Synthesis of ferrocenylacetylide derivatives of gold-ruthenium and gold-osmium clusters. Crystal structures of $M_3(AuPPh_3)(C{\equiv}CFc)(CO)_9$ (M = Ru or Os; Fc is ferrocenyl)

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The synthesis and crystal structures of the clusters $M_3(AuPPh_3)(C{\equiv}CFc)(CO)_9$ (M = Ru, **3a**; or M = Os, **3b**) are described. Compound **3a** was synthesized by deprotonation of $Ru_3H(C{\equiv}CFc)(CO)_9$ under the action of KOH/EtOH followed by treatment of the anionic complex $[Ru_3(C{\equiv}CFc)(CO)_9]^-$ with chloro(triphenylphosphine)gold. Compound **3b** was prepared by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $FcC{\equiv}CAuPPh_3$, which was synthesized by the reaction of $FcC{\equiv}CNa$ with $ClAuPPh_3$. The pentanuclear cluster $Ru_4(AuPPh_3)(C{\equiv}CFc)(CO)_{12}$ (**4a**), which was prepared by the reaction of **3a** with $Ru_3(CO)_{12}$, was characterized by spectral methods.

Key words: gold-ruthenium clusters; gold-osmium clusters; acetylide derivatives of gold, ruthenium, and osmium; ferrocenylacetylene; X-ray diffraction analysis.

Recently, it has been demonstrated[1] that the reaction of $Ru_3H(C{\equiv}CFc)(CO)_9$ (**1a**) with $Ru_3(CO)_{12}$ in refluxing hexane affords a tetraruthenium cluster of a new type, *viz.*, $Ru_4H(C_2Fc)(CO)_{12}$ (**2a**). Analogously, the reaction of $Os_3H(C{\equiv}CFc)(CO)_9$ (**1b**) with ruthenium carbonyl yields the heteronuclear cluster $RuOs_3H(C_2Fc)(CO)_{12}$ (**2b**). Green clusters **2a** and **2b** are unstable both in the solid state and in solutions. These clusters slowly decompose to form the starting trinuclear acetylide complexes and ruthenium carbonyl. Because of this, attempts to prepare single crystals of cluster **2a** suitable for X-ray diffraction study from a hexane solution led to mixed crystals containing molecules **1a** and **2a** in a ratio of 1 : 1.

According to the data of X-ray diffraction analysis,[1a] the acetylide ligand in cluster **2a** is coordinated to the "butterfly" Ru_4 core in a complex mode. Thus, the α-carbon atom is coordinated to three ruthenium atoms of one of the "butterfly wings" and the β-carbon atom is bound to the wing-tip ruthenium atom of the second Ru_3 wing. In addition to these four Ru—C bonds (2.07—2.18 Å), molecule **2a** has two contacts between the ruthenium atoms and the above-mentioned carbon atoms ($Ru{\cdots}C_\alpha$ is 2.58(1) Å and $Ru{\cdots}C_\beta$ is 2.76(1) Å).

Previously, clusters of type **2a** have not been isolated in reactions of alkynes with metal carbonyls of the iron subgroup.[2,3] Hence, we suggested that the formation (stability) of clusters **2a** and **2b** is determined by the presence of the ferrocenyl group in the acetylide ligand. To verify this suggestion and to obtain new X-ray diffraction data on the mode of coordination of the acetylide ligand μ_4-C_2Fc, it was necessary to prepare complexes related to clusters **2a** and **2b**. Since it is known[4] that the H ligand is isolobal to $AuPPh_3$, goldphosphine analogs of hydrides **2a** and **2b** can serve as such complexes. This work was aimed at synthesizing these complexes.

Results and Discussion

Goldphosphine derivatives of Ru_3 and Os_3 clusters with the ferrocenylacetylide ligand, *viz.*, the complexes $M_3(AuPPh_3)(C{\equiv}CFc)(CO)_9$ (M = Ru, **3a**; M = Os, **3b**), were synthesized from complexes **1a** and **1b** using different procedures (Scheme 1).

Then complexes **3a** and **3b** were introduced into the reactions with $Ru_3(CO)_{12}$ to prepare complexes $Ru_4(AuPPh_3)(C_2Fc)(CO)_{12}$ (**4a**) and $RuOs_3(AuPPh_3)(C_2Fc)(CO)_{12}$ (**4b**), respectively (Scheme 2).

Deprotonation of complex **1a** dissolved in THF was carried out under the action of an ethanolic solution of KOH analogously to a procedure[5] used for deprotonation of the complex $Ru_3H(C{\equiv}CBu^t)(CO)_9$ (**5**). The addition of $(Ph_3P)_2NBr$ to a solution of the anionic complex afforded the $[(PPh_3)_2N][Ru_3(C{\equiv}CFc)(CO)_9]$ salt (**3c**) in quantitative yield. Treatment of this salt with $ClAuPPh_3$ in the presence of $AgBF_4$ gave rise to red-brown cluster **3a** in 56% yield.

Red cluster **3b** was synthesized in low yield by the reaction of $Os_3(CO)_{10}(NCMe)_2$ with alkyne $FcC{\equiv}CAuPPh_3$. The latter was prepared by the reaction of $FcC{\equiv}CNa$ with $ClAuPPh_3$.

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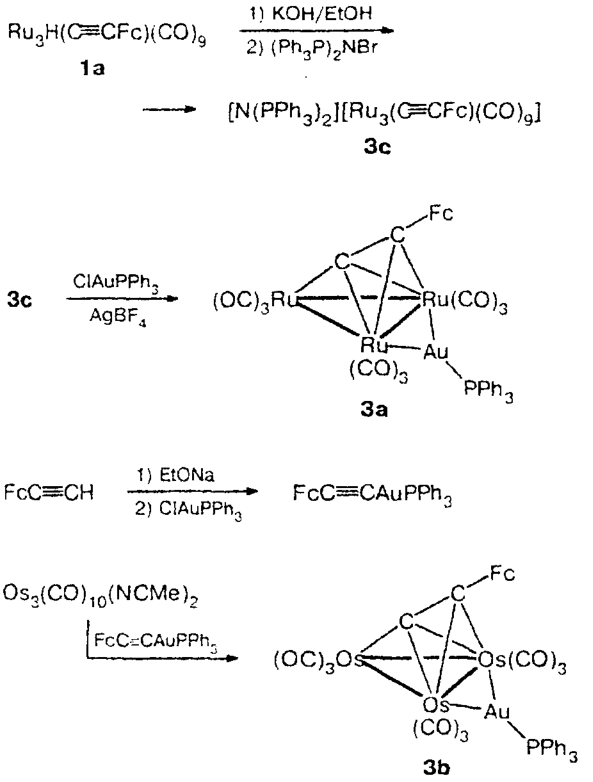
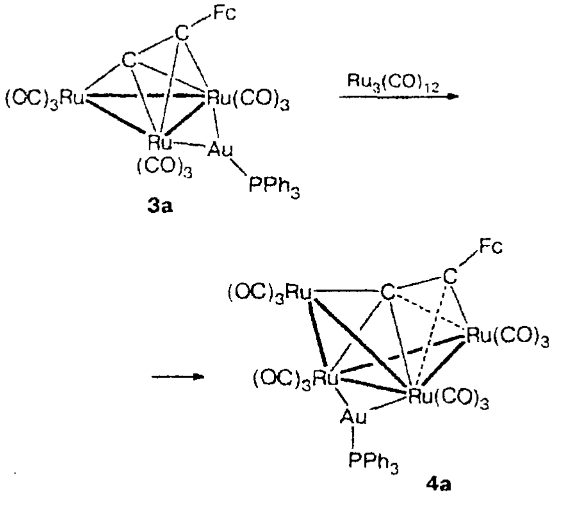
Scheme 1



Scheme 2



Complexes **3a** and **3b** are rather stable in solutions and in the crystalline state. These compounds were characterized by ^1H and ^{31}P NMR and IR spectroscopy and by X-ray diffraction analysis. Isostructural complexes **3a** and **3b** are shown in Fig. 1. The principal geometric parameters are given in Table 1.

As expected, clusters **3a** and **3b** contain a "butterfly" metal core and are structurally similar to the complex $Ru_3(AuPPh_3)(C{\equiv}CBu^t)(CO)_9$ (**6**) studied previously.[6] The dihedral angles between the "butterfly" wings, *viz.*, between Ru(1)—Ru(2)—Ru(3) and Ru(1)—Ru(2)—Au(1) in **3a** and between Os(1)—Os(2)—Os(3) and Os(1)—Os(2)—Au(1) in **3b**, are 122.5 and 123.6°, respectively. These angles are noticeably smaller than that observed in complex **6** (129.3°). A comparison of the structures of clusters **3a**, **3b**, and **6** revealed yet another substantial difference, *viz.*, the difference in the Au—P bond length (2.303(2), 2.302(3), and 2.276(3) Å, respectively), whereas the Ru—Au distances in clusters **3a** and **6** differ only slightly (2.7731(8) and 2.7685(11) Å in **3a** and 2.763(1) and 2.757 (1) Å in **6**).

The mode of bonding of the ferrocenylacetylide ligand with the metal core in clusters **3a** and **3b** is similar to that observed in hydride clusters **1a** [1a] and **1b**.[7] In the crystal structures, molecules **3a** and **3b** are asymmetrical with atoms of the ferrocenyl group located on the same side relative to the plane passing through the M(3)—Au(1)—P(1) atoms. However, the ferrocenyl substituent should be readily rotated with respect to the C(11)—C(12) bond in solutions. This rotation leads to averaging of the stereochemical environment about the pairs of the H(2) and H(5) atoms and the H(3) and

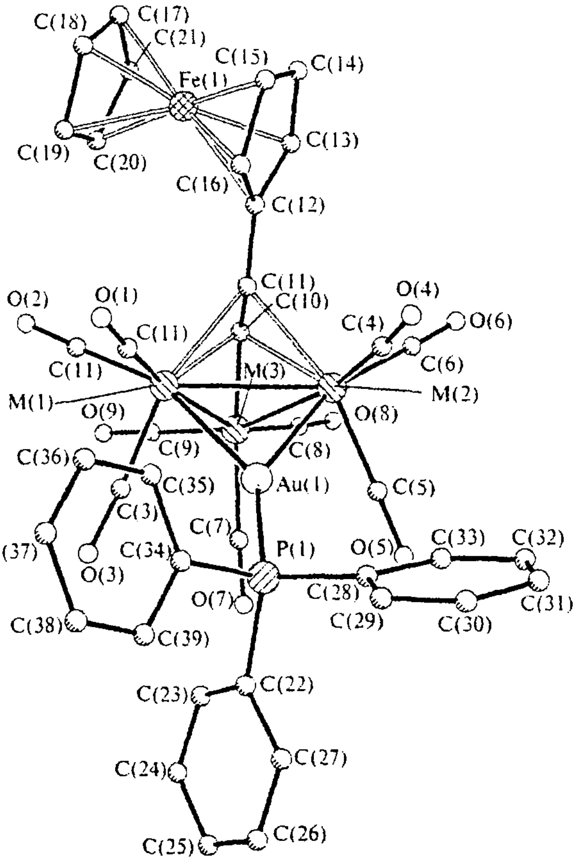


Fig 1. Structures of complexes **3a** (M = Ru) and **3b** (M = Os).

Table 1. Principal bond lengths (*d*) and bond angles (ω) in complexes **3a** (M = Ru) and **3b** (M = Os)

Parameter	**3a**	**3b**
Bond	*d*/Å	
M(1)—M(2)	2.837(1)	2.863(1)
M(1)—M(3)	2.802(1)	2.840(2)
M(2)—M(3)	2.798(1)	2.833(1)
Au(1)—M(1)	2.773(1)	2.783(1)
Au(1)—M(2)	2.769(1)	2.780(1)
Au(1)—P(1)	2.303(2)	2.302(3)
M(1)—C(10)	2.195(6)	2.197(11)
M(1)—C(11)	2.233(6)	2.233(10)
M(2)—C(10)	2.202(6)	2.230(12)
M(2)—C(11)	2.268(6)	2.244(12)
M(3)—C(10)	1.962(6)	1.937(12)
C(10)—C(11)	1.296(8)	1.32(2)
C(11)—C(12)	1.459(9)	1.43(2)
Angle	ω/deg	
M(3)—M(1)—M(2)	59.50(3)	59.56(3)
M(3)—M(2)—M(1)	59.63(4)	59.83(4)
M(2)—M(3)—M(1)	60.87(3)	60.61(3)
Au(1)—M(1)—M(2)	59.13(3)	58.97(3)
Au(1)—M(2)—M(1)	59.28(3)	59.09(3)
Au(1)—M(1)—M(3)	97.85(3)	98.49(3)
Au(1)—M(2)—M(3)	98.04(3)	98.75(3)
M(2)—Au(1)—M(1)	61.59(2)	61.94(3)
P(1)—Au(1)—M(1)	148.57(4)	148.1(1)
P(1)—Au(1)—M(2)	149.80(4)	149.9(1)
C(11)—C(10)—M(3)	153.2(5)	153(1)
C(10)—C(11)—C(12)	145.1(6)	144(1)

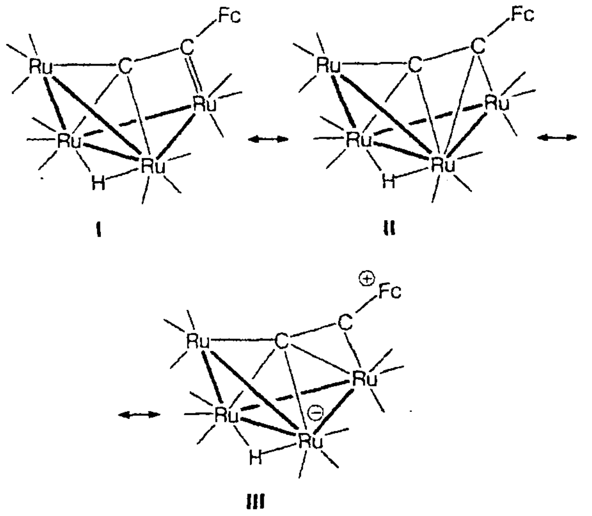
H(4) atoms in the substituted cyclopentadienyl ring of the ferrocenyl group because these protons are manifested as two signals in the ^{1}H NMR spectrum.

Thermal reactions of clusters **3a** and **3b** with $Ru_3(CO)_{12}$ were performed (see Scheme 2). In the case of the reaction of cluster **3a**, green complex **4a** was isolated. This complex is less stable compared to hydride complex **2a**. For this reason, complex **4a** was not characterized by elemental analysis and X-ray diffraction study. However, the green color (which is very rarely observed for cluster ruthenium complexes) and the results of ^{31}P NMR and, particularly, of ^{1}H NMR spectroscopy indicate that complex **4a** is a goldphosphine analog of hydride complex **2a** and, apparently, has the composition $Ru_4(AuPPh_3)(C_2Fc)(CO)_{12}$. Thus, the ^{1}H NMR spectrum of complex **4a** ($CDCl_3$, 25 °C) exhibits signals of the ferrocenyl fragment and three phenyl groups. It is remarkable that the signals for the protons of the substituted cyclopentadienyl ring of the ferrocenyl group are broadened, like in the spectrum of complex **2a** at room temperature, which is indicative of the fluctuation of the μ_4-acetylide ligand in complex **4a**.[1]

An attempt to prepare the complex of composition $RuOs_3(AuPPh_3)(C_2Fc)(CO)_{12}$ (**4b**) by the reaction of cluster **3b** with $Ru_3(CO)_{12}$ was unsuccessful due, apparently, to the even lower stability of **4b** compared to the stabilities of complexes **2a**, **2b**, and **4a**.

Recently,[8] it has been suggested that bonding of the ligand μ_4-C_2Fc in cluster **2a** should be considered by taking into account three resonance structures **I**, **II**, and **III** (Scheme 3). Bipolar structure **III** reflects the role of the ferrocenyl group, famed for its high ability to delocalize a positive charge. The significance of the contribution of structure **III** to the formation (stabilization) of green clusters **2a** and **2b** is evidenced by the fact[9] that the reaction of the acetylide triosmium complex $Os_3H(C{\equiv}CMe)(CO)_9$ (**7**), which is isostructural to the complex $Os_3H(C{\equiv}CFc)(CO)_9$ (**1b**), with $Ru_3(CO)_{12}$ afforded a red alkyne cluster of the well-known type with the "butterfly" core, *viz.*, $RuOs_3(HC_2Me)(CO)_{12}$ (**9**), rather than hydridoacetylide $RuOs_3H(C_2Me)(CO)_{12}$ (**8**).

Scheme 3



It is of interest to consider the change in the contribution of structure **III** to the bonding of the ligand μ_4-C_2Fc with the Ru_4 core on going from **2a** to **4a**.

Based on the data of IR spectroscopy of derivatives of tetranuclear cluster iron carbonyls, it was established[10] that the accepting strength of the bridging groups increases in the series $CuL^+ \approx AuPR_3^+ < CH_3Hg < H^+$. This fact agrees also with our data for clusters **1a**[11] and **3a**. Thus, the most intense ν(CO) band in the IR spectra of these complexes is observed at 2078 and 2037 cm^{-1}, respectively. Hence, the electron density at the Ru_4 core would be expected to increase on going from **2a** to **4a**, which, in turn, should lead to a decrease in the transfer of the electron density from the ferrocenyl group to this core. To put it differently, the contribution of bipolar structure **III** to the bonding of the acetylide ligand with the Ru_4 core decreases on going from **2a** to **4a**.

Therefore, it can be believed that unusual hydridoacetylide clusters of types **2a**, **2b**, and **4a** are formed and are rather stable due to the high ability of the ferrocenyl group to delocalize the positive charge. As for the reactions of metal carbonyls with the complexes $M_3H(C{\equiv}CR)(CO)_9$ containing an alkyl or aryl group as the R substituent, they afforded alkyne complexes $M_4(HC_2R)(CO)_{12}$ with the "butterfly" core as a result of migration of the hydride ligand from the metal core to the acetylide carbon atom. These complexes are among typical products of reactions of alkynes with metal carbonyls of the iron subgroup.

Experimental

The ^1H and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.13 and 161.98 MHz, respectively). The IR spectra were measured on a Bruker IFS-113v instrument. The reactions were carried out under an atmosphere of argon. Chromatographic separation was performed in air. Preparative chromatographic separation of the products was carried out with the use of silica gel L (100/160 μm) (Chemapol). The organic solvents were distilled under an atmosphere of argon over the corresponding drying agents (CH_2Cl_2 over P_2O_5; THF over sodium benzophenone ketyl; benzene over sodium; and EtOH over Mg/I_2); $AgBF_4$ was purchased from Aldrich.

Bis(triphenylphosphoranylidene)ammonium 1,1,1,2,2,2,3,3,3-nonacarbonyl-μ$_3$-[ferrocenylethynyl-C^1(Ru^1)C^{1-2}(Ru^2,Ru^3)]-*triangulo*-triruthenate (3c). A solution of KOH (10 mg, 0.172 mmol) in anhydrous EtOH (5 mL) was added dropwise to a stirred solution of $Ru_3H(C{\equiv}CFc)(CO)_9$[11] (120 mg, 0.157 mmol) in THF (30 mL) over 4 min. Then a solution of $(Ph_3P)_2NBr$[12] (97 mg, 0.157 mmol) in anhydrous EtOH (2 mL) was added to the reaction mixture. In the course of the reaction, the color of the solution changed from red-brown to brown. The reaction mixture was stirred for 4 h, the solvent was evaporated to dryness, the residue was dissolved in EtOH (20 mL), and the product was crystallized at −78 °C. The complex $[(PPh_3)_2N][Ru_3(C{\equiv}CFc)(CO)_9]$ (**3c**) was obtained as brown crystals in a yield of 200 mg (98%). IR (THF), ν(CO)/cm^{-1}: 2046 m, 2001 v.s, 1991 v.s, 1966 s, 1942 (sh).

1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-[(triphenylphosphine)gold]-μ$_3$-[ferrocenylethynyl-C^1(Ru^1)C^{1-2}(Ru^2,Ru^3)]-*triangulo*-triruthenium (3a). $ClAuPPh_3$[13] (76 mg, 0.154 mmol) and $AgBF_4$ (30 mg, 0.154 mmol) were added to a solution of compound **3c** (200 mg, 0.154 mmol) in THF (30 mL) cooled to −15 °C. The reaction mixture was stirred for 7 h and kept for 15 h. Then the solvent was evaporated. Two major fractions were isolated from the residue by chromatography, *viz.*, a red-yellow fraction (hexane as the eluent) containing the complex $Ru_3(AuPPh_3)(C{\equiv}CFc)(CO)_9$ (**3a**, the yield was 105 mg, 56%) and a red-brown fraction (MeCN as the eluent) containing an unidentified compound.

Complex **3a** was obtained as red-brown crystals. IR (hexane), ν(CO)/cm^{-1}: 2070 m, 2037 v.s, 1994 s, 1976 v.w, 1964 w. ^1H NMR ($CDCl_3$, 25 °C), δ: 4.21 (s, 5 H, C_5H_5); 4.25 (t, 2 H, C_5H_4, J = 2.0 Hz); 4.41 (t, 2 H, C_5H_4, J = 2.0 Hz); 7.10—7.40 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 61.57 (s).

1-[(Triphenylphosphine)gold]-2-ferrocenylethyne, $FcC{\equiv}CAuPPh_3$. A solution of freshly prepared EtONa (19.5 mg) in EtOH (2 mL) and ferrocenylacetylene[14] (169 mg, 0.808 mmol) were added to a suspension of $ClAuPPh_3$ (400 mg, 0.808 mmol) in anhydrous EtOH (40 mL). The resulting solution was refluxed for 1 h, cooled, and concentrated. The orange precipitate that formed was filtered off. The product was obtained as orange crystals in a yield of 430 mg (80%). ^1H NMR ($CDCl_3$, 25 °C), δ: 4.10 (t, 2 H, C_5H_4, J = 2.0 Hz); 4.21 (s, 5 H, C_5H_5); 4.43 (t, 2 H, C_5H_4, J = 2.0 Hz); 7.40—7.60 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 43.18 (s).

1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2-μ-[(triphenylphosphine)gold]-μ$_3$-[ferrocenylethynyl-C^1(Os^1)C^{1-2}(Os^1,Os^3)]-*triangulo*-triosmium (3b). A solution of $Os_3(CO)_{10}(NCMe)_2$[15] (230 mg, 0.247 mmol) and $FcC{\equiv}CAuPPh_3$ (165 mg, 0.247 mmol) in CH_2Cl_2 (40 mL) was stirred at −20 °C for 1 h. The color of the solution changed from orange to red-brown. After evaporation of the solvent, six fractions were isolated from the residue by chromatography, *viz.*, an orange-yellow fraction containing the starting complex $Os_3(CO)_{10}(NCMe)_2$, a yellow fraction (hexane as the eluent) containing the complex $(Ph_3PAu)Os_3Cl(CO)_9$,[16] a red fraction (a 20 : 1 hexane—benzene system as the eluent) containing complex **3b** (the yield was 50 mg, 14%), and then orange, red, and orange-red zones containing unidentified complexes, which were obtained in low yields.

Complex **3b** was obtained as dark-red crystals. IR (hexane), ν(CO)/cm^{-1}: 2088 w, 2073 m, 2040 v.s, 2005 s, 1991 s, 1974 (sh), 1963 (sh). ^1H NMR ($CDCl_3$, 25 °C), δ: 4.20 (s, 5 H, C_5H_5); 4.27 (t, 2 H, C_5H_4, J = 2.0 Hz); 4.41 (t, 2 H, C_5H_4, J = 2.0 Hz); 7.40—7.70 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 72.86 (s).

Reaction of $Ru_3(AuPPh_3)(C{\equiv}CFc)(CO)_9$ (3a) with $Ru_3(CO)_{12}$. $Ru_3(CO)_{12}$ (52 mg, 0.0817 mmol) was added to a

Table 2. Crystallographic data, details of X-ray diffraction study, and characteristics of the refinement of compounds **3a** and **3b**

Parameter	**3a**	**3b**
Molecular formula	$C_{39}H_{24}AuFeO_9PRu_3$	$C_{39}H_{24}AuFeO_9POs_3$
Molecular weight	1223.58	1490.97
Space group	$P\bar{1}$	$P\bar{1}$
Temperature/K	293(2)	293(2)
a/Å	10.743(2)	10.742(2)
b/Å	12.543(3)	12.543(3)
c/Å	16.383(3)	16.301(3)
α/deg	77.98(3)	77.83(3)
β/deg	80.98(3)	81.43(3)
γ/deg	65.71(3)	65.39(3)
V/Å^3	1961.8(7)	1947.3(7)
Z	2	2
d_{calc}/g cm^{-3}	2.071	2.543
Diffractometer	CAD-4	CAD-4
Radiation (λ/Å)	Mo-Kα (0.71073)	
μ/cm^{-1}	53.09	139.63
Absorption correction	—	ψ-curves
T_{min}/T_{max}	—	0.254/1.000
Scanning mode	θ-5/3θ	θ-5/3θ
2θ$_{max}$/deg	52	52
Number of independent reflections (R_{int})	6919 (0.0971)	6840 (0.0522)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0427 (5779 reflections)	0.0627 (5817 reflections)
wR_2 (based on F^2 for all reflections)	0.1152	0.1995
Number of refinable parameters	487	487
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (1/3)(F_o^2 + 2F_c^2)$	
a	0.0820	0.1519
b	0.4223	3.8862

solution of complex **3a** (100 mg, 0.0817 mmol) in benzene (30 mL). The reaction mixture was stirred at 70—75 °C for 6 h. The color of the solution changed from orange-red to dark-brown. After evaporation of the solvent, four major fractions were isolated from the residue by chromatography, *viz.*, a yellow fraction containing $Ru_3(CO)_{12}$, a violet-red fraction (hexane as the eluent) containing an unidentified compound, a yellow-brown fraction containing a mixture of complex **3a** and $Ru_4(AuPPh_3)(C{\equiv}CFc)(CO)_{12}$ (**4a**), and a dark-brown fraction (benzene as the eluent) containing an unidentified compound. **Complex 4a** was additionally purified by chromatography and was obtained as a dark-green crystalline compound in a yield of 20 mg (35%), which decomposed to form **3a** and $Ru_3(CO)_{12}$. ^1H NMR ($CDCl_3$, 25 °C), δ: 4.38 (s, 5 H, C_5H_5); 4.83 (br.s, 2 H, C_5H_4); 5.29 (br.s, 2 H, C_5H_4); 7.10—7.40 (m, 15 H, C_6H_5). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 65.21 (s).

X-ray diffraction study of complexes 3a and 3b. Single crystals of complexes **3a** and **3b** suitable for X-ray diffraction study were prepared by crystallization from hexane. The crystallographic data and the principal details of the refinement of compounds **3a** and **3b** are given in Table 2. Both structures were solved by the direct method. The positional and thermal parameters of the nonhydrogen atoms were refined first isotropically and then anisotropically by the full-matrix least-squares method. The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model. For the structure of **3b**, the absorption correction was applied using experimental azimuth scanning curves. All calculations were carried out on a PC computer using the SHELXTL PLUS 5 program package.[17]

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