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Preparation and X-ray Structure Determination of Tris[bis(diphenylphosphino)methane]diiodotetragold

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The reaction of $Au_4(PPh_3)_4(\mu\text{-}I)_2$ with dppmH (molar ratio 1:3.5; dppmH = $PPh_2CH_2PPh_2$) in THF yields instantaneously $Au_4(dppmH)_3I_2$, whose crystal and molecular structure has been investigated by X-ray analysis. It crystallizes in space group $P\bar{1}$, with unit cell dimensions a = 12.305 (2) Å, b = 14.693 (2) Å, c = 21.238 (3) Å, α = 94.85 (10)°, β = 90.70 (12)°, γ = 67.90 (12)°, V = 3544.2 Å^3, and Z = 2. The gold skeleton can be described as a slightly distorted tetrahedron. One Au atom is coordinated to an iodine (Au–I = 2.593 (2) Å), while the remaining Au triangle is surrounded not only by three bridging dppmH ligands but also by another iodine that caps asymmetrically at rather long distances (3.13–3.67 Å). The Au–Au distances (2.72–2.95 Å) and Au–P distances (2.33–2.39 Å) are normal for gold phosphine clusters. The final R value is 0.072. The ^{197}Au Mössbauer spectrum shows two different Au sites with parameters in accordance with their structural characteristics. $^{31}P[^1H]$ NMR spectra show a fast intramolecular equilibration of the P sites even at −60 °C.

Introduction

Gold clusters with monodentate phosphine ligands have been intensively studied,[1] whereas the use of bidentate phosphine ligands has led to a limited number of clusters, occasionally with most peculiar and interesting structural and physical properties. Well-characterized gold clusters with bidentate phosphine ligands are $[Au_5(dppmH)_3(dppm)](NO_3)_2$[2,3] (dppmH = $PPh_2CH_2PPh_2$, dppm = $PPh_2CHPPh_2^-$), $[Au_6(dppp)_4](NO_3)_2$[4] (dppp = $PPh_2(CH_2)_3PPh_2$), $[Au_{11}(dppp)_5](SCN)_3$,[5,6] and $[Au_{13}(dppmH)_6]^{n+}$.[3]

The title compound $Au_4(dppmH)_3I_2$ can be prepared by the substitution of the phosphine ligands in $Au_4(PPh_3)_4(\mu\text{-}I)_2$[7] with dppmH. Physical data including ^{197}Au Mössbauer and $^{31}P[^1H]$ NMR are described in this report.

Experimental Section

The commercially available bis(diphenylphosphino)methane (dppmH) was used without further purification. Analyses were carried out by Dr. A. Bernhardt, Elbach über Engelskirchen, West Germany. ^{1}H NMR spectra were recorded on a Bruker WH-90 and $^{31}P[^1H]$ NMR spectra on a Varian XL-100 FT spectrometer. Infrared spectra were recorded with a Perkin-Elmer 283 spectrometer. The ^{197}Au Mössbauer spectra were recorded at 4.2 K with the apparatus described earlier.[8] The molecular weight was determined on a Knauer Typ 11.00 vapor pressure osmometer in THF at 37 °C.

$Au_4(PPh_3)_4(\mu\text{-}I)_2$ was prepared according to the literature.[7]

Preparation of $Au_4(dppmH)_3I_2$. To 60 mg of the yellow $Au_4(PPh_3)_4(\mu\text{-}I)_2$ was added 40 mg of dppmH (mole ratio 1:3.5) in 5 mL of THF. Immediately the reaction mixture turned orange-red, and after 5 min 15 mL of petroleum ether (bp 40–60 °C) was added, causing the precipitation of an orange-yellow powder. The yellow supernatant was removed carefully, to the remaining precipitate was added 15 mL of diethyl ether, and after some time the supernatant was removed again. The remaining crude product was purified by washing with small volumes of acetone (3 × 5 mL) and subsequently diethyl ether (2 × 5 mL). Yield: 30–40 mg (50–60%). At room temperature the compound is stable in the solid state and in a solution of THF. Slow decomposition occurs in pyridine and methylene chloride. Red crystals suitable for an X-ray analysis were obtained by slow diffusion of diethyl ether into a THF solution. Anal. Calcd for $Au_4(dppmH)_3I_2$ ($C_{75}H_{66}Au_4I_2P_6$, M_r = 2194.875): C, 41.04; H, 3.03; Au, 35.90; I, 11.56; P, 8.47. Found: C, 41.00; H, 3.10; Au, 35.65; I, 11.38; P, 8.65. $^{31}P[^1H]$ NMR: one sharp peak (line width = 3 Hz) in THF at −37.7 ppm downfield relative to TMP ($OP(OMe)_3$). ^{1}H NMR ($CDCl_3$): aromatic protons, 6.4–7.6 ppm, multiplet (60 H); aliphatic protons, 1.8–4.8 ppm, multiplet (6 H); chemical shifts relative to Me_4Si. IR (CsI pellet): only bands originating from coordinated dppmH could be assigned. Any Au–I is not within the range of the apparatus. The ^{197}Au Mössbauer data can be fitted adequately with two pairs of lines (see Figure 1 and Table II for the parameters). The molecular weight, 2240, is in good agreement with the theoretical molecular weight of 2194.

Table I. Experimental Details of the X-ray Diffraction Study of Tris[bis(diphenylphosphino)methane]diiodotetragold

formula	$C_{75}H_{66}Au_4I_2P_6$
space group	$P\bar{1}$
a, Å	12.305 (2)
b, Å	14.693 (2)
c, Å	21.238 (3)
α, deg	94.85 (10)
β, deg	90.70 (12)
γ, deg	67.90 (12)
V, Å^3	3544.2
Z	2
instrument	Nonius CAD-4 diffractometer
radiation used	Cu Kα graphite monochromated (λ = 1.5418 Å)
type of scan	ω–2θ
no. of measured reflcns	20 524
no. of independent reflcns	12 063
no. of data with $I > 3\sigma(I)$	9743
final R value	0.072

Crystal Structure Determination of $Au_4(PPh_2CH_2PPh_2)_3I_2$. a. Collection and Reduction of the Data. Crystallographic data were collected on a single-crystal CAD-4 diffractometer using Cu Kα radiation (λ = 1.54018 Å), monochromated with a graphite-crystal monochromator. The unit cell dimensions were calculated from the setting angles of 25 reflections having 26° < 2θ < 30°. The lattice constants are a = 12.305 (2) Å, β = 14.693 (2) Å, c = 21.238 (3) Å, α = 94.85 (10)°, β = 90.70 (12)°, γ = 67.90 (12)°, and V = 3544.2 Å^3; space group is $P\bar{1}$, with ρ_c = 2.06 g·cm^{-3} and Z = 2, and the linear absorption coefficient μ(Cu) is 240.0 cm^{-1}. The data were collected by using the ω–2θ scan mode with a variable scan speed, with a maximum of 30 s/reflection. A total of 20 524 reflections with 1° < θ < 65° were recorded ($\pm h,\pm k,\pm l$). Three standard reflections were measured after every 1800 s of X-ray exposure time. Their intensities decreased to about 80% of their initial values. After averaging of equivalent reflections (R_{av} [$=\sum(|I| - |\bar{I}|)/\sum|I|$] = 0.049, including all reflections) 12 063 reflections remained of which 9743

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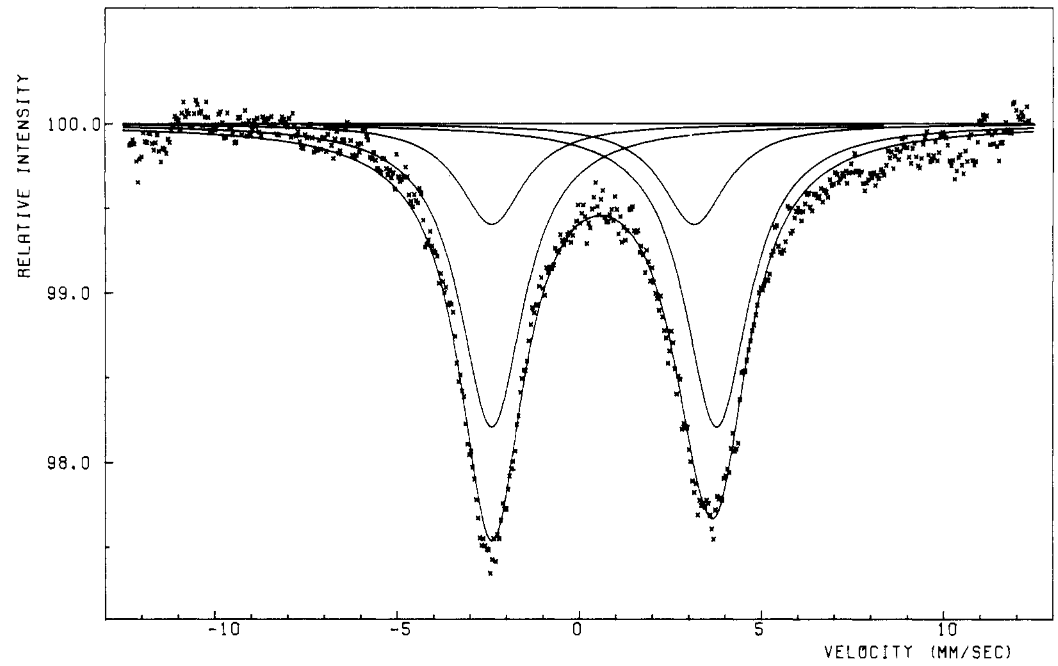

Figure 1. ^{197}Au Mössbauer spectrum of $Au_4(dppmH)_3I_2$.

Table II. ^{197}Au Mössbauer Parameters for Some Gold Clusters

compd	Au site	attributed to Au atoms no.	QS, mm/s	IS,[a] mm/s	line width, mm/s	rel intens
$Au_4(dppmH)_3I_2$	1	1, 2, 3	6.18	0.69	2.15	3
	2	4	5.56	0.38	2.15	1
$[Au_5(dppmH)_3(dppm)]^{2+}$	1	1, 2, 3	7.38	1.43	2.22	3
	2	4	6.65	2.45	2.22	1
	3	5	9.03	3.62	2.22	1
$Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$	Au-I		4.12	0.00	2.2	

[a] Relative to ^{197}Pt source.

had $I > 3\sigma_I$ (σ_I based on counting statistics). The intensity data of the remaining 12063 reflections were corrected for Lorentz and polarization effects and then reduced to $|F_o|$ values. Absorption correction was not done, as the crystal faces could not be measured accurately.

b. Solution and Refinement of the Structure. The positions of three gold atoms were found in a Patterson map. One more gold atom and the iodine and phosphorus atoms were positioned by the DIRDIF procedure.[9] The carbon atoms were located in several consecutive Fourier maps. All 9743 observed reflections were used in the refinement by full-matrix least-squares methods, with anisotropic temperature factors for the gold, iodine, and phosphorus atoms and constrained phenyl rings. The weight for each reflection was calculated according to the formula $w = (\sigma_I^2 \pm 0.005F^2)^{-1}$ (σ_I based on counting statistics). The refinement converged to disagreement factors R $[=\sum(|F_o| - |F_c|)/\sum|F_o|] = 0.072$ and R_w $[=[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}] = 0.104$. A final difference Fourier map showed a residual electron density of 1.1 e/Å^3 near the gold atoms.

All routine crystallographic calculations were performed with use of the X-ray 76 programs.[10] The atomic scattering factors and the dispersion correction for the gold atoms were taken from Tables 2.2 B and 2.3.1 of ref 11. Positional and thermal parameters for Au, P, I, and bridge carbon atoms are provided in Table III. A selection of bond distances and angles is given in Table IV. Furthermore, the structure factor table and the positional thermal parameters for the phenyl atoms are available as supplementary material.

Table III. Positional Coordinates and Isotropic Thermal Parameters (×10^2, Å^2) for Au, P, I, and Bridging Carbon Atoms of $Au_4(dppmH)_3I_2$ (Esd's within Parentheses)[a]

	x	y	z	U_{eq}	U_{iso}
Au (1)	0.45317 (5)	0.12320 (4)	0.27135 (2)	2.19 (2)	
(2)	0.31304 (5)	0.31996 (4)	0.31940 (2)	1.95 (2)	
(3)	0.41868 (5)	0.28026 (4)	0.19126 (2)	1.89 (2)	
(4)	0.24031 (5)	0.22122 (4)	0.22117 (3)	2.59 (2)	
1 (1)	0.58155 (9)	0.27041 (8)	0.33800 (5)	3.94 (4)	
(2)	0.0725 (2)	0.1747 (2)	0.17176 (7)	9.12 (9)	
P (11)	0.5577 (4)	0.0118 (2)	0.1881 (2)	1.8 (1)	
(12)	0.4505 (4)	0.0555 (3)	0.3676 (2)	3.2 (1)	
(21)	0.2717 (3)	0.2591 (3)	0.4126 (2)	2.4 (1)	
(22)	0.2735 (3)	0.4882 (3)	0.3142 (1)	1.7 (1)	
(31)	0.4140 (3)	0.4401 (2)	0.1912 (2)	1.9 (1)	
(32)	0.4927 (3)	0.1706 (3)	0.0984 (2)	2.1 (1)	
C (1)	0.498 (1)	0.048 (1)	0.1099 (6)		2.4 (3)
(2)	0.395 (1)	0.149 (1)	0.4356 (7)		3.8 (3)
(3)	0.385 (1)	0.512 (1)	0.2689 (7)		3.3 (3)

[a] $U_{eq} = {}^1/_3 \Sigma_i \Sigma_j a_i a_j U_{ij}$.

Results and Discussion

The Au skeleton forms a slightly distorted tetrahedron (see Figure 2). The top Au(4) atom is coordinated to an iodine with a bond distance of 2.593 (2) Å, which is normal for a terminal Au–I in gold clusters (Au–I = 2.600 (5) Å in $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$)[12]). The I(2)–Au(4) vector lies almost perpendicular (82.5°) to the basal plane of the tetrahedron. The Au–Au distances from top to base are shorter (2.72–2.77 Å) than within the base (2.86–2.95 Å) but at normal values

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Table IV. Selected Bond Distances (Å) and Angles (deg) for $Au_4(dppmH)_3I_2$ (Esd's within Parentheses)

	Au-Au (0.001)		
1-2	2.858	2-3	2.947
1-3	2.883	2-4	2.771
1-4	2.724	3-4	2.744
	Au-I (0.002)		
1-1	3.343	3-1	3.668
2-1	3.132	4-2	2.593
	Au-P (0.004)		
1-11	2.334	2-22	2.345
1-12	2.354	3-31	2.327
2-21	2.375	3-32	2.391
	P-C all between 1.81 and 1.85		
	Au-Au-Au all between 57.27 and 64.59		
	Au-I-Au (0.02)		
1-1-2	52.25	2-1-3	50.61
1-1-3	48.28		
	Au-Au-I (0.05)		
1-4-2	136.25	3-4-2	142.50
2-4-2	147.71		
	Au-P-C all between 110.5 and 115.3		
	P-C-P all between 109.8 and 111.0		

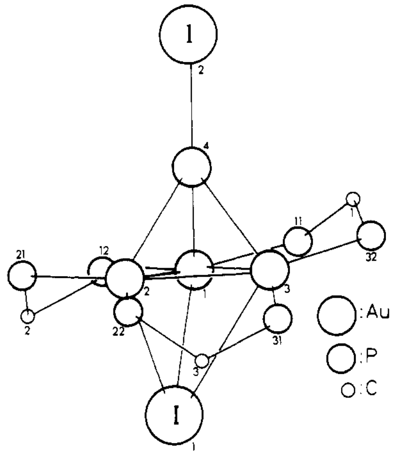

Figure 2. Molecular structure of $Au_4(dppmH)_3I_2$ with numbering scheme; phenyl rings have been omitted for clarity.

for gold clusters (see Table IV).

Each gold atom in the basal triangle is coordinated to two phosphorus atoms of bridging dppmH ligands and to I(1), which is asymmetrically μ_3-coordinated at rather long Au-I(1) distances (3.13–3.67 Å). This is the first example of a triply bridging iodine, capping a triangular metal face in a gold cluster compound. A μ_2-bridging iodine has been reported for $Au_4(PPh_3)_4(\mu\text{-}I)_2$[7] with a mean Au-I distance of 2.945 Å. The increase in Au-I bond length in going from terminal via bridging to capping geometries is not surprising, since bond weakening is to be expected in this order. The differences in the structures of $Au_4(PPh_3)_4I_2$ and $Au_4(dppmH)_3I_2$ are probably due to the steric constraint of the ligands (see Figures 2 and 4). The Au–P distances (2.33–2.39 Å) lie in the range normally found for gold phosphine clusters.

The structural similarity with $Cu_3(dppmH)_2(\mu\text{-}I)(\mu_3\text{-}I)_2$[13] and $[Au_5(dppmH)_3(dppm)]^{2+}$[2,3] (dppm = $PPh_2CHPPh_2^-$; see Figure 3) is interesting. $Cu_3(dppmH)_2(\mu\text{-}I)(\mu_3\text{-}I)_2$ has been described as a triangle of copper atoms connected by triple-bridging iodine atoms above and below the plane of the copper atoms. $[Au_5(dppmH)_3(dppm)]^{2+}$ and $Au_4(dppmH)_3I_2$ contain a triangle of gold atoms [Au(1), Au(2), and Au(3)] with three bridging dppmH ligands. In the Au_5 cluster Au(4) is bonded to a phosphino group.

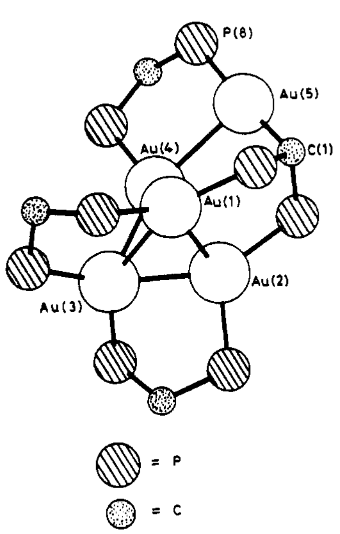

Figure 3. Molecular structure of $[Au_5(dppmH)_3(dppm)]^{2+}$ (dppm = $PPh_2CHPPh_2^-$); phenyl rings have been omitted for clarity.

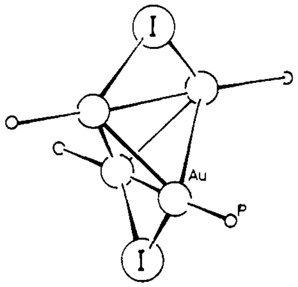

Figure 4. Molecular structure of $Au_4(PPh_3)_4I_2$; phenyl rings have been omitted for clarity.

The ^{197}Au Mössbauer spectrum (Figure 1) of $Au_4(dppmH)_3I_2$ could be fitted with two pairs of lines with an intensity ratio of 3:1. From the Mössbauer parameters listed in Table II, it can be seen that the set of gold atoms [Au(1), Au(2), and Au(3)] coordinated to phosphines and capping I(1) have parameters smaller than those of the similar Au triangle in $[Au_5(dppmH)_3(dppm)]^{2+}$. This is caused by a more spherical environment for these gold atoms in $Au_4(dppmH)_3I_2$, since an extra ligand (I(1)) is present in this case. The pair of lines attributable to the Au(4)–I(2) site has parameters larger than those of an Au–I site in $Au_{11}[P(p\text{-}ClC_6H_4)_3]_7I_3$.[5] This is probably due to the lower connectivity for the Au(4)–I(2) site resulting in a less spherical environment. The $^{31}P[^1H]$ NMR spectrum of $Au_4(dppmH)_3I_2$ at room temperature in THF gives one sharp peak at −37.7 ppm (downfield relative to TMP), which indicates a magnetic equivalence of the phosphorus sites in solution. The solid-state $^{31}P[^1H]$ NMR spectrum is however broad and complicated, indicating an equilibration of the phosphorus sites in solution.[14] Furthermore, no fast intermolecular exchange reactions do occur since the peak position of the singlet of $Au_4(dppmH)_3I_2$ in the solution $^{31}P[^1H]$ NMR spectrum does not shift upon addition of free dppmH. Variable-temperature $^{31}P[^1H]$ NMR measurements in CD_2Cl_2 down to −60 °C show only a slight broadening (line width = 5 Hz), indicating a fast equilibration process even at low temperatures. Internal rearrangement of

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the molecule involving Au–P bond breaking and formation is not very probable in view of the energies involved in such a process. A fluxional behavior without bond breaking is more appropriate, since the structure of the molecule in the crystalline state needs only slight displacements in the gold–ligand system for the equilibration of the P atoms. A more detailed report describing the fluxionality of gold phosphine clusters in solution as studied by variable-temperature and solid-state $^{31}P[^1H]$ NMR will be submitted shortly.

Acknowledgment. We thank Prof. Dr. Ir. J. J. Steggerda and Prof. Dr. P. T. Beurskens for their continuous interest and useful discussions. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Pure Research (ZWO).

Registry No. $Au_4(dppmH)_3I_2$, 86885-93-0; $Au_4(PPh_3)_4(\mu\text{-}I)_2$, 78519-63-8.

Supplementary Material Available: Listings of structure factors, anisotropic thermal parameters, and positional and thermal parameters for the phenyl C atoms (77 pages). Ordering information is given on any current masthead page.

Contribution from the Centro di Studio del CNR sulla Sintesi e Struttura dei Composti
dei Metalli di Transizione nei Bassi Stati di Ossidazione, 20133 Milano, Italy

Stepwise Degradation of the Unsaturated Cluster Tetrakis(μ-hydrido)decacarbonyltrirhenate(1−) by Reaction with Iodine. Crystal and Molecular Structures of the Tetraethylammonium Salts of the New Anions Bis(μ-hydrido)bis(μ-iodo)decacarbonyltrirhenate(1−) and (μ-Hydrido)bis(μ-iodo)hexacarbonyldirhenate(1−)

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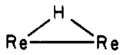
The reactions of the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with iodine have been investigated in various solvents. While in donor solvents, such as ethanol, the only product obtained is the anion $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$, in dichloromethane and similar solvents the reaction proceeds with evolution of H_2, giving mixtures of products of variable composition, depending on the amounts of iodine. The process implies stepwise degradation, with progressive substitution of



bonds by Re–I–Re ones, leading, as a final result, to the dimeric species $[Re_2(\mu\text{-}I)_3(CO)_6]^-$ and $Re_2(\mu\text{-}I)_2(CO)_8$. The intermediate products have been isolated and characterized as $[Re_3(\mu\text{-}H)_3(\mu\text{-}I)(CO)_{10}]^-$ (first step), $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ (second step), and $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$ *plus* $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$ (third step). All the compounds have been spectroscopically characterized, and the crystal structures of the novel anions $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ and $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$, as their tetraethylammonium salts, have been investigated by single-crystal X-ray analysis. The former species gives monoclinic crystals, space group $P2_1/n$, with $a = 9.685$ (2) Å, $b = 12.679$ (3) Å, $c = 24.439$ (5) Å, $\beta = 98.18$ (1)°, and $Z = 4$. The structure solution and refinements were based on 2646 significant counter data, the final R value being 0.025. The second species is monoclinic, space group $C2/c$, with $a = 14.601$ (1) Å, $b = 11.794$ (1) Å, $c = 14.548$ (1) Å, $\beta = 110.88$ (1)°, and $Z = 4$. Refinements, performed with 1353 significant counter intensities, led to a final R value of 0.030. The anion $[Re_3(\mu\text{-}H)_2(\mu\text{-}I)_2(CO)_{10}]^-$ contains an open trimetal array, derived from a triangle with one broken edge bridged by an iodine atom. It shows one long hydrogen-bridged Re–Re interaction with 3.321 (1) Å, while the other Re–Re bond, double-bridged by one hydride and one iodide ligand, is shorter, 3.107 (1) Å. The values of the Re–I interactions are in the range 2.797 (1)–2.841 (1) Å. In the dinuclear anion $[Re_2(\mu\text{-}H)(\mu\text{-}I)_2(CO)_6]^-$, of idealized C_{2v} symmetry, the rhenium atoms display an almost octahedral coordination with three CO groups and the bridging I and H atoms. Differently from other known $Re(\mu\text{-}X)_3Re$ systems, where X is a three-electron donor group, in this anion a formal direct metal–metal bond is required and this is reflected in the value of the Re–Re distance of 2.954 (1) Å. Also in the dinuclear compound $Re_2(\mu\text{-}H)(\mu\text{-}I)(CO)_8$, mainly characterized by mass spectroscopy, a Re–Re bond is considered to be present, representing a situation intermediate between those of $Re_2(\mu\text{-}H)_2(CO)_8$ and of $Re_2(\mu\text{-}I)_2(CO)_8$.

Introduction

The current interest in carbonyl cluster chemistry, after a fruitful period during which the principal aims were the synthesis and the characterization of new species, is now focused on the study of their reactivity. In the field of low-nuclearity clusters a particular interest is devoted to unsaturated compounds, such as $Os_3(\mu\text{-}H)_2(CO)_{10}$,[1a] whose chemistry has been widely studied:[1b] it contains a formally double metal–metal bond on the basis of the 18-electron rule, and the $Os(\mu\text{-}H)_2Os$ system has been described as a four-center four-electron bond[1c] or as a partially protonated double bond.[1d] Another member of this class of compounds is the anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ (**1**)[2] (represented hereafter with a formal Re=Re double bond), and we are presently investigating its reactivity.

Unlike the isoelectronic $Os_3(\mu\text{-}H)_2(CO)_{10}$, it does not readily add nucleophilic ligands such as CO, PR_3, and unsaturated hydrocarbons, but it reacts rather easily with molecules that

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(1) (a) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859. (b) See for instance: Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1978**, *25*, 145. Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304 and references therein. (c) Broach, R. W.; Williams, J. W. *Ibid.* **1979**, *18*, 314. (d) Churchill, M. R.; De Boer, B. G.; Rotella, F. J. *Ibid.* **1976**, *15*, 1843.

(2) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1977**, *136*, C49.