Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and spectroscopic data for (1) and (2) have been deposited with the IUCr (Reference: CF1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(η^3-Allyl)dicarbonyl(1,10-phenanthroline)(trifluoroacetato)molybdenum, (I), and [*syn*(1,2,3-η)-2-Butenyl]dicarbonyl(1,10-phenanthroline)(trifluoroacetato)molybdenum, (II)

Lars Eriksson,[a] Magnus P. T. Sjögren[b] and Björn Åkermark[c]

[a]*Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden,* [b]*ASTRA Production Chemicals AB, S-151 85 Södertälje, Sweden, and* [c]*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*

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Abstract

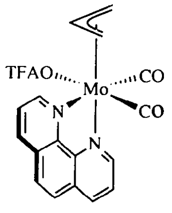
This structure determination shows that in the two molybdenum complexes of the title, (I), $[Mo(C_2F_3O_2)(C_3H_5)(C_{12}H_8N_2)(CO)_2]$, and (II), $[Mo(C_2F_3O_2)(C_4H_7)(C_{12}H_8N_2)(CO)_2]$, the phenanthroline ligand is perpendicular to the molybdenum–dicarbonyl plane. This is in contrast to similar molybdenum complexes, where the ligand is in the plane.

Comment

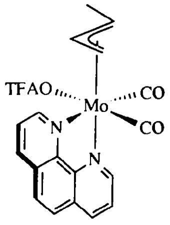
We have studied the nucleophilic substitution of allylic substrates for some time (Tsuji, 1980; Trost & Verhoeven, 1982; Heck, 1985; Collman, Hegedus, Norton & Finke, 1987; Godleski, 1991). A long-term goal is to find alternatives to the commonly used palladium catalyst by replacing palladium with other metals.

We have shown recently that (η^3-allyl)dicarbonyl(1,10-phenanthroline)molybdenum complexes are catalytically active in the nucleophilic substitution of allylic substrates, although there were major differences between the catalyses when the ligands were 1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline (Sjögren, Frisell, Åkermark, Vitagliano & Eriksson, 1995). We postulate that the difference in the catalytic activities depends on the different geometries of the catalysts.

We have also shown that in solution, dicarbonyl(1,10-phenanthroline)[(1,2,3-η)-2-propenyl]molybdenum trifluoroacetate, which is one probable active catalyst, exists as an equilibrium of two complexes in a ratio of 1:2 (Sjögren, 1993). Similar behaviour has been reported earlier (Faller, Haitko, Adams & Chodosh, 1977, 1979) for a dicarbonyl(*P*–*P*)(η^3-allyl)molybdenum complex.



(I)



(II)

By the NOE technique it was shown that the major phenanthroline complex had the same geometry at Mo as that reported here for (I), and the geometry of the minor phenanthroline complex was shown to be the same as the earlier known dicarbonyl(*N*–*N*)(η^3-allyl)complexes. The work described here establishes that dicarbonyl(1,10-phenanthroline)[(1,2,3-η)-2-propenyl](trifluoroacetato)molybdenum, (I), and [*syn*-(1,2,3-η)-2-butenyl]dicarbonyl(1,10-phenanthroline)(trifluoroacetato)molybdenum, (II), each have the molybdenum–phenanthroline plane perpendicular to the molybdenum–dicarbonyl plane. This is the same arrangement at Mo as reported for the dicarbonyl(*P*–*P*)(η^3-allyl)molybdenum complex but quite different from the earlier known dicarbonyl(*N*–*N*)(η^3-

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allyl)molybdenum complexes (Graham & Fenn, 1969, 1970; Fenn & Graham, 1972), which all have the *N–N* ligand, Mo and CO groups in the same plane.

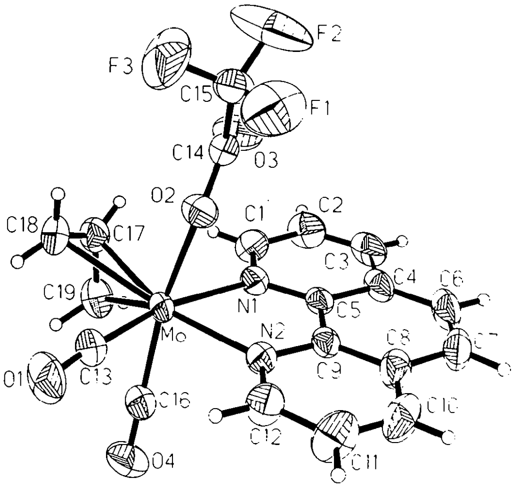

Fig. 1. A perspective view of (I) with 50% probability ellipsoids. H atoms are drawn as small circles of arbitrary size.

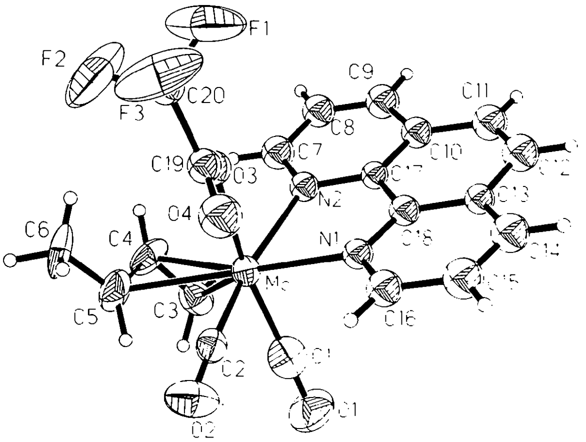

Fig. 2. A perspective view of (II) with 50% probability ellipsoids. H atoms are drawn as small circles of arbitrary size.

Experimental

Compounds (I) and (II) were prepared by refluxing tetracarbonyl(1,10-phenanthroline)molybdenum with 3-trifluoroacetoxy-1-butene and 3-trifluoro-1-propene, respectively, in dry THF for 3 h under N_2. The reaction mixture was rotary evaporated *in vacuo* to dryness. The crude solid formed deep-red crystals upon slow crystallization (Sjögren, Hansson, Norrby, Åkermark, Cucciolito & Vitagliano, 1992) from dichloromethane/diethyl ether.

Compound (I)

Crystal data

$[Mo(C_2F_3O_2)(C_3H_5)$-
$(C_{12}H_8N_2)(CO)_2]$
$M_r = 486.25$
Triclinic
$P\bar{1}$
$a = 8.848\,(4)$ Å
$b = 10.770\,(5)$ Å
$c = 11.335\,(6)$ Å
$\alpha = 100.27\,(2)^\circ$
$\beta = 101.96\,(2)^\circ$
$\gamma = 113.93\,(2)^\circ$
$V = 923.3\,(8)$ Å^3
$Z = 2$
$D_x = 1.749$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5.8–12.1^\circ$
$\mu = 0.769$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.30 \times 0.266 \times 0.076$ mm
Red

Data collection

Stoe Siemens AED-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*SHELX76*; Sheldrick, 1976)
$T_{\min} = 0.858$, $T_{\max} = 0.950$
5046 measured reflections
2421 independent reflections

2154 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0233$
$\theta_{\max} = 22.5^\circ$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 5$
4 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0302$
$wR(F^2) = 0.0715$
$S = 1.072$
2421 reflections
315 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.6215P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.628$ e Å^{-3}
$\Delta\rho_{\min} = -0.877$ e Å^{-3}
Extinction correction: $F_c^* = kF_c[1 + (0.001x \times F_c^2\lambda^3/\sin2\theta)]^{-1/4}$
Extinction coefficient: $x = 0.0033\,(10)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo	0.40357 (4)	0.18437 (3)	0.81470 (3)	0.0306 (2)
N1	0.4073 (4)	0.1690 (3)	0.6121 (3)	0.0339 (7)
N2	0.6072 (4)	0.3915 (3)	0.8182 (3)	0.0350 (7)
C1	0.3079 (5)	0.0596 (5)	0.5096 (4)	0.0449 (10)
C2	0.3113 (6)	0.0638 (5)	0.3887 (4)	0.0540 (11)
C3	0.4207 (6)	0.1857 (5)	0.3715 (4)	0.0529 (12)
C4	0.5285 (5)	0.3054 (5)	0.4758 (4)	0.0432 (10)
C5	0.5160 (4)	0.2917 (4)	0.5952 (3)	0.0327 (8)
C6	0.6466 (6)	0.4372 (5)	0.4670 (5)	0.0570 (12)
C7	0.7503 (6)	0.5493 (5)	0.5700 (5)	0.0558 (12)
C8	0.7422 (5)	0.5383 (4)	0.6935 (4)	0.0458 (10)
C9	0.6236 (4)	0.4107 (4)	0.7049 (3)	0.0338 (8)
C10	0.8496 (6)	0.6488 (5)	0.8043 (5)	0.0609 (13)
C11	0.8333 (6)	0.6292 (5)	0.9170 (5)	0.0644 (14)
C12	0.7112 (6)	0.5003 (4)	0.9208 (4)	0.0500 (10)
C13	0.4491 (5)	0.2377 (4)	0.9963 (4)	0.0441 (9)
C14	0.1280 (5)	0.2743 (4)	0.6837 (4)	0.0373 (9)
C15	0.0305 (5)	0.3613 (5)	0.7037 (4)	0.0477 (10)
C16	0.5886 (5)	0.1338 (4)	0.8704 (4)	0.0430 (9)
C17	0.1646 (5)	−0.0206 (4)	0.7483 (4)	0.0429 (10)
C18	0.1567 (6)	0.0438 (5)	0.8631 (4)	0.0482 (10)
C19	0.2978 (6)	−0.0600 (5)	0.7539 (5)	0.0524 (11)

O1	0.4858 (4)	0.2690 (4)	1.1053 (3)	0.0701 (9)
O2	0.2480 (3)	0.3004 (3)	0.7807 (2)	0.0412 (6)
O3	0.0769 (4)	0.1909 (3)	0.5803 (3)	0.0614 (8)
O4	0.7008 (4)	0.1087 (4)	0.9098 (3)	0.0662 (9)
F1	0.1339 (4)	0.4979 (3)	0.7586 (4)	0.1001 (11)
F2	−0.0691 (6)	0.3548 (5)	0.5987 (3)	0.130 (2)
F3	−0.0650 (5)	0.3210 (4)	0.7757 (4)	0.1139 (13)

Table 2. *Selected geometric parameters (Å, °) for* (I)

Mo—C13	1.943 (4)	N2—C12	1.330 (5)
Mo—C16	1.948 (4)	N2—C9	1.365 (5)
Mo—C17	2.207 (4)	C5—C9	1.430 (5)
Mo—N2	2.214 (3)	C13—O1	1.159 (5)
Mo—O2	2.225 (3)	C14—O3	1.208 (5)
Mo—N1	2.280 (3)	C14—O2	1.257 (5)
Mo—C19	2.316 (5)	C16—O4	1.155 (5)
Mo—C18	2.339 (4)	C17—C18	1.391 (6)
N1—C1	1.327 (5)	C17—C19	1.399 (6)
N1—C5	1.358 (5)		

C13—Mo—C16	78.7 (2)	C16—Mo—C18	110.0 (2)
C13—Mo—C17	103.0 (2)	C17—Mo—C18	35.5 (2)
C16—Mo—C17	103.8 (2)	N2—Mo—C18	152.7 (1)
C13—Mo—N2	93.9 (1)	O2—Mo—C18	79.8 (2)
C16—Mo—N2	87.6 (1)	N1—Mo—C18	122.3 (1)
C17—Mo—N2	161.1 (1)	C19—Mo—C18	61.2 (2)
C13—Mo—O2	94.2 (1)	C1—N1—C5	117.0 (3)
C16—Mo—O2	164.6 (1)	C1—N1—Mo	128.0 (3)
C17—Mo—O2	91.0 (1)	C5—N1—Mo	114.7 (2)
N2—Mo—O2	79.2 (1)	C12—N2—C9	117.2 (3)
C13—Mo—N1	166.8 (1)	C12—N2—Mo	125.7 (3)
C16—Mo—N1	98.0 (1)	C9—N2—Mo	117.1 (2)
C17—Mo—N1	90.2 (1)	N1—C5—C9	117.6 (3)
N2—Mo—N1	73.2 (1)	N2—C9—C5	117.0 (3)
O2—Mo—N1	85.8 (1)	O1—C13—Mo	175.8 (4)
C13—Mo—C19	105.0 (2)	O4—C16—Mo	176.3 (3)
C16—Mo—C19	69.3 (2)	C18—C17—C19	116.3 (4)
C17—Mo—C19	35.9 (2)	C18—C17—Mo	77.5 (2)
N2—Mo—C19	146.1 (2)	C19—C17—Mo	76.3 (3)
O2—Mo—C19	126.0 (1)	C17—C18—Mo	67.1 (2)
N1—Mo—C19	85.4 (2)	C17—C19—Mo	67.8 (2)
C13—Mo—C18	70.4 (2)	C14—O2—Mo	128.5 (2)

Compound (II)

Crystal data

$[Mo(C_2F_3O_2)(C_4H_7)(C_{12}H_8N_2)(CO)_2]$
$M_r = 500.28$
Monoclinic
$A2/n$
$a = 20.191$ (9) Å
$b = 7.009$ (3) Å
$c = 28.944$ (17) Å
$\beta = 109.40$ (2)°
$V = 3863.5$ (33) Å^3
$Z = 8$
$D_x = 1.720$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 30 reflections
$\theta = 11.3$–12.3°
$\mu = 0.738$ mm^{-1}
$T = 293$ (2) K
Prism
$0.342 \times 0.049 \times 0.030$ mm
Red

Data collection

Stoe Siemens AED-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.967$, $T_{\max} = 0.983$
2796 measured reflections
1664 independent reflections

1032 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0767$
$\theta_{\max} = 20.0$°
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 6$
$l = -27 \rightarrow 26$
3 standard reflections
frequency: 90 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0697$
$wR(F^2) = 0.0791$
$S = 1.191$
1664 reflections
184 parameters
H atoms riding, C—H 0.93–0.97Å
$w = 1/[\sigma^2(F_o^2) + (0.0169P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.370$ e Å^{-3}
$\Delta\rho_{\min} = -0.352$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo	0.08011 (6)	0.1705 (2)	0.16595 (4)	0.0298 (3)
C1	0.1342 (7)	0.356 (2)	0.2127 (5)	0.051 (4)
O1	0.1634 (5)	0.4781 (15)	0.2397 (4)	0.074 (4)
C2	0.0051 (6)	0.343 (2)	0.1661 (4)	0.035 (3)
O2	−0.0374 (6)	0.4562 (15)	0.1684 (3)	0.065 (4)
C3	0.1265 (7)	0.0425 (19)	0.2426 (4)	0.046 (4)
C4	0.0676 (8)	−0.0626 (19)	0.2146 (4)	0.049 (4)
C5	0.0022 (8)	0.0298 (19)	0.2040 (5)	0.052 (4)
C6	−0.0645 (6)	−0.0596 (19)	0.1741 (5)	0.059 (5)
N1	0.1102 (4)	0.3369 (16)	0.1106 (3)	0.030 (2)
N2	0.1702 (5)	0.0083 (14)	0.1512 (3)	0.031 (3)
C7	0.1975 (6)	−0.162 (2)	0.1697 (4)	0.043 (3)
C8	0.2556 (6)	−0.2374 (17)	0.1599 (4)	0.044 (4)
C9	0.2838 (6)	−0.141 (2)	0.1321 (4)	0.046 (4)
C10	0.2590 (6)	0.0359 (18)	0.1118 (4)	0.037 (4)
C11	0.2887 (6)	0.1412 (19)	0.0813 (4)	0.047 (4)
C12	0.2571 (6)	0.304 (2)	0.0608 (4)	0.048 (4)
C13	0.1953 (6)	0.3787 (16)	0.0691 (4)	0.031 (3)
C14	0.1589 (7)	0.5424 (19)	0.0464 (5)	0.047 (4)
C15	0.1014 (6)	0.5987 (18)	0.0564 (4)	0.051 (4)
C16	0.0768 (6)	0.4947 (18)	0.0885 (4)	0.041 (4)
C17	0.1987 (6)	0.1054 (15)	0.1208 (4)	0.027 (3)
C18	0.1673 (6)	0.2797 (17)	0.0999 (4)	0.033 (3)
O3	0.0174 (4)	0.0022 (12)	0.1012 (3)	0.038 (2)
C19	−0.0381 (6)	0.068 (2)	0.0696 (4)	0.035 (4)
O4	−0.0620 (4)	0.2286 (12)	0.0636 (3)	0.054 (3)
C20	−0.0772 (7)	−0.0811 (19)	0.0346 (5)	0.038 (4)
F1	−0.0440 (4)	−0.1641 (18)	0.0094 (4)	0.144 (5)
F2	−0.1049 (6)	−0.2130 (16)	0.0522 (3)	0.165 (6)
F3	−0.1319 (5)	−0.0160 (14)	−0.0016 (3)	0.118 (4)

Table 4. *Selected geometric parameters (Å, °) for* (II)

Mo—C1	1.93 (2)	C3—C4	1.40 (2)
Mo—C2	1.94 (2)	C4—C5	1.41 (2)
Mo—O3	2.220 (8)	C5—C6	1.48 (2)
Mo—N1	2.224 (9)	N1—C16	1.342 (14)
Mo—C4	2.225 (12)	N1—C18	1.350 (12)
Mo—C3	2.284 (12)	N2—C7	1.35 (2)
Mo—N2	2.301 (10)	N2—C17	1.380 (13)
Mo—C5	2.411 (13)	C17—C18	1.416 (14)
C1—O1	1.18 (2)	O3—C19	1.276 (12)
C2—O2	1.186 (15)	C19—O4	1.212 (13)

C1—Mo—C2	80.7 (5)	N1—Mo—C5	156.9 (4)
C1—Mo—O3	168.5 (5)	C4—Mo—C5	35.1 (4)
C2—Mo—O3	96.1 (4)	C3—Mo—C5	61.0 (4)
C1—Mo—N1	85.7 (5)	N2—Mo—C5	123.9 (4)
C2—Mo—N1	94.3 (4)	O1—C1—Mo	175 (1)
O3—Mo—N1	83.5 (3)	O2—C2—Mo	176 (1)
C1—Mo—C4	102.0 (5)	C4—C3—Mo	69.6 (7)
C2—Mo—C4	101.8 (5)	C3—C4—C5	116 (1)
O3—Mo—C4	89.5 (4)	C3—C4—Mo	74.2 (8)
N1—Mo—C4	163.1 (5)	C5—C4—Mo	79.7 (8)
C1—Mo—C3	68.4 (5)	C4—C5—C6	123 (1)
C2—Mo—C3	108.1 (4)	C4—C5—Mo	65.2 (7)
O3—Mo—C3	123.0 (4)	C6—C5—Mo	121 (1)
N1—Mo—C3	141.6 (4)	C16—N1—C18	118 (1)

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: *DIF*4 (Stoe & Cie, 1988*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93.

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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Ethynyltetrakis(trimethylphosphine)cobalt(I), $[Co(CCH)\{P(CH_3)_3\}_4]$

Graham Stringer, Nicholas J. Taylor and Todd B. Marder*

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

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Abstract

The title compound consists of a neutral $[Co(C_2H)(C_3H_9P)_4]$ 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: $[Co(CC^tBu)(HCCH^tBu)(MeCN)\{P(CH_3)_3\}_3]BPh_4$ (Habadie, Dartiguenave, Dartiguenave, Britten & Beauchamp, 1989), $[Co(CCCN)_2(\eta^5\text{-}C_5H_5)\{P(C_6H_5)_3\}]$ (Kergoat, Gomes de Lima, Jégat, Le Berre & Kubicki, 1990), $[Co\{CCSi(CH_3)_3\}\{(DO)(DOH)pn\}I]$, where (DO)(DOH)pn is 1,3-bis(diacetylmonooximeimino)propane (Giese, Zehnder, Neuberger & Trach, 1991), $[CoH(CCPh)_2\{P(CH_3)_3\}_3]$ (Klein *et al.*, 1991) and $[CoH(CCSiMe_3)\{P(CH_2CH_2PPh_2)_3\}]BPh_4$ (Bianchini, Peruzzini, Vacca & Zanobini, 1991). To date, however, no structures, either of a parent ethynyl complex or of any Co^I–