

C(50)	0.2855 (6)	0.3032 (4)	0.4963 (7)	0.052 (3)
O(1s)	-0.0286 (22)	0.5234 (19)	1.0370 (23)	0.184 (10)
C(1s)	-0.0389 (21)	0.4548 (16)	1.0297 (23)	0.241 (11)
C(2s)	-0.0500 (16)	0.3829 (11)	1.0445 (18)	0.228 (9)

Table 2. Selected geometric parameters (Å, °)

Au(1)—S(1)	2.324 (2)	Au(2)—P(2)	2.266 (2)
Au(2)—S(2)	2.296 (2)	S(2)—C(9)	1.797 (8)
S(1)—C(2)	1.773 (7)	P(1)—C(21)	1.808 (7)
P(1)—C(15)	1.816 (6)	P(2)—C(33)	1.845 (6)
P(1)—C(27)	1.803 (7)	P(2)—C(45)	1.822 (7)
P(2)—C(39)	1.802 (7)	O(1)—C(3)	1.363 (10)
O(1)—C(1)	1.427 (10)	O(2)—C(10)	1.341 (10)
O(2)—C(8)	1.410 (15)	C(2)—C(7)	1.385 (11)
C(2)—C(3)	1.430 (9)	C(4)—C(5)	1.397 (14)
C(3)—C(4)	1.375 (11)	C(6)—C(7)	1.413 (12)
C(5)—C(6)	1.361 (11)	C(9)—C(14)	1.394 (12)
C(9)—C(10)	1.392 (11)	C(11)—C(12)	1.333 (14)
C(10)—C(11)	1.408 (13)	C(13)—C(14)	1.415 (15)
C(12)—C(13)	1.324 (15)	O(1s)—C(1s)	1.233 (44)
Au(1)—P(1)	2.283 (2)	C(1s)—C(2s)	1.323 (35)
S(1)—Au(1)—P(1)	175.2 (1)	C(39)—P(2)—C(45)	104.7 (3)
Au(1)—S(1)—C(2)	105.0 (2)	C(8)—O(2)—C(10)	117.3 (8)
Au(1)—P(1)—C(15)	116.8 (2)	S(1)—C(2)—C(7)	123.2 (5)
C(15)—P(1)—C(21)	104.4 (3)	O(1)—C(3)—C(2)	117.0 (6)
C(15)—P(1)—C(27)	106.0 (3)	C(2)—C(3)—C(4)	120.2 (8)
Au(2)—P(2)—C(33)	113.9 (2)	C(4)—C(5)—C(6)	121.8 (8)
C(33)—P(2)—C(39)	104.2 (3)	C(2)—C(7)—C(6)	120.2 (7)
C(33)—P(2)—C(45)	108.2 (3)	S(2)—C(9)—C(14)	123.3 (6)
C(1)—O(1)—C(3)	119.7 (6)	O(2)—C(10)—C(9)	115.8 (7)
S(1)—C(2)—C(3)	117.8 (6)	C(9)—C(10)—C(11)	119.1 (8)
C(3)—C(2)—C(7)	119.0 (7)	C(11)—C(12)—C(13)	120.8 (10)
O(1)—C(3)—C(4)	122.8 (7)	C(9)—C(14)—C(13)	122.3 (9)
C(3)—C(4)—C(5)	119.4 (7)	P(1)—C(15)—C(20)	123.3 (5)
C(5)—C(6)—C(7)	119.5 (9)	P(1)—C(21)—C(22)	121.9 (6)
S(2)—C(9)—C(10)	120.2 (6)	P(1)—C(27)—C(28)	118.1 (5)
C(10)—C(9)—C(14)	116.3 (8)	P(2)—C(33)—C(34)	118.1 (5)
O(2)—C(10)—C(11)	125.1 (8)	P(2)—C(39)—C(40)	117.8 (5)
C(10)—C(11)—C(12)	122.4 (9)	P(2)—C(45)—C(46)	122.6 (5)
C(12)—C(13)—C(14)	118.9 (9)	C(1s)—O(1s)—O(1sa)	53.2 (26)
P(1)—C(15)—C(16)	118.6 (5)	O(1s)—C(1s)—C(2s)	169.4 (27)
S(2)—Au(2)—P(2)	176.2 (1)	P(1)—C(21)—C(26)	118.1 (5)
Au(2)—S(2)—C(9)	103.0 (2)	P(1)—C(27)—C(32)	122.9 (5)
Au(1)—P(1)—C(21)	107.4 (2)	P(2)—C(33)—C(38)	123.5 (6)
Au(1)—P(1)—C(27)	115.5 (2)	P(2)—C(39)—C(44)	121.7 (6)
C(21)—P(1)—C(27)	105.7 (3)	P(2)—C(45)—C(50)	118.9 (5)
Au(2)—P(2)—C(39)	113.7 (2)	C(1s)—O(1s)—C(1sa)	107.5 (28)
Au(2)—P(2)—C(45)	111.4 (2)		

The ether molecule is generated by an inversion center located at $0, \frac{1}{2}, 0$ such that the O atom was placed at 50% occupancy. Atoms in the ether molecule are the only non-H atoms to be modeled isotropically. Calculations were performed using *SHELXTL* (Sheldrick, 1978) on a Data General Eclipse 140 computer.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71576 (48 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1072]

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Acta Cryst. (1994). **C50**, 525–528

Dichloro(2,6-diacetylpyridine dioxime- κ^3N,N',N'')copper(II) 1.5-Hydrate

K. A. ABBOUD,* R. C. PALENIK AND G. J. PALENIK*

Department of Chemistry, University of Florida,
Gainesville, FL 32611, USA

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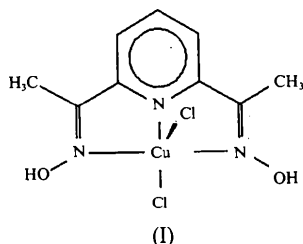
Abstract

The reaction of hydroxylamine with aquachloro-(2,6-diacetylpyridine disemicarbazone)copper(II) results in a displacement of the semicarbazide group and the formation of dichloro(2,6-diacetylpyridine dioxime- κ^3N,N',N'')copper(II) 1.5-hydrate $\{[\text{CuCl}_2(\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2)]_2 \cdot 3\text{H}_2\text{O}\}$. A triclinic dihydrate form has been reported previously. The Cu atom is in the center of a square pyramid consisting of a Cl and three N atoms in the base and an apical Cl. An analysis of the five-coordinate CuCl_2N_3 structures in the 1992 release of the Cambridge Crystallographic Database revealed a linear relationship between the displacement of the Cu atom from the basal plane and the apical Cu—Cl distance.

Comment

Dichloro(2,6-diacetylpyridine dioxime- κ^3N,N',N'')copper(II) dihydrate (I), $[\text{CuCl}_2(\text{dapdH}_2)] \cdot 2\text{H}_2\text{O}$, was reported by Nicholson, Petersen & McCormick (1982) to crystallize in a triclinic form with one molecule per asymmetric unit. Our form is found to be monoclinic with two molecules of $\text{CuCl}_2(\text{DAPDH}_2) \cdot 1.5\text{H}_2\text{O}$ per asymmetric unit (see Fig. 1). The analytical data for C, H and N are in agreement with 1.5 waters per Cu atom: found (calculated) C

30.29 (30.48), H 3.71 (3.98), N 11.89% (11.85%). There appear to be slight differences in the basal *versus* the apical Cu—Cl bond lengths in the two studies, which may be related to differences in the hydrogen-bonding patterns in the two forms. The remaining bond lengths and angles in both studies do not differ significantly.



The average basal Cu—Cl bonds in our study are significantly shorter than the average apical Cu—Cl bonds, 2.237 (2) *versus* 2.428 (2) Å. This appears to be a common effect in five-coordinate Cu—Cl complexes. We found 16 examples of five-coordinate square-pyramidal CuCl_2 complexes with three N

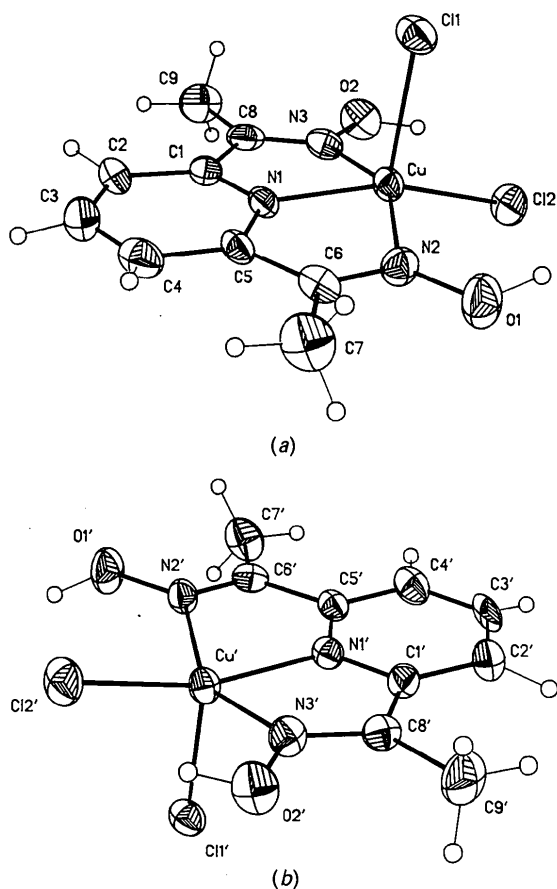


Fig. 1. A view of the two molecules, (a) molecule *A* and (b) molecule *B*, in the asymmetric unit, illustrating the atomic numbering and the displacements ellipsoids at 50% probability.

atoms completing the coordination sphere in the 1992 release of the Cambridge Structural Database, henceforth CSD (Allen, Kennard & Taylor, 1983). A scatter plot of the deviation of the Cu atom from the plane of the Cl and three N atoms is shown in Fig. 2. There is an approximately linear relationship; the correlation coefficient (r^2) is 0.80, but if the points for JEKAL2 and GAYMUO are excluded, the value of r^2 is 0.95. Orpen, Brammer, Allen, Kennard, Watson & Taylor (1989), in a compilation from the September 1985 CSD, divided the Cu—Cl distances in five-coordinate complexes into two groups, one below and one above 2.4 Å. Our results suggest that averaging Cu—Cl bond lengths in square-pyramidal complexes is probably not justified.

Gawron, Palenik & Palenik (1986) reported a linear relationship between the axial Cu—O distance and the displacement of the Cu atom from an N_2O_2 donor-set plane. These results suggest that in five-coordinate Cu complexes the axial Cu—donor distance is dependent on the deviations of the Cu atom from the plane of the other four donor atoms. Further studies are in progress to extend this generalization to other five-coordinate Cu complexes.

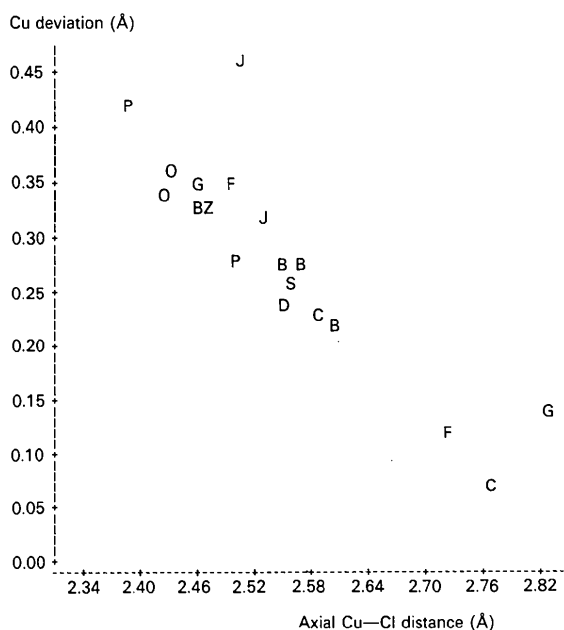


Fig. 2. A scatter plot of the deviation of the Cu atom from the CuClN_3 plane *versus* the axial Cu—Cl distance. The letter corresponds to the first letter of the CSD REFCODE. The points *J* at 2.503 and *G* at 2.831 Å were omitted from the analysis.

Experimental

Crystal data

$[\text{CuCl}_2(\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2)]_2 \cdot 3\text{H}_2\text{O}$
 $M_r = 709.34$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic
 $I2/a$
 $a = 27.048 (6) \text{ \AA}$
 $b = 10.298 (2) \text{ \AA}$
 $c = 20.300 (3) \text{ \AA}$
 $\beta = 102.62 (2)^\circ$
 $V = 5518 (2) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.708 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 10-11^\circ$
 $\mu = 1.98 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Needles
 $0.36 \times 0.22 \times 0.20 \text{ mm}$
 Green

Data collection

Siemens P3m/V diffractometer
 $R_{\text{int}} = 0.0167$
 $\theta_{\text{max}} = 25^\circ$
 ω scans
 $h = 0 \rightarrow 32$
 Absorption correction: empirical
 $l = -24 \rightarrow 24$
 $T_{\text{min}} = 0.736$, $T_{\text{max}} = 0.927$
 4 standard reflections monitored every 96 reflections
 5282 measured reflections
 4870 independent reflections
 2934 observed reflections
 $[F > 4\sigma(F)]$
 intensity variation: 1%

Refinement

Refinement on F^2
 $R = 0.0526$
 $wR = 0.0544$
 $S = 1.45$
 2934 reflections
 362 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F) + 0.0004F]^2$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$

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}
Cu	0.06039 (3)	0.26099 (9)	0.12358 (4)	0.0357 (3)
Cl1	-0.01102 (8)	0.1153 (2)	0.11724 (11)	0.0516 (8)
Cl2	0.02243 (8)	0.4539 (2)	0.10206 (11)	0.0522 (8)
O1	0.0649 (3)	0.3079 (7)	0.2780 (3)	0.071 (3)
O2	0.0493 (2)	0.3137 (6)	-0.0270 (3)	0.061 (3)
N1	0.1141 (2)	0.1329 (6)	0.1352 (3)	0.033 (2)
N2	0.0833 (3)	0.2474 (7)	0.2279 (3)	0.044 (3)
N3	0.0732 (2)	0.2438 (7)	0.0283 (3)	0.042 (3)
C1	0.1281 (3)	0.0883 (8)	0.0797 (4)	0.040 (3)
C2	0.1645 (3)	-0.0097 (9)	0.0843 (6)	0.055 (3)
C3	0.1860 (4)	-0.0540 (10)	0.1484 (6)	0.066 (4)
C4	0.1729 (4)	-0.0034 (10)	0.2049 (6)	0.057 (4)
C5	0.1356 (3)	0.0917 (8)	0.1970 (4)	0.037 (3)
C6	0.1162 (3)	0.1585 (8)	0.2501 (4)	0.045 (3)
C7	0.1338 (4)	0.1212 (11)	0.3235 (4)	0.071 (5)
C8	0.1031 (3)	0.1530 (9)	0.0179 (4)	0.046 (3)
C9	0.1110 (4)	0.1192 (10)	-0.0501 (4)	0.065 (4)
Cu'	0.18740 (3)	-0.50133 (9)	0.13818 (4)	0.0342 (3)
Cl1'	0.25716 (8)	-0.3511 (2)	0.14165 (10)	0.0458 (7)
Cl2'	0.22601 (8)	-0.6946 (2)	0.15408 (11)	0.0530 (8)
O1'	0.1794 (2)	-0.5513 (6)	-0.0155 (3)	0.059 (3)
O2'	0.1997 (2)	-0.5640 (6)	0.2893 (3)	0.054 (2)
N1'	0.1332 (2)	-0.3743 (6)	0.1294 (3)	0.033 (2)
N2'	0.1620 (2)	-0.4898 (6)	0.0347 (3)	0.038 (2)
N3'	0.1750 (2)	-0.4933 (7)	0.2341 (3)	0.040 (2)
Cl1'	0.1181 (3)	-0.3361 (7)	0.1852 (4)	0.039 (3)
C2'	0.0807 (3)	-0.2441 (9)	0.1804 (5)	0.051 (3)
C3'	0.0597 (3)	-0.1965 (9)	0.1176 (6)	0.053 (3)
C4'	0.0743 (3)	-0.2387 (9)	0.0598 (5)	0.048 (3)
C5'	0.1119 (3)	-0.3306 (7)	0.0676 (4)	0.034 (3)
C6'	0.1306 (3)	-0.3960 (8)	0.0136 (3)	0.038 (3)

C7'	0.1160 (3)	-0.3546 (10)	-0.0584 (4)	0.061 (4)
C8'	0.1443 (3)	-0.4067 (8)	0.2465 (4)	0.037 (3)
C9'	0.1345 (4)	-0.3810 (10)	0.3152 (4)	0.064 (4)
O11	-0.0116 (3)	0.4696 (7)	0.2433 (3)	0.079 (3)
O12	1/4	-0.2108 (10)	0	0.122 (8)
O13	1/4	-0.7390 (10)	0	0.126 (4)
O14	0.2682 (6)	-0.970 (2)	0.0482 (6)	0.292 (13)

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

Cu—Cl1	2.427 (2)	Cl1'—Cu'	2.429 (2)
Cu—Cl2	2.235 (2)	Cl2'—Cu'	2.238 (2)
Cu—N1	1.939 (6)	N1'—Cu'	1.944 (6)
Cu—N2	2.077 (6)	N2'—Cu'	2.065 (6)
Cu—N3	2.045 (7)	N3'—Cu'	2.047 (6)
Cl1—Cu—Cl2	102.28 (8)	Cl1'—Cu'—Cl2'	103.13 (8)
Cl1—Cu—N1	98.8 (2)	Cl1'—Cu'—N1'	98.0 (2)
Cl1—Cu—N2	94.0 (2)	Cl1'—Cu'—N2'	94.4 (2)
Cl1—Cu—N3	101.2 (2)	Cl1'—Cu'—N3'	103.5 (2)
Cl2—Cu—N1	158.2 (2)	Cl2'—Cu'—N1'	158.5 (2)
Cl2—Cu—N2	106.3 (2)	Cl2'—Cu'—N2'	103.8 (2)
Cl2—Cu—N3	93.3 (2)	Cl2'—Cu'—N3'	93.8 (2)
N1—Cu—N2	77.4 (3)	N1'—Cu'—N2'	78.0 (3)
N1—Cu—N3	77.2 (3)	N1'—Cu'—N3'	77.5 (3)
N2—Cu—N3	152.1 (3)	N2'—Cu'—N3'	151.3 (3)

The ω -scan width was symmetrical over 1.2° about the $K\alpha_{1,2}$ maximum and the background was offset 1.0 and -1.0° in ω from the $K\alpha_{1,2}$ maximum. The scan speed was a variable $3-6^\circ \text{ min}^{-1}$ (depending upon intensity). The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV). The methyl H atoms were calculated in idealized positions and their displacement parameters fixed, while the aromatic H atoms were refined freely. Hydroxy H atoms H01, H01' and H02' and the water H atoms were located from a difference Fourier map and refined riding on their respective O atoms. H02 was placed in an idealized position and its displacement parameter fixed. O11 is located about a twofold axis and thus only one H atom was found. The O13 water molecule is disordered about a twofold axis, with H13a on the axis and H13b disordered. Atomic scattering factors were from Cromer & Mann (1968) for the non-H atoms, with anomalous-dispersion corrections from Cromer & Liberman (1970), while those of the H atoms were from Stewart, Davidson & Simpson (1965). Cell refinement, data collection and reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Software used to prepare material for publication: *FUER* (S. B. Larson, personal communication).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71634 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1070]

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Acta Cryst. (1994). **C50**, 528–530

**[AuCo₃Ru(C₈H₁₁P)(C₁₈H₁₅P)(CO)₁₁]-
½CH₂Cl₂**

HEIKKI J. KAKKONEN, MARKKU AHLGRÈN AND
TAPANI A. PAKKANEN

*University of Joensuu, Department of Chemistry,
PO Box 111, SF-80101 Joensuu, Finland*

JOUNI PURSIAINEN

*University of Oulu, Department of Chemistry,
Linnanmaa, SF-90570 Oulu, Finland*

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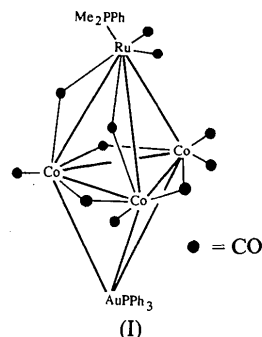
Abstract

HRuCo₃(CO)₁₁PMe₂Ph reacts with AuPPh₃Cl giving a substitution product, penta-μ-carbonyl-1:2κ²C;-1:3κ²C;2:3κ²C;2:4κ²C;3:4κ²C-hexacarbonyl-1κ²C,-2κC,3κC,4κ²C-dimethylphenylphosphine-1κP-triphenylphosphine-5κP-tricobaltgoldruthenium(3 Au—Co)(3 Co—Co)(3 Co—Ru), where the [AuPPh₃]⁺ moiety shields the basal Co₃ face. The PMe₂Ph ligand changes coordination from an axial site of the basal Co₃ plane to the apical Ru atom.

Comment

HRuCo₃(CO)₁₂ (Hidai, Orisaku, Ue, Koyasu, Kodama & Uchida, 1983) reacts with PMe₂Ph forming a phosphine derivative HRuCo₃(CO)₁₁PMe₂Ph (Pursiainen & Pakkanen, 1989), where the phosphine ligand is axially coordinated to a basal Co atom (Pursiainen, Ahlgrèn, Pakkanen & Valkonen, 1990). For HRuCo₃(CO)₁₂, mainly derivatives with axial coordination of phosphine ligands are found. A bridging hydride ligand (μ-H) is bound to the basal Co₃ plane. In the present work we have studied the replacement of the hydride ligand with [AuPPh₃]⁺.

The structure determination of the title compound, (I) by X-ray diffraction, reveals that the crystal is composed of Ph₃PAuRuCo₃(CO)₁₁PMe₂Ph and CH₂Cl₂ molecules in a 2:1 ratio. The [AuPPh₃]⁺



moiety has replaced the hydride ligand from the parent cluster and capped the basal Co₃ face. Opening of the Co—Co—C(axial) bond angles by the triphenylphosphinegold ligand can be seen from the bond-angle data in Table 2. Co(1)—Co(2)—C(7), Co(2)—Co(3)—C(9) and Co(3)—Co(1)—C(5) angles are 132.6 (4), 138.6 (4) and 122.1 (4)°, respectively. In HRuCo₃(CO)₁₁PMe₂Ph the average value of the corresponding angles to the axial carbonyls is 116.8°, and in HRuCo₃(CO)₁₂ it is 118° (Pursiainen, Hirva & Pakkanen, 1991). Replacement of the hydride is also evidenced by the ¹H NMR spectrum, which shows no indication of the presence of the hydride ligand. Compared to the starting material, the coordination site of PMe₂Ph is different. It is obvious that the AuPPh₃ moiety shields the basal coordination sites and therefore PMe₂Ph coordinates to the apical Ru atom. Carbonyl arrangement has also changed with two of the terminal carbonyls now semibridging Ru—Co edges [Ru(1)—C(6) 2.458 (12), Co(2)—C(6) 1.786 (13), Ru(1)—C(8) 2.344 (11) and Co(3)—C(8)

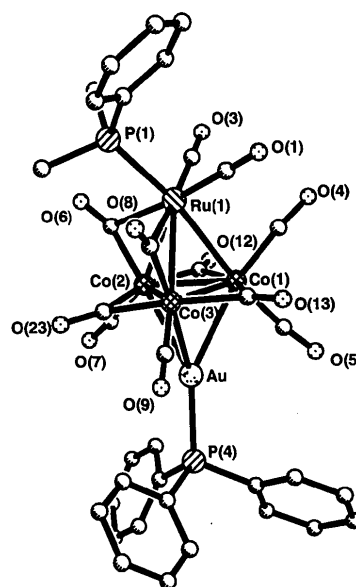


Fig. 1. View of [AuRuCo₃(C₈H₁₁P)(C₁₈H₁₅P)(CO)₁₁].