drogen bonded both to the chlorine of an adjacent $[(CH_3)_2SnCl_4]^{2-}$ unit and to the oxygen atom of an adjacent water molecule. These N–H--O hydrogen bonds are at 2.603 (3) Å (intramolecular) and 2.721 (3) Å (intermolecular) vs. 2.89 Å for 989 known examples.[17] The benzamido nitrogen atom, on the other hand, uses only one of its hydrogens to make an adjacent benzamide into a dimeric unit and produces a three-coordinated situation. These N–H--O═C hydrogen bonds are longer, at *d*(N–H--O) = 2.904 (2) Å. Thus, only one potential hydrogen-bonding site at the benzamide nitrogen [H(14)] is left unutilized in the structure.

The carbonyl oxygen atoms are also three-coordinated, making hydrogen bonds both intra- and intermolecularly to anilinium and benzamido nitrogen atoms, respectively, as are the oxygen atoms of the water molecules, which utilize both their hydrogen atoms in binding to chlorines and are bound by a hydrogen bond from an adjacent anilinium nitrogen.

The network of hydrogen bonds efficiently fills space with dimeric anthranilamide, water, and dimethyltetrachlorostannate(IV) units, delocalizing the anilinium cation and tin dianion charges through the lattice.

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Registry No. $[2\text{-}H_3NC_6H_4C(O)NH_2]^+{}_2[(CH_3)_2SnCl_4]^{2-}(H_2O)_2$, 88336-79-2; $(CH_3)_2SnCl_2$, 753-73-1; $2\text{-}H_2NC_6H_4C(O)NH_2$, 88-68-6.

Supplementary Material Available: A listing of structure factor amplitudes, Tables V and IX–XI, showing anisotropic thermal parameters, C–C distances, C–C–C angles, least-squares plane parameters, and hydrogen atom parameters, and Figure 3, showing the coordination geometries and dimer dimensions (12 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie de Coordination du CNRS,
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Synthesis and Structural Characterization of a New Ruthenium–Gold Cluster Complex: $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$

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The tetranuclear mixed-metal cluster complex $Ru_3(\mu_3\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ has been synthesized from the reaction of $Ru_3(CO)_{12}$ with $AuPPh_3Cl$ in refluxing dichloromethane and characterized by analysis, IR, ^1H NMR, and X-ray diffraction at low temperature. X-ray data (−155 °C): monoclinic, space group $P2_1/n$, a = 12.697 (2) Å, b = 16.748 (3) Å, c = 16.078 (3) Å, β = 113.0 (1)°, V = 3147 Å^3, Z = 4. R = 0.022, R_w = 0.024 for 3249 reflections with $F_o^2 > 3\sigma(F_o)^2$. The complex has a butterfly metal framework with the gold atom occupying one of the wing tips. Bond distances of interest: (i) Ru–Ru (unsupported) 2.8197 (7) and 2.8125 (8) Å; (ii) (μ-Au)(μ-Cl)Ru–Ru 2.8742 (6) Å; (iii) Ru–Au 2.7523 (6) and 2.7549 (6) Å. In terms of isolobal analogy, this complex is shown to have a structure similar to that of the hydrido cluster complexes of general formula $M_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}$ (M = Ru, Os; X = Cl, Br, I). The complex is shown to have low stability since thermolysis at 80 °C leads to extrusion of the gold atom and affords the complex $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$.

Introduction

The isolobal relationship between the hydride lignad and the $AuPR_3$ group[1] has been exemplified in a series of syntheses of mixed-metal cluster complexes.[2-16]

While the first osmium–gold cluster complex, $Os_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, was reported in the literature 13 years ago, attempts to prepare the ruthenium analogue were unsuccessful.[2]

As part of a new research program directed to the synthesis of ruthenium-containing mixed-metal clusters,[17] we have now found a facile synthetic route to $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$. The complex has been characterized by spectroscopic and crystallographic techniques.[18] Additional interest in this

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complex stems from the analogy with the series of reactive hydrido cluster complexes $Ru_3(\mu\text{-}H,\mu\text{-}X)(CO)_{10}$ (X = Cl, Br, I) that have been recently reported.[19]

Experimental Section

General Comments. All reactions were performed under an atmosphere of prepurified nitrogen; Schlenk techniques were used. All organic solvents were reagent grade. $Ru_3(CO)_{12}$ was prepared by a published procedure.[20] Chloro(triphenylphosphine)gold(I) was purchased from Stream Chemicals. Analytical data were obtained from the Service Central de Microanalyse du C.N.R.S.

Spectroscopic Data. Solution IR spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrophotometer with cyclohexane as a solvent. ^{1}H NMR spectra were recorded on a Bruker WH90 spectrometer. Chemical shifts δ given in this paper are relative to internal Me_4Si reference. Attempts to obtain mass spectra were made on a Varian MAT 311A by using a direct inlet probe (EI) at 65 °C.

Preparation of the Complex. $Ru_3(\mu\text{-}AuP(C_6H_5)_3)(\mu\text{-}Cl)(CO)_{10}$. In a typical experiment, 310 mg of $Ru_3(CO)_{12}$ (0.48 mmol) and 240 mg of $AuP(C_6H_5)_3Cl$ (0.48 mmol) were dissolved in 50 mL of dichloromethane. The solution was carefully deaerated by several freeze–pump–thaw cycles and was then refluxed for 18 h, while a color change from orange to violet was observed. After cooling and solvent removal under vacuum, the reaction mixture was chromatographed on silica gel 60 (Fluka). Elution with toluene–hexane (1–4) afforded two bands: (a) orange, $Ru_3(CO)_{12}$, 39 mg; (b) violet, $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, 252 mg (yield 55%). Further elution with toluene–hexane (1:1) afforded a yellow band (c), 12 mg. A brown material (d) was retained at the top of the column and could be only partially eluted with tetrahydrofuran (97 mg; unidentified mixture of products). Infrared peaks of the four fractions chromatographed are given below.

IR (νCO, cm^{-1}, cyclohexane): (a) $Ru_3(CO)_{12}$, 2060 (s), 2030 (vs), 2010 (m); (b) $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, 2095 (m), 2045 (vs), 2025 (s), 2010 (s), 1995 (m), 1985 (sh), 1967 (m); (c) yellow fraction, 2080 (ms), 2022 (s), 2015 (vs), 1956 (m); (d) indefinite broad bands. Suitable crystals of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ were obtained by slow evaporation of fraction b (toluene–hexane 1:4). Anal. Calcd: Au, 18.28; Cl, 3.3; P, 2.87; C, 31.21; H, 1.40. Found: Au, 16.08; Cl, 3.0; P, 2.8; C, 31.70; H, 1.40. ^{1}H NMR (CD_2Cl_2): δ C_6H_5 7.51, 7.48. Mass spectrometry: Attempts to obtain a mass spectrum of this complex by using a direct inlet probe (EI) were unsuccessful. Decomposition seemed to have occurred in the spectrometer.

Thermal Decomposition of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$. In a typical experiment, 100 mg of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ was dissolved in 50 mL of cyclohexane. A color change from violet to brown was observed upon refluxing for 24 h. Chromatographic workup allowed separation of the same compounds as mentioned above, but in different yields: fraction a, $Ru_3(CO)_{12}$, traces; fraction b, $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, traces; fraction c, yellow, 45 mg. Traces of other uncharacterized complexes could be eluted with dichloromethane while a black residue was retained at the top of the column.

We were able to get single crystals of the yellow complex (yield 47%) which was subsequently formulated as $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$ from an X-ray structure determination.[21]

Table I. Summary of Experimental Data for the X-ray Diffraction Study

Crystal Data

formula: $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$
$M_r = 1077.63$
cryst system: monoclinic
space group: $P2_1/n$
$\mu = 63$ cm^{-1}
cryst shape: parallelepipedic
cryst vol: 7×10^{-4} mm^3
cell parameters (at −155 ± 1 °C)
$a = 12.697$ (2) Å
$b = 16.748$ (3) Å
$c = 16.078$ (3) Å
$\beta = 113.0$ (1)°
$V = 3147$ Å^3
$d_{calcd} = 2.27$ g·cm^{-3}

Intensity Data

radiation: Mo Kα (λ = 0.709 30 Å) from monochromator
takeoff angle: 2.8°
θ limits: 1–22°
scan mode: ω–θ
scan range: 0.6° below Kα_1 to 0.6° above Kα_2
reflcns collected: 4012
reflcns used: 3249 ($F_o^2 > 3\sigma(F_o)^2$)
no. of variable parameters: 274
secondary extinction parameter: 0.17×10^{-8}
final agreement factors: $R = 0.022$; $R_w = 0.024$

Table II. Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters for $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$

atom	x	y	z	B, Å^2
Au(1)	0.58761 (2)	0.22085 (1)	0.82018 (2)	1.16 (2)
Ru(1)	0.25086 (4)	0.27574 (3)	0.74724 (3)	1.32 (3)
Ru(2)	0.40710 (4)	0.16086 (3)	0.85494 (3)	1.17 (4)
Ru(3)	0.46292 (4)	0.32798 (3)	0.87494 (3)	1.10 (3)
Cl	0.4324 (1)	0.24250 (9)	0.98631 (10)	1.84 (7)
P	0.7431 (1)	0.20310 (9)	0.7817 (1)	1.18 (7)
C(1)	0.2077 (5)	0.2926 (4)	0.8488 (5)	2.04 (5)
O(1)	0.1759 (4)	0.3050 (3)	0.9044 (3)	2.95 (4)
C(2)	0.3245 (5)	0.2653 (3)	0.6611 (5)	1.64 (4)
O(2)	0.3625 (4)	0.2615 (2)	0.6076 (3)	1.98 (3)
C(3)	0.1336 (5)	0.1972 (4)	0.6899 (4)	1.88 (5)
O(3)	0.0658 (4)	0.1482 (3)	0.6607 (3)	2.70 (3)
C(4)	0.1752 (5)	0.3739 (4)	0.6932 (4)	2.12 (5)
O(4)	0.1289 (4)	0.4309 (3)	0.6630 (3)	2.91 (4)
C(5)	0.2822 (6)	0.1018 (4)	0.8616 (4)	1.76 (4)
O(5)	0.2071 (4)	0.0652 (3)	0.8653 (3)	2.88 (4)
C(6)	0.3926 (5)	0.1105 (4)	0.7471 (4)	1.49 (4)
O(6)	0.3843 (4)	0.0760 (2)	0.6831 (3)	2.08 (3)
C(7)	0.5292 (5)	0.0902 (4)	0.9287 (4)	1.59 (4)
O(7)	0.5955 (4)	0.0444 (3)	0.9679 (3)	2.43 (3)
C(8)	0.3952 (5)	0.4218 (4)	0.9014 (4)	1.89 (5)
O(8)	0.3582 (4)	0.4784 (3)	0.9166 (3)	3.13 (4)
C(9)	0.4811 (5)	0.3816 (4)	0.7793 (4)	1.42 (4)
O(9)	0.4940 (4)	0.4187 (3)	0.7246 (3)	2.36 (3)
C(10)	0.6193 (6)	0.3474 (3)	0.9571 (4)	1.40 (4)
O(10)	0.7108 (4)	0.3649 (3)	1.0024 (3)	2.32 (3)

X-ray Structure Analysis of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$. Collection and Reduction of X-ray Data. Preliminary Laue and precession photographs showed that the complex crystallized in a monoclinic unit cell. Systematic extinction patterns ($0k0$, $k = 2n + 1$) and $h0l$, $h + l = 2n + 1$) were consistent with space group $P2_1/n$. The crystals selected for intensity data collection were glued on a glass fiber with Apiezon N grease and transferred to a Nonius CAD4 diffractometer equipped with a low-temperature device.[22] Intensity measurements were made at −155 ● 1 °C. The setting angles of 25 reflections within the range 24° < 2θ(Mo) < 26° were refined by least-squares procedure, leading to the cell constants that are reported in Table I along with pertinent crystal and intensity data. Intensities were corrected for Lorentz and polarization effects and reduced to observed structure factor amplitudes, by using a p value of 0.03.[23] Owing to their fragility at low temperature, crystals were incidentally broken during data collection. A complete data set was obtained from three independent crystals. Intensities were first scaled by using standard reflections. Three independent scale factors were then used in structure refinements.

Solution and Refinement of the Structure. The direct-method approach[24] based on 320 normalized structure factors yielded the

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(18) The X-ray crystal structure in the osmium analogue $Os_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ mentioned in ref 2 has never been reported in full.

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(22) The low-temperature device has been designed in this laboratory and will be soon commercially available from SOTEREM (Zone Industrielle de Vic, 31000 Castanet Tolosan, France).

(23) The intensity data were processed as described in "1980 Update CAD4 Operation Manual"; Enraf-Nonius: Delft, Holland. The net intensity $I = (K/(\mathrm{NPI})(C - 2B)$, where K is 15.44x (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurements, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/(\mathrm{NPI})^2[C + 4B + (p_1)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2(\sigma(I)/I)F_o$.

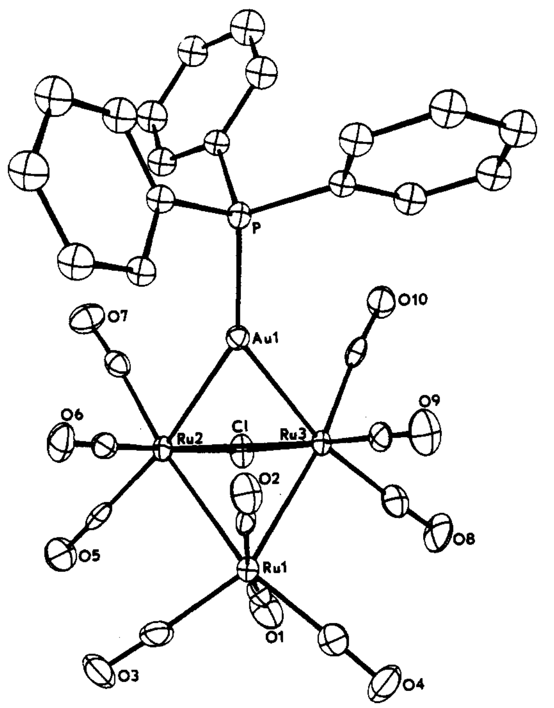


Figure 1. Geometry and labeling of the butterfly cluster complex $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$. Thermal ellipsoids are taken at the 60% probability level.

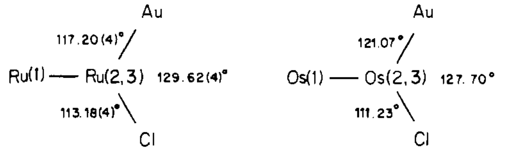
Table III. Selected Interatomic Distances (Å) with Esd's

	Gold-Ruthenium		
Au(1)-Ru(2)	2.7523 (6)	Au(1)-Ru(3)	2.7549 (6)
	Ruthenium-Ruthenium		
Ru(1)-Ru(2)	2.8197 (7)	Ru(1)-Ru(3)	2.8125 (8)
Ru(2)-Ru(3)	2.8742 (6)		
	Ruthenium-Bridging Ligand		
Ru(2)-Cl	2.430 (1)	Ru(3)-Cl	2.439 (1)
	Gold-Phosphorus		
Au(1)-P	2.307 (1)		
	Ruthenium-Carbon		
Ru(1)-C(1)	1.936 (7)		
Ru(1)-C(2)	1.958 (7)		
Ru(1)-C(3)	1.930 (7)	Ru(1)-C(4)	1.930 (7)
Ru(2)-C(5)	1.907 (7)	Ru(3)-C(8)	1.916 (7)
Ru(2)-C(6)	1.871 (7)	Ru(3)-C(9)	1.872 (7)
Ru(2)-C(7)	1.942 (7)	Ru(3)-C(10)	1.935 (7)
	Carbon-Oxygen		
C(1)-O(1)	1.134 (7)		
C(2)-O(2)	1.140 (7)		
C(3)-O(3)	1.148 (7)	C(4)-O(4)	1.127 (7)
C(5)-O(5)	1.154 (7)	C(8)-O(8)	1.128 (7)
C(6)-O(6)	1.148 (7)	C(9)-O(9)	1.140 (7)
C(7)-O(7)	1.132 (7)	C(10)-O(10)	1.142 (7)
	Selected Nonbonding Distances		
Au(1)···C(2)	3.402 (7)		
Au(1)···C(6)	2.941 (6)	Au(1)···C(9)	2.968 (6)
Au(1)···C(7)	3.064 (6)	Au(1)···C(10)	2.968 (6)

Table IV. Selected Interatomic Angles (deg) with Esd's

	Angles Involving the Metal Framework		
Ru(2)-Au(1)-Ru(3)	62.92 (2)		
Ru(2)-Ru(1)-Ru(3)	61.37 (2)		
Au(1)-Ru(2)-Ru(3)	58.58 (1)	Au(1)-Ru(3)-Ru(2)	58.50 (1)
Ru(1)-Ru(2)-Ru(3)	59.19 (2)	Ru(1)-Ru(3)-Ru(2)	59.44 (2)
Au(1)-Ru(2)-Ru(1)	93.90 (2)	Au(1)-Ru(3)-Ru(1)	94.00 (2)
	Angles Involving the Bridging Chloride		
Ru(2)-Cl-Ru(3)	72.36 (4)		
Cl-Ru(2)-Ru(3)	53.97 (4)	Cl-Ru(3)-Ru(2)	53.67 (4)
Cl-Ru(2)-Au(1)	97.67 (4)	Cl-Ru(3)-Au(1)	97.38 (4)
Cl-Ru(2)-Ru(1)	88.40 (4)	Cl-Ru(3)-Ru(1)	88.38 (4)
Cl-Ru(2)-C(5)	94.2 (2)	Cl-Ru(3)-C(8)	96.0 (2)
Cl-Ru(2)-C(6)	172.2 (2)	Cl-Ru(3)-C(9)	172.3 (2)
Cl-Ru(2)-C(7)	90.5 (2)	Cl-Ru(3)-C(10)	90.7 (2)
	Ru-Ru-CO		
Ru(2)-Ru(1)-C(1)	86.8 (2)	Ru(3)-Ru(1)-C(1)	81.1 (2)
Ru(2)-Ru(1)-C(2)	87.6 (2)	Ru(3)-Ru(1)-C(2)	87.6 (2)
Ru(2)-Ru(1)-C(3)	93.1 (2)	Ru(3)-Ru(1)-C(4)	103.3 (2)
Ru(1)-Ru(2)-C(5)	89.3 (2)	Ru(1)-Ru(3)-C(8)	91.9 (2)
Ru(1)-Ru(2)-C(6)	87.0 (2)	Ru(1)-Ru(3)-C(9)	86.5 (2)
Ru(3)-Ru(2)-C(5)	132.3 (2)	Ru(2)-Ru(3)-C(8)	135.3 (2)
Ru(3)-Ru(2)-C(6)	118.2 (2)	Ru(2)-Ru(3)-C(9)	118.6 (2)
Ru(3)-Ru(2)-C(7)	114.9 (2)	Ru(2)-Ru(3)-C(10)	112.5 (2)
	Au-Ru-CO		
Au(1)-Ru(2)-C(6)	76.4 (2)	Au(1)-Ru(3)-C(9)	77.2 (2)
Au(1)-Ru(2)-C(7)	79.5 (2)	Au(1)-Ru(3)-C(10)	76.3 (2)
	CO-Ru-CO		
C(3)-Ru(1)-C(4)	102.1 (2)		
C(1)-Ru(1)-C(3)	94.7 (2)	C(1)-Ru(1)-C(4)	90.0 (3)
C(2)-Ru(1)-C(3)	95.4 (2)	C(2)-Ru(1)-C(4)	92.8 (2)
C(5)-Ru(2)-C(6)	92.1 (3)	C(8)-Ru(3)-C(9)	90.0 (3)
C(5)-Ru(2)-C(7)	97.6 (2)	C(8)-Ru(3)-C(10)	98.0 (2)
C(6)-Ru(2)-C(7)	93.3 (2)	C(9)-Ru(3)-C(10)	93.3 (2)
	Ru-C-O		
Ru(1)-C(1)-O(1)	175.3 (6)		
Ru(1)-C(2)-O(2)	175.2 (5)		
Ru(1)-C(3)-O(3)	175.9 (5)	Ru(1)-C(4)-O(4)	177.9 (6)
Ru(2)-C(5)-O(5)	179.1 (5)	Ru(3)-C(8)-O(8)	177.7 (5)
Ru(2)-C(6)-O(6)	176.6 (5)	Ru(3)-C(9)-O(9)	175.4 (5)
Ru(2)-C(7)-O(7)	174.8 (5)	Ru(3)-C(10)-O(10)	174.4 (5)
	Angles Involving the Phosphine Ligand		
Ru(2)-Au(1)-P(1)	151.05 (4)	Ru(3)-Au(1)-P	145.94 (4)
Au(1)-P-C(11)	115.0 (1)	C(11)-P-C(21)	104.0 (2)
Au(1)-P-C(21)	115.8 (1)	C(11)-P-C(31)	104.9 (2)
Au(1)-P-C(31)	109.0 (1)	C(21)-P-C(31)	107.4 (2)

Chart I. Selected Interplanar Dihedral Angles in $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ and Relevant Angles in $Os_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$[a]



[a] Calculated from ref 2.

correct coordinates for Au and Ru atoms. A subsequent Fourier difference map then allowed the location of all nonhydrogen atoms. Atomic scattering factors for all atoms were taken from Cromer and Waber's tabulation.[25] Anomalous dispersion terms for Au, Ru, Cl, and P atoms were included in F_c.[26] Phenyl rings attached to the phosphorus atom were treated as rigid groups (D_{6h} symmetry, C–C 1.495 Å, C–H 0.95 Å). Refinement of an isotropic model including 25 atoms and 3 rigid groups converged to $R = 0.035$ and $R_w = 0.041$. The final cycles of full-matrix least-squares refinement included anisotropic thermal parameters for all independent atoms. On the basis of 3249 reflections for 274 variables (including a secondary isotropic extinction parameter), final conventional R values are $R(F) = 0.022$ and $R_w(F) = 0.025$.

Final atomic positional and equivalent thermal parameters are listed in Table II.

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(24) The main programs used were the following: Germain's MULTAN; Zalkin's FORDAP Fourier summation program; Johnson's ORTEP; Busing's and Levy's ORFFE error function program; Iber's NUCLS full-matrix least-squares program, which in its non-group form closely resembles the Busing–Levy ORFLS.

(25) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(26) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

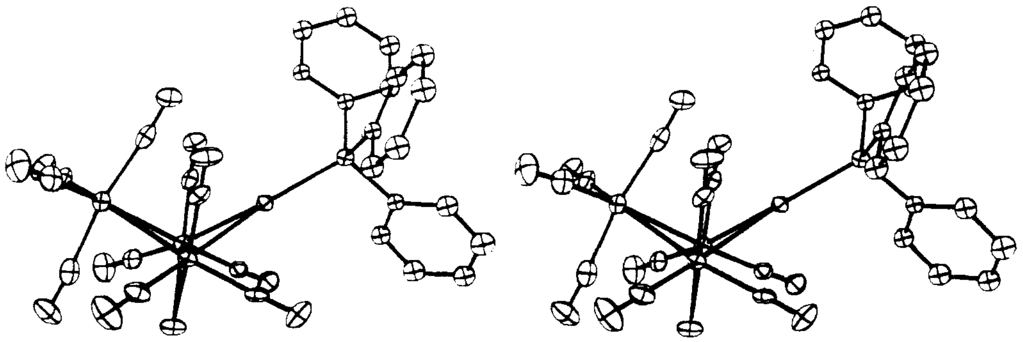

Figure 2. Stereoscopic view of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$.

Table V. *Comparison of Doubly Bridged Metal–Metal Bonds (Å) (μ-H)(μ-X)MM with the Corresponding (μ-AuPPh₃)(μ-X)MM in Trinuclear Complexes of Ruthenium and Osmium*

$(\mu\text{-}H)(\mu\text{-}H)Os\text{–}Os$ in $Os_3(\mu\text{-}H)_2(CO)_{10}$[29]	2.683 (1)	$(\mu\text{-}AuPPh_3)(\mu\text{-}H)Os\text{–}Os$ in $(\mu\text{-}AuPPh_3)(\mu\text{-}H)Os_3(CO)_{10}$[5]	2.699 (1)
$(\mu\text{-}H)(\mu\text{-}Cl)Os\text{–}Os$ in $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$[27]	2.846 (1)	$(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)Os\text{–}Os$ in $Os_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$[2]	2.86
$(\mu\text{-}H)(\mu\text{-}COMe)Ru\text{–}Ru$ in $Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}$[30]	2.803 (2)	$(\mu\text{-}AuPPh_3)(\mu\text{-}COMe)Ru\text{–}Ru$ in $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}COMe)(CO)_{10}$[6]	2.879 (2)

Description of the Structure and Discussion

The structure consists of four discrete ordered units of $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ separated by normal van der Waals distances. Figure 1 shows an ORTEP diagram of the molecule, while a stereoscopic view is given in Figure 2. Interatomic distances and bond angles are given in Tables III and IV, respectively. Selected interplanar angles are given in Chart I.

The molecule has a "butterfly" metal framework with the gold atom occupying one of the wing tips. In terms of isolobal analogy, the molecular structure is similar to that of $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$,[19] with one bridging hydrido ligand in the latter replaced by an $AuPPh_3$ group. The structure is also closely related to that of the osmium cluster $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$.[27] Details exemplifying this structure analogy are discussed below.

(1) The doubly bridged metal–metal vector, (μ-Au,μ-Cl)-Ru(2)–Ru(3), 2.8742 (6) Å, is slightly longer than a "normal" Ru–Ru bond (average 2.854 Å) in $Ru_3(CO)_{12}$[28] while both nonbridged bonds, Ru(1)–Ru(2) 2.8197 (7) and Ru(1)–Ru(3) 2.8125 (8) Å are shorter. Although no crystallographic data are available for the corresponding hydrido cluster complex $Ru_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$, a (μ-H,μ-Cl)Ru–Ru bond may be reasonably expected to be shorter than the value 2.819 (1) Å found for the (μ-H)(μ-Br)Ru–Ru bond in $Ru_3(\mu\text{-}H)(\mu\text{-}Br)(CO)_{10}$.[19] It thus appears that the bond lengthening influence induced by the bridging gold atom is higher than the related influence of a bridging hydride ligand.

This observation is in full agreement with structural data available from gold-containing cluster complexes and relevant hydrido analogues (see Table V). Such a lengthening influence can be related to the polarity of Ru–Ru bonds.[13]

(2) The distribution of carbonyl ligands in the present structure is closely similar to that one found in trinuclear complexes of general formula $M_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}$ (M = Ru, Os).[19,27]

The following features should be noted: (i) the axial carbonyl ligand C(2)O(2) on Ru(1) is slightly bent toward the gold atom, as shown by the relatively low values found for the angles Ru(2)–Ru(1)–C(2) = 87.6(2) and Ru(3)–Ru(1)–C(2) = 87.6 (2)°. Nevertheless, the distance C(2)···Au(1) of 3.402 Å is clearly non bonding, unlike the weakly bonding distance of 3.22 Å in $Os_3(\mu\text{-}H)(\mu\text{-}AuPPh_3)(CO)_{10}$.[5]

(ii) The distribution of carbonyl ligands reached to Ru(2) and Ru(3) clearly reflects the influence of gold and chlorine atoms: the presence of these bridging atoms induces a semiaxial position for the carbonyl ligands C(5)O(5), C(6)O(6), C(8)O(8), and C(9)O(9). Noticeably, both carbonyl ligands trans to the chloride atom exhibit the shortest metal–carbon distances (Ru(2)–C(6) = 1.871 (7) Å; Ru(3)–C(9) = 1.872 (7) Å), while the longest pair of carbonyl groups involves equatorial carbonyls trans to Ru(1) (Ru(2)–C(7) = 1.942 (7) Å; Ru(3)–C(10) = 1.935 (7) Å).

The orientation of carbonyl groups in hydrido cluster complexes has been used as a probe to estimate the stereochemical influence of bridging hydride ligands.[31] The observation of relevant geometric features in a gold complex allows a precise evaluation of the isolobal analogy. In the present cluster, the gold atom is adjacent to both pairs of carbonyl ligands, with C(7)O(7) and C(10)O(10) occupying equatorial positions relative to the Ru(3) framework and C(6)O(6) and C(9)O(9) in semiaxial positions.

For equatorial carbonyl groups, the values of both angles Ru(3)–Ru(2)–C(7), 114.9 (2)°, and Ru(2)–Ru(3)–C(10), 112.5 (2)°, are significantly larger than the corresponding average Ru–Ru–CO(equatorial) angle, 97.95°, in $Ru_3(CO)_{12}$.[28] Comparison with the corresponding angles adjacent to a bridging hydride ligand in $(\mu\text{-}H,\mu\text{-}Cl)Os_3(CO)_{10}$[27] (Os–Os–CO 112.1 (4)° and 112.7 (4)°) clearly indicates a close similarity in the stereochemical influence induced by either a gold–phosphine group or a hydride ligand. This structural analogy can be also inferred from the values of Ru–Ru–CO (semiaxial) angles, i.e., Ru(3)–Ru(2)–C(6), 118.2 (2)°, and Ru(2)–Ru(3)–C(9), 118.6 (2), which compare well with the corresponding angles Os(1)–Os(3)–C(31), 117.8 (4)°, and Os(3)–Os(1)–C(11), 118.4 (4)°, in $Os_3(\mu\text{-}H)(\mu\text{-}Cl)(CO)_{10}$.[27] Such geometric features clearly indicate that the gold–phosphine group even duplicates the apparent size of a bridging hydride ligand.

It should be noted that the mixed-metal cluster complex $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ has low stability and can be only accessed under very mild conditions. Earlier attempts to prepare this complex have likely failed because of too severe reaction conditions. Indeed, we have shown that $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$ decomposes in refluxing cyclohexane with extrusion of the gold atom, yielding $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$ as the main product. The structure of the latter

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complex is closely similar to that reported for $FeRu_2(\mu\text{-}Cl)_2(CO)_8(PR_3)_2$.[32]

Interestingly, abstraction of the gold atom can be also realized upon nucleophilic attack: simple addition of tetraethylammonium chloride at ambiant temperature is sufficient to induce degradation of the mixed-metal cluster, yielding a mixture of anionic and neutral complexes among which we were able to again isolate $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$.[33]

While a number of hydrido cluster complexes have now their gold analogue,[2–16] it should be of interest to know whether a gold–phosphine group can be designed to stabilize complexes for which the corresponding postulated hydrido derivative is unstable. Such studies are currently under investigation in this laboratory.

Registry No. $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, 88181-31-1; $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$, 88181-32-2; $Ru_3(CO)_{12}$, 15243-33-1; $AuPPh_3Cl$, 14243-64-2; Au, 7440-57-5; Ru, 7440-18-8.

Supplementary Material Available: Anisotropic thermal parameters for independent atoms (Table S1), rigid-group parameters (Table S2), root-mean-square amplitudes of vibration (Table S3), and a complete listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

The Molybdenum–Molybdenum Triple Bond. 13.[1] Preparations and Characterization of Bis(β-diketonato)tetraalkoxydimolybdenum and -ditungsten Compounds

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Dinuclear tungsten and molybdenum alkoxides of formula $M_2(OR)_6$ ($M{\equiv}M$) react in hydrocarbon solvents at room temperature with β-diketones, $R'COCH_2COR''$, to give mixed alkoxide–β-diketonate complexes of formula $M_2(OR)_4(R'COCHCOR'')_2$. Various combinations of R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu and R′, R″ = Me, *t*-Bu, and Ph have been made in order to elucidate structures and dynamic solution behavior of this class of compounds. The molecular structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$, determined from a single-crystal X-ray diffraction study, provides the basis for a discussion of the above. There are unbridged $Mo{\equiv}Mo$ bonds united by four ligated metal atoms. The Mo—O bonds, two to OR ligands and two to the didentate acac ligand, lie roughly in a plane. In solution, there is rapid rotation about the $M{\equiv}M$ bonds. From variable-temperature NMR studies of compounds with R′ = Me and R″ = Ph, the bidentate nature of the β-diketonate ligand is established. Only at +110 °C for M = Mo is there evidence for rapid reversible chelate ⇌ monodentate behavior for the β-diketonate ligands. Crystal data for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ at −143 °C: $a = 14.008$ (4) Å, $b = 11.462$ (3) Å, $c = 11.497$ (3) Å, $\alpha = 87.84$ (1)°, $\beta = 92.94$ (1)°, $\gamma = 88.82$ (1)°, $Z = 2$, $d_{calcd} = 1.332$ g cm^{-3} in space group $P\bar{1}$.

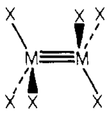
Introduction

The compound $M_2(OR)_6$, where M = Mo[2] and W[3] and R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu, are coordinatively unsaturated and provide good starting materials for the exploration of dinuclear molybdenum and tungsten chemistry.[4] They react reversibly with neutral donor ligands, L, such as amines or tertiary phosphines according to eq 1. The position of

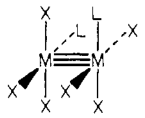
$$M_2(OR)_6 + 2L \rightleftharpoons M_2(OR)_6L_2 \quad K \qquad (1)$$

equilibrium is sensitive to the steric constraints imposed by R and L, and for related compounds $K_W > K_{Mo}$. Indeed the compounds $W_2(OR)_6$, where R = *i*-Pr and CH_2-*t*-Bu, are not known in the absence of coordinating ligands (L = $HNMe_2$, py, or PMe_3) though UV–visible spectra recorded at dilute concentrations (ca. 10^{-4} M) support their free existence according to (1).[4–6]

In reaction 1, ethane-like dimers (I) are converted to compounds where metal atoms are each coordinated to four ligand atoms and are united by unbridged M–M triple bonds (II). The four σ bonds formed to each metal atom in II lie roughly in a plane, and the conformation of the dinuclear species reflects the interactions of the ligands across the Mo–Mo triple bonds. In general, steric repulsive interactions favor staggered conformations, though hydrogen bonding (e.g. L = $HNMe_2$, R = *i*-Pr, and M = W) may cause an eclipsed conformation.[4,5]



I



II

X = OR

The M–M triple bond of configuration $\sigma^2\pi^4$ provides a reservoir of electrons for oxidative-addition reactions[7–9] and also for reactions with π-acid ligands.[4] $M_2(OR)_6$ compounds have been shown to react with CO,[10,11] NO,[12,13] and alkyl and aryl isocyanides[14] to give products in which the $M{\equiv}M$ bond has been cleaved. Similarly, $W_2(O\text{-}t\text{-}Bu)_6$ has been found to

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