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(I)

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

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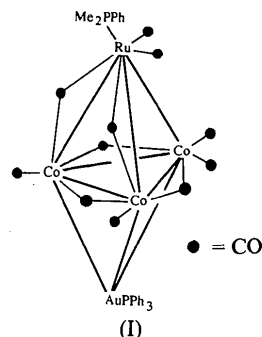(*Received* 19 *February* 1993; *accepted* 15 *September* 1993)

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)
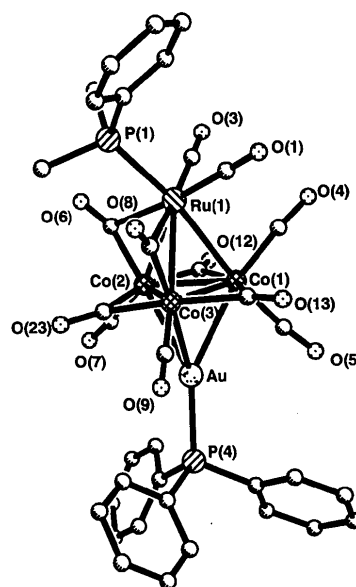

Fig. 1. View of [AuRuCo₃(C₈H₁₁P)(C₁₈H₁₅P)(CO)₁₁].

1.783 (11) Å]. In $HRuCo_3(CO)_{11}PMe_2Ph$ all the bridging carbonyls are located in the basal Co_3 plane.

Experimental

Synthesis was carried out under an N_2 atmosphere by refluxing (2 h) the starting material (0.24 mmol) in tetrahydrofuran with solid [AuPPh₃Cl] (0.24 mmol) in the presence of TlPF₆. The reaction led to several compounds, which were separable with silica gel. Elution with a hexane/dichloromethane (5:1) mixture gave a red fraction of unreacted starting material (0.13 mmol), followed by a red fraction of $[AuCo_3Ru(C_8H_{11}P)(C_{18}H_{15}P)(CO)_{11}].0.5CH_2Cl_2$ (0.10 mmol). The compound was crystallized from CH_2Cl_2/n-hexane (1:1).

Crystal data

$[AuCo_3Ru(C_8H_{11}P)(C_{18}H_{15}P)-(CO)_{11}].0.5CH_2Cl_2$
$M_r = 1225.8$
Monoclinic
$P2_1/c$
$a = 20.182$ (6) Å
$b = 9.062$ (3) Å
$c = 24.028$ (6) Å
$\beta = 90.79$ (2)°
$V = 4394$ (2) Å³
$Z = 4$

$D_x = 1.853$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5-12.5°$
$\mu = 4.941$ mm^{-1}
$T = 294$ K
Prism
$0.45 \times 0.40 \times 0.30$ mm
Brown

Data collection

Nicolet $R3m/V$ diffractometer
ω scans
Absorption correction: none
11 682 measured reflections
10 089 independent reflections
5179 observed reflections [$I \geq 3\sigma(I)$]

$R_{int} = 0.041$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 11$
$l = -31 \rightarrow 31$
2 standard reflections monitored every 98 reflections intensity variation: ±4%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.058$
$S = 1.51$
5179 reflections
472 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0005F^2]$

$(\Delta/\sigma)_{max} = 0.271$
$\Delta\rho_{max} = 1.27$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

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

	x	y	z	U_{eq}
Au	0.1996 (1)	0.2360 (1)	0.1695 (1)	0.054 (1)
Ru(1)	0.3417 (1)	0.3791 (1)	0.3120 (1)	0.043 (1)
Co(2)	0.2910 (1)	0.4285 (2)	0.2084 (1)	0.045 (1)
Co(3)	0.2156 (1)	0.3228 (2)	0.2785 (1)	0.044 (1)
Co(1)	0.3035 (1)	0.1629 (2)	0.2372 (1)	0.046 (1)
P(1)	0.3606 (2)	0.5872 (3)	0.3685 (1)	0.053 (1)
P(4)	0.1206 (2)	0.1778 (3)	0.1047 (1)	0.050 (1)
O(3)	0.4877 (5)	0.3600 (12)	0.2862 (4)	0.102 (5)
O(1)	0.3519 (4)	0.1650 (11)	0.4074 (4)	0.079 (4)
O(6)	0.3782 (5)	0.6679 (11)	0.2358 (3)	0.088 (4)
O(7)	0.2709 (5)	0.5752 (11)	0.1017 (4)	0.094 (4)
O(8)	0.2149 (4)	0.4385 (10)	0.3890 (3)	0.072 (3)
O(9)	0.0760 (5)	0.2851 (12)	0.2979 (4)	0.101 (4)
O(5)	0.2753 (5)	−0.1031 (11)	0.1722 (4)	0.092 (4)
O(4)	0.4149 (5)	0.0114 (10)	0.2887 (4)	0.083 (4)
O(23)	0.1790 (5)	0.6172 (11)	0.2384 (4)	0.89 (4)
O(12)	0.3993 (4)	0.2692 (10)	0.1550 (4)	0.082 (4)
O(13)	0.2208 (4)	0.0192 (10)	0.3192 (3)	0.076 (4)
C(3)	0.4335 (6)	0.3669 (14)	0.2950 (5)	0.062 (4)
C(1)	0.3481 (5)	0.2446 (13)	0.3715 (5)	0.055 (4)
C(6)	0.3480 (6)	0.5607 (15)	0.2363 (5)	0.064 (5)
C(7)	0.2767 (6)	0.5151 (15)	0.1423 (5)	0.065 (5)
C(8)	0.2335 (5)	0.4008 (12)	0.3452 (5)	0.052 (4)
C(9)	0.1313 (6)	0.2995 (13)	0.2880 (5)	0.057 (4)
C(5)	0.2833 (6)	0.0019 (15)	0.1948 (5)	0.062 (5)
C(4)	0.3719 (6)	0.0756 (13)	0.2699 (5)	0.060 (4)
C(23)	0.2105 (6)	0.5109 (14)	0.2407 (4)	0.057 (4)
C(12)	0.3548 (6)	0.2858 (13)	0.1837 (4)	0.054 (4)
C(13)	0.2370 (6)	0.1170 (13)	0.2917 (5)	0.052 (4)
C(102)	0.3068 (3)	0.6028 (9)	0.4763 (3)	0.071 (5)
C(103)	0.3059	0.5663	0.5327	0.092 (7)
C(104)	0.3557	0.4775	0.5556	0.105 (8)
C(105)	0.41/2	0.4251	0.5220	0.092 (7)
C(106)	0.4074	0.4616	0.4656	0.071 (5)
C(101)	0.3575	0.5504	0.4428	0.055 (4)
C(112)	0.4428 (6)	0.6707 (15)	0.3607 (5)	0.075 (5)
C(111)	0.3034 (7)	0.7442 (13)	0.3538 (5)	0.076 (5)
C(412)	0.1198 (4)	−0.0623 (11)	0.0310 (3)	0.078 (6)
C(413)	0.1175	−0.2127	0.0186	0.125 (9)
C(414)	0.1125	−0.3159	0.0614	0.130 (10)
C(415)	0.1097	−0.2687	0.1166	0.132 (10)
C(416)	0.1119	−0.1184	0.1290	0.098 (7)
C(411)	0.1170	−0.0152	0.0862	0.064 (5)
C(422)	0.0701 (3)	0.3061 (10)	0.0067 (3)	0.076 (5)
C(423)	0.2/3	0.3781	−0.0442	0.096 (7)
C(424)	0.1393	0.4184	−0.0627	0.102 (7)
C(425)	0.1954	0.3867	−0.0303	0.098 (7)
C(426)	0.1888	0.3147	0.0206	0.074 (5)
C(421)	0.1262	0.2744	0.0392	0.052 (4)
C(432)	0.0312 (5)	0.3516 (9)	0.1611 (4)	0.083 (6)
C(433)	−0.0305	0.3885	0.1826	0.113 (8)
C(434)	−0.0848	0.2961	0.1732	0.123 (9)
C(435)	−0.0774	0.1668	0.1424	0.129 (10)
C(436)	−0.0157	0.1299	0.1210	0.096 (7)
C(431)	0.0386	0.2223	0.1303	0.057 (4)
Cl(1)†	0.4532 (11)	0.6738 (26)	0.1074 (8)	0.111 (6)
Cl(2)†	0.4020 (11)	0.5496 (25)	0.0052 (9)	0.123 (7)
Cl(3)†	0.4740 (12)	0.5987 (30)	0.1020 (10)	0.106 (7)
Cl(4)†	0.4024 (13)	0.4796 (32)	0.0283 (11)	0.122 (8)
Cl(5)†	0.4946 (33)	0.5171 (75)	0.0227 (20)	0.152 (21)
Cl(10)†	0.4466 (17)	0.6413 (40)	0.0487 (14)	0.109 (10)

† Site occupation factors are 0.25, 0.25, 0.20, 0.20, 0.10, 0.50 for Cl(1), Cl(2), Cl(3), Cl(4), Cl(5) and Cl(10), respectively.

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

Au—Co(2)	2.697 (2)	Au—Co(3)	2.751 (2)
Au—Co(1)	2.718 (2)	Au—P(4)	2.275 (3)
Ru(1)—Co(2)	2.716 (2)	Ru(1)—Co(3)	2.708 (2)
Ru(1)—Co(1)	2.762 (2)	Ru(1)—P(1)	2.351 (3)
Ru(1)—C(3)	1.907 (12)	Ru(1)—C(1)	1.881 (12)
Ru(1)—C(6)	2.458 (12)	Ru(1)—C(8)	2.344 (11)
Co(2)—Co(3)	2.478 (2)	Co(2)—Co(1)	2.516 (2)
Co(2)—C(6)	1.786 (13)	Co(2)—C(7)	1.792 (12)
Co(2)—C(23)	1.957 (12)	Co(2)—C(12)	1.925 (11)
Co(3)—Co(1)	2.506 (2)	Co(3)—C(8)	1.783 (11)
Co(3)—C(9)	1.732 (11)	Co(3)—C(23)	1.934 (12)
Co(3)—C(13)	1.939 (12)	Co(1)—C(5)	1.822 (13)
Co(1)—C(4)	1.766 (12)	Co(1)—C(12)	2.001 (11)
Co(1)—C(13)	1.933 (11)		
Co(2)—Au—Co(3)	54.1 (1)	Ru(1)—Co(3)—C(23)	91.0 (4)
Co(3)—Au—Co(1)	54.5 (1)	Co(1)—Co(3)—C(23)	110.9 (3)
Co(3)—Au—P(4)	142.2 (1)	C(9)—Co(3)—C(23)	97.1 (5)

Co(2)—Ru(1)—Co(3)	54.4 (1)	Ru(1)—Co(3)—C(13)	85.8 (3)
Co(3)—Ru(1)—Co(1)	54.5 (1)	Co(1)—Co(3)—C(13)	49.6 (3)
Co(3)—Ru(1)—P(1)	117.8 (1)	C(9)—Co(3)—C(13)	94.5 (5)
Co(2)—Ru(1)—C(3)	99.7 (4)	Au—Co(1)—Ru(1)	115.0 (1)
Co(1)—Ru(1)—C(3)	94.8 (4)	Ru(1)—Co(1)—Co(2)	61.7 (1)
Co(2)—Ru(1)—C(1)	145.5 (4)	Ru(1)—Co(1)—Co(3)	61.6 (1)
Co(1)—Ru(1)—C(1)	92.9 (4)	Au—Co(1)—C(5)	72.3 (4)
C(3)—Ru(1)—C(1)	94.0 (5)	Co(2)—Co(1)—C(5)	126.3 (4)
Co(3)—Ru(1)—C(6)	87.9 (3)	Au—Co(1)—C(4)	165.3 (4)
P(1)—Ru(1)—C(6)	83.2 (3)	Co(2)—Co(1)—C(4)	128.7 (4)
C(1)—Ru(1)—C(6)	172.9 (4)	C(5)—Co(1)—C(4)	93.3 (5)
Co(3)—Ru(1)—C(8)	40.5 (3)	Ru(1)—Co(1)—C(12)	83.1 (3)
P(1)—Ru(1)—C(8)	83.2 (3)	Co(3)—Co(1)—C(12)	108.0 (3)
C(1)—Ru(1)—C(8)	81.4 (4)	C(4)—Co(1)—C(12)	97.2 (5)
Au—Co(2)—Ru(1)	117.3 (1)	Ru(1)—Co(1)—C(13)	84.4 (3)
Ru(1)—Co(2)—Co(3)	62.7 (1)	Co(3)—Co(1)—C(13)	49.8 (3)
Ru(1)—Co(2)—Co(1)	63.6 (1)	C(4)—Co(1)—C(13)	98.5 (5)
Au—Co(2)—C(6)	176.9 (4)	Ru(1)—C(6)—Co(2)	77.8 (5)
Co(3)—Co(2)—C(6)	113.8 (4)	Co(2)—C(23)—Co(3)	79.1 (5)
Au—Co(2)—C(7)	82.8 (4)	Co(3)—C(13)—Co(1)	80.7 (4)
Co(2)—Au—Co(1)	55.4 (1)	Co(1)—Co(2)—C(7)	132.6 (4)
Co(2)—Au—P(4)	149.0 (1)	Au—Co(2)—C(23)	79.5 (4)
Co(1)—Au—P(4)	151.7 (1)	Co(3)—Co(2)—C(23)	50.0 (4)
Co(2)—Ru(1)—Co(1)	54.7 (1)	C(6)—Co(2)—C(23)	97.4 (5)
Co(2)—Ru(1)—P(1)	116.9 (1)	Au—Co(2)—C(12)	85.2 (3)
Co(1)—Ru(1)—P(1)	170.5 (1)	Co(3)—Co(2)—C(12)	111.7 (3)
Co(3)—Ru(1)—C(3)	146.9 (4)	C(6)—Co(2)—C(12)	97.8 (5)
P(1)—Ru(1)—C(3)	91.1 (4)	C(23)—Co(2)—C(12)	160.2 (5)
Co(3)—Ru(1)—C(1)	99.1 (3)	Au—Co(3)—Co(2)	61.8 (1)
P(1)—Ru(1)—C(1)	94.1 (4)	Au—Co(3)—Co(1)	62.1 (1)
Co(2)—Ru(1)—C(6)	40.0 (3)	Co(2)—Co(3)—Co(1)	60.6 (1)
Co(1)—Ru(1)—C(6)	90.6 (3)	Ru(1)—Co(3)—C(8)	58.7 (3)
C(3)—Ru(1)—C(6)	79.6 (5)	Co(1)—Co(3)—C(8)	116.7 (3)
Co(2)—Ru(1)—C(8)	87.5 (3)	Ru(1)—Co(3)—C(9)	154.8 (4)
Co(1)—Ru(1)—C(8)	91.6 (3)	Co(1)—Co(3)—C(9)	133.1 (4)
C(3)—Ru(1)—C(8)	172.3 (4)	Au—Co(3)—C(23)	78.4 (3)
C(6)—Ru(1)—C(8)	104.7 (4)	Co(2)—Co(3)—C(23)	50.9 (3)
Au—Co(2)—Co(3)	64.1 (1)	C(8)—Co(3)—C(23)	94.7 (5)
Au—Co(2)—Co(1)	62.7 (1)	Au—Co(3)—C(13)	84.5 (3)
Co(3)—Co(2)—Co(1)	60.2 (1)	Co(2)—Co(3)—C(13)	110.2 (3)
Ru(1)—Co(2)—C(6)	62.2 (4)	C(8)—Co(3)—C(13)	101.1 (5)
Co(1)—Co(2)—C(6)	118.5 (4)	C(23)—Co(3)—C(13)	159.1 (5)
Ru(1)—Co(2)—C(7)	159.9 (4)	Au—Co(1)—Co(2)	61.9 (1)
Co(3)—Co(2)—C(7)	132.8 (4)	Au—Co(1)—Co(3)	63.4 (1)
C(6)—Co(2)—C(7)	97.7 (6)	Co(2)—Co(1)—Co(3)	59.1 (1)
Ru(1)—Co(2)—C(23)	90.2 (3)	Ru(1)—Co(1)—C(5)	171.9 (4)
Co(1)—Co(2)—C(23)	109.7 (4)	Co(3)—Co(1)—C(5)	122.1 (4)
C(7)—Co(2)—C(23)	93.4 (5)	Ru(1)—Co(1)—C(4)	79.5 (4)
Ru(1)—Co(2)—C(12)	85.8 (3)	Co(3)—Co(1)—C(4)	129.5 (4)
Co(1)—Co(2)—C(12)	51.5 (3)	Au—Co(1)—C(12)	83.2 (3)
C(7)—Co(2)—C(12)	97.0 (5)	Co(2)—Co(1)—C(12)	48.8 (3)
Au—Co(3)—Ru(1)	115.7 (1)	C(5)—Co(1)—C(12)	101.6 (5)
Ru(1)—Co(3)—Co(2)	63.0 (1)	Au—Co(1)—C(13)	85.5 (3)
Ru(1)—Co(3)—Co(1)	63.8 (1)	Co(2)—Co(1)—C(13)	108.9 (4)
Au—Co(3)—C(8)	171.4 (4)	C(5)—Co(1)—C(13)	93.2 (5)
Co(2)—Co(3)—C(8)	109.8 (4)	C(12)—Co(1)—C(13)	157.7 (5)
Au—Co(3)—C(9)	89.3 (4)	Ru(1)—C(8)—Co(3)	80.8 (4)
Co(2)—Co(3)—C(9)	138.6 (4)	Co(2)—C(12)—Co(1)	79.7 (4)
C(8)—Co(3)—C(9)	96.8 (5)		

All crystallographic calculations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1987). The structure was determined by direct methods and subsequent ΔS calculations. Metal, P and O atoms were refined anisotropically as were C atoms in the methyl groups, C(111) and C(112), and in the carbonyl groups. Phenyl rings were refined as rigid groups with anisotropic displacement parameters. H atoms were placed in calculated positions (C—H = 0.96 Å, U_{iso} = 0.09 Å^2).

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A New Phase of Bis[2-(Diphenylphosphino-κP)phenylazanido-κN](ethanolato)(oxo)-rhenium(V)

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Abstract

The title compound, $[Re(C_{18}H_{15}NP)_2(C_2H_5O)O]$, was synthesized by the oxidation–substitution reaction of $[Re^{III}(PNH)_2(PNH_2)]Cl$, where PNH_2 is 2-(diphenylphosphino)phenylamine, with NEt_3 in EtOH. The X-ray diffraction study of this new triclinic phase, designated β, confirms the molecular structural details for the monoclinic α isomer, which crystallized in space group $P2_1/c$ with $a = 12.056$ (3), $b = 26.303$ (6), $c = 11.005$ (3) Å, $\beta = 102.32$ (2)° [Refosco, Tisato, Bandoli, Bolzati, Dolmella, Moresco & Nicolini (1993). *J. Chem. Soc. Dalton Trans.* pp. 605–618].

Comment

The structure contains discrete monomeric neutral units (I), with the coordination geometry around the Re atom being highly distorted octahedral. The fitted