C7—N2—C17	119 (1)
O3—Mo—N2	81.1 (3)	C7—N2—Mo	127.4 (8)
N1—Mo—N2	72.8 (3)	C17—N2—Mo	113.4 (8)
C4—Mo—N2	91.0 (5)	N2—C17—C18	118 (1)
C3—Mo—N2	83.8 (4)	N1—C18—C17	117 (1)
C1—Mo—C5	105.0 (5)	C19—O3—Mo	122.1 (8)
C2—Mo—C5	68.0 (5)	O4—C19—O3	131 (1)
O3—Mo—C5	83.8 (4)		

The F atoms in the trifluoroacetate groups are highly anisotropic in both compounds. Splitting one trifluoroacetate group into two different positions did not produce any significant improvement in the refinements and was therefore not used. Compound (II) was solved in the C2 space group, a subgroup of A2/n; even in this subgroup the F atoms exhibited large anisotropic displacement parameters. The H atoms were positioned geometrically and allowed to ride during the least-squares refinements.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1988a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1988b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXL-Plus* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 80–82

Ethynyltetrakis(trimethylphosphine)-cobalt(I), [Co(CCH){P(CH₃)₃]₄]

GRAHAM STRINGER, NICHOLAS J. TAYLOR AND TODD B. MARDER*

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 15 June 1994; accepted 24 July 1995)

Abstract

The title compound consists of a neutral [Co(C₂H)-(C₃H₉P)₄] unit, with the ligands arranged in a distorted trigonal bipyramidal configuration, retaining threefold axial symmetry. The C≡CH ligand occupies an axial position, with a C≡C bond length of 1.185 (6) Å. This compound represents the first structurally characterized example of a cobalt(I)-ethynyl complex.

Comment

Ethynyl complexes are known for many of the transition metals. Relatively few, however, have been structurally characterized (Atwood, Tsutsui, Ely & Gebala, 1976; Bianchini, Mealli, Peruzzini, Vizza & Zanobini, 1988; Bianchini *et al.*, 1989; Akita, Terada, Oyama & Morooka, 1990; Phillips, Miller & Trogler, 1990; Sun, Taylor & Carty, 1992; Haquette, Pirio, Touchard, Toupet & Dixneuf, 1993).

Only five cobalt-alkynyl complexes have been reported, all of which are Co^{III} complexes: [Co(CC'Bu)(HCCH'Bu)(MeCN){P(CH₃)₃]₃]BPh₄ (Habadie, Dartiguenave, Dartiguenave, Britten & Beauchamp, 1989), [Co(CCCN)₂(η⁵-C₅H₅){P(C₆H₅)₃}] (Kergoat, Gomes de Lima, Jégat, Le Berre & Kubicki, 1990), [Co{CCSi(CH₃)₃}{(DO)(DOH)pn}]I, where (DO)(DOH)pn is 1,3-bis(diacetylmonooximeimino)propane (Giese, Zehnder, Neuberger & Trach, 1991), [CoH(CCPh)₂{P(CH₃)₃]₃] (Klein *et al.*, 1991) and [CoH(CCSiMe₃){P(CH₂CH₂PPh₂)₃]BPh₄ (Bianchini, Peruzzini, Vacca & Zanobini, 1991). To date, however, no structures, either of a parent ethynyl complex or of any Co^I-

alkynyl complex, have appeared. In this article, we report the first crystal structure analysis of a $\text{Co}^{\text{I}}-\text{C}\equiv\text{CH}$ mononuclear complex, (I).

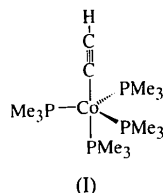


Fig. 1 presents a view of the molecular structure of (I) with the atomic numbering scheme. The title compound is made up of neutral $[\text{Co}(\text{CCH})\{\text{P}(\text{CH}_3)_3\}_4]$ units in which the metal center has a distorted trigonal bipyramidal environment. The metal is displaced 0.265 Å out of the plane of the three equatorial phosphine ligands and the $\text{P}(1)-\text{Co}-\text{P}(2)$ angle is $96.9(1)^\circ$. This distortion from a perfect bipyramid arises from the greater steric bulk of the phosphine ligand compared to the ethynyl ligand. Threefold rotational symmetry is retained about the phosphine-metal-ethynyl axis. The metal-phosphorus bond length for the phosphine ligand *trans* to the ethynyl ligand is significantly shorter than that for the equatorial phosphine ligands, *i.e.* 2.168(2) versus 2.190(1) Å. These distances contrast with the range 2.193(2)–2.252(2) Å reported for $\text{Co}-\text{P}$ distances in $[\text{Co}\{\text{P}(\text{CH}_3)_3\}_4]\text{BPh}_4$ (Ananias de Carvalho, Dartiguenave, Dartiguenave & Beauchamp, 1984).

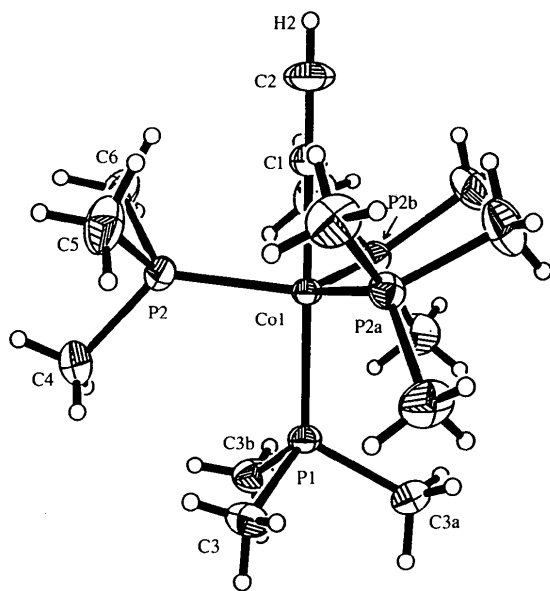


Fig. 1. ORTEP (Johnson, 1965) drawing of $[\text{Co}(\text{CCH})\{\text{P}(\text{CH}_3)_3\}_4]$ showing the atomic numbering scheme and 50% probability displacement ellipsoids.

The $\text{C}\equiv\text{C}$ bond length of 1.185(6) Å is not significantly shorter than the 1.209(6) Å bond length reported for the alkynyl bond in $[\text{Co}(\text{CC}'\text{Bu})(\text{HCCH}'\text{Bu})-(\text{MeCN})\{\text{P}(\text{CH}_3)_3\}_3]\text{BPh}_4$ (Habadie, Dartiguenave, Dartiguenave, Britten & Beauchamp, 1989) and is comparable to the distance of 1.2033(2) Å found in free acetylene (Fast & Welsh, 1972). The $\text{C}-\text{H}$ bond lengths in this structure are in the range 0.78(4)–1.04(4) Å (average 0.93 Å), *i.e.* 0.78 Å for $\equiv\text{CH}$ and 0.88–1.04 Å for CH_3 $\text{C}-\text{H}$ bonds (average 0.94 Å).

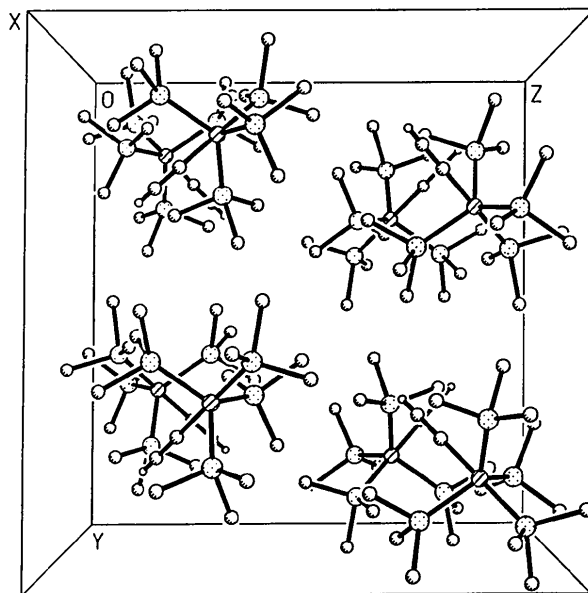


Fig. 2. Packing diagram for $[\text{Co}(\text{CCH})\{\text{P}(\text{CH}_3)_3\}_4]$.

Experimental

The title complex, $[\text{Co}(\text{CCH})\{\text{P}(\text{CH}_3)_3\}_4]$, was prepared by reacting $[\text{Co}\{\text{P}(\text{CH}_3)_3\}_4]\text{BF}_4$ (Klein & Karsch, 1975) with $\text{LiCCH}_2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ in tetrahydrofuran under a blanket of N_2 at room temperature. After stirring for 14 h, the reaction mixture was filtered and the solvent removed *in vacuo*. The residue was dissolved in hexane and concentrated. Dark brown crystals of the product were obtained after cooling to 243 K.

Crystal data

$[\text{Co}(\text{C}_2\text{H})(\text{C}_3\text{H}_9\text{P})_4]$
 $M_r = 388.2$
 Cubic
 $Pa\bar{3}$
 $a = 16.216(3)$ Å
 $V = 4264.2(13)$ Å³
 $Z = 8$
 $D_x = 1.209$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 11-16^\circ$
 $\mu = 1.089$ mm⁻¹
 $T = 170$ K
 Truncated octahedron
 $0.42 \times 0.42 \times 0.39$ mm
 Brown

Data collection

Siemens R3m/V diffractometer
 ω scans
 Absorption correction:
 8 ψ scans (XEMP in
 SHELXTL-Plus; Sheldrick,
 1990)
 $T_{\min} = 0.485$, $T_{\max} =$
 0.543
 4205 measured reflections
 1258 independent reflections

885 observed reflections
 $[F \geq 6\sigma(F)]$
 $R_{\text{int}} = 0.0302$
 $\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 19$
 $k = 0 \rightarrow 19$
 $l = 0 \rightarrow 19$
 2 standard reflections
 monitored every 100
 reflections
 intensity decay: 2%

Refinement

Refinement on F
 $R = 0.0349$
 $wR = 0.0331$
 $S = 1.41$
 885 reflections
 108 parameters
 All H-atom parameters
 refined

$w = 1/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\max} = 0.015$
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Co(1)—P(2)—C(6) 116.2 (2) C(4)—P(2)—C(5) 98.0 (2)
 C(4)—P(2)—C(6) 96.3 (2) C(5)—P(2)—C(6) 99.5 (2)
 Co(1)—C(1)—C(2) 180.0 (1)

Symmetry code: (i) y, z, x .

Crystallographic computations were performed using the
 SHELXTL-Plus program package (Sheldrick, 1990).

This work was supported by the Natural Sciences and
 Engineering Research Council of Canada.

Lists of structure factors, anisotropic displacement parameters, H-
 atom coordinates and complete geometry have been deposited with
 the IUCr (Reference: BK1075). Copies may be obtained through The
 Managing Editor, International Union of Crystallography, 5 Abbey
 Square, Chester CH1 2HU, England.

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 4293–4300.

Table 1. Fractional atomic coordinates and equivalent
 isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Co(1)	0.18024 (2)	x	x	0.0190 (1)
P(1)	0.10304 (5)	x	x	0.0227 (2)
P(2)	0.29190 (5)	0.17243 (6)	0.10468 (6)	0.0252 (3)
C(1)	0.2475 (2)	x	x	0.0291 (8)
C(2)	0.2897 (3)	x	x	0.046 (1)
C(3)	0.0861 (3)	0.1342 (3)	-0.0043 (3)	0.035 (1)
C(4)	0.3063 (3)	0.1072 (3)	0.0130 (3)	0.045 (2)
C(5)	0.3282 (3)	0.2698 (3)	0.0606 (3)	0.049 (2)
C(6)	0.3854 (3)	0.1399 (3)	0.1576 (3)	0.044 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Co(1)—P(1)	2.168 (2)	Co(1)—P(2)	2.190 (1)
Co(1)—C(1)	1.890 (3)	P(1)—C(3)	1.833 (4)
P(2)—C(4)	1.840 (5)	P(2)—C(5)	1.830 (5)
P(2)—C(6)	1.821 (5)	C(1)—C(2)	1.185 (6)
P(1)—Co(1)—P(2)	96.9 (1)	P(1)—Co(1)—C(1)	180.0 (1)
P(2)—Co(1)—C(1)	83.1 (1)	P(2)—Co(1)—P(2')	118.6 (1)
Co(1)—P(1)—C(3)	118.4 (2)	C(3)—P(1)—C(3')	99.2 (2)
Co(1)—P(2)—C(4)	126.2 (2)	Co(1)—P(2)—C(5)	115.8 (2)