Heterobimetallic Complexes of Gold and Mercury. Syntheses and Characterizations of $Hg^{II}(CH_2P(S)Ph_2)_2(Au^ICl)_2$ and $Hg^{II}Au^I(CH_2P(S)Ph_2)_2Au^{III}Cl_4$

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The trinuclear compound $Hg^{II}(CH_2P(S)Ph_2)_2(Au^ICl)_2$ (2) was synthesized by the reaction of $Hg^{II}(CH_2P(S)Ph_2)_2$ (1) with 2 equiv of Au(THT)Cl (THT = tetrahydrothiophene) in a CH_2Cl_2 solution. Oxidation of 2 by 1 equiv of $C_6H_5ICl_2$ yielded the mixed-valence trinuclear compound $Hg^{II}Au^I(CH_2P(S)Ph_2)_2Au^{III}Cl_4$ (3). The crystal structures of 2 and 3 were determined by single-crystal X-ray diffraction analyses. 2 and 3 have one-dimensional chain structures in the solid. Crystal data: 2, $C_{26}H_{24}HgAu_2Cl_2S_2P_2\cdot{}^1/_2C_5H_{12}$, space group $P\bar{1}$, $a = 11.930$ (4) Å, $b = 13.452$ (4) Å, $c = 10.516$ (4) Å, $\alpha = 108.44$ (2)°, $\beta = 90.61$ (3)°, $\gamma = 81.06$ (2)°, $V = 1580.1$ (8) Å^3, $Z = 2$, $R = 0.0432$ and $R_w = 0.0489$ for refinement of 154 least-squares parameters with 2744 reflections ($F_o^2 \geq 3\sigma(F_o^2)$); 3, $C_{26}H_{24}HgAu_2Cl_4S_2P_2\cdot CH_2Cl_2$, space group $P\bar{1}$, $a = 10.199$ (6) Å, $b = 12.340$ (3) Å, $c = 15.064$ (4) Å, $\alpha = 74.17$ (2)°, $\beta = 82.76$ (3)°, $\gamma = 82.27$ (3)°, $V = 1799$ (1) Å^3, $Z = 2$, $R = 0.0505$ and $R_w = 0.0501$ for refinement of 178 least-squares parameters with 1680 reflections ($F_o^2 \geq 3\sigma(F_o^2)$).

Introduction

Syntheses of heterobimetallic compounds and the study of their reactivities continue to be strong in organometallic chemistry, promoted by the unique role of bimetallic catalysts in industry.[1] Mankind continues to be fascinated by the mythical metal, gold, and the many mysterious functions of this noble metal and its metal alloys in medicine and industry.[2] Metal-metal interactions in gold compounds and the role these interactions play in catalysis are of special interest to us. Some unique reactions of multinuclear gold complexes have been discovered recently. Studies of dimeric Au-Au systems have demonstrated that the chemical and physical behavior of one metal center can be greatly influenced by the presence of the other metal centers. However, many fundamental questions remain unanswered related to the specific influence of one metal center on the other metal center. What are the controlling factors? In order to understand this question, the design and syntheses of heterobimetallic compounds are the crucial first steps.

Syntheses of heterobimetallic compounds with the bidentate methylenediphenylphosphine sulfide anionic (MTP) ligand, $CH_2P(S)Ph_2^-$, have been developed in our laboratory. Compounds such as $Au^I_2Pt^{II}(MTP)_4$, $Au^I_2Pb^{II}(MTP)_4$, and $Au^ITl^I(MTP)_2$ have been obtained. Their interesting chemical and physical properties have been described in previous papers.[3b,4] Recently, in a preliminary communication,[5] we reported the synthesis and crystal structure of $Hg(MTP)_2$ (1) and its use as a precursor for the synthesis of $Hg^{II}Au^I(MTP)_2PF_6$. Here we report the synthesis and structure of the novel trimetallic compound $Hg^{II}(MTP)_2(Au^ICl)_2$ (2) obtained by the reaction of $Hg^{II}(MTP)_2$ with $Au^I(THT)Cl$ (THT = tetrahydrothiophene) and also a the mixed-valence trimetallic compound $Hg^{II}Au^I(MTP)_2Au^{III}Cl_4$ obtained by the oxidation of 2 with $C_6H_5ICl_2$.

Experimental Section

All reactions were carried out under a nitrogen atmosphere at 22 °C. All solvents were dried and freshly distilled before use. Au(THT)Cl and $Hg(MTP)_2$ were prepared according to the literature.[4,6] ^{1}H NMR spectra were taken on a Varian XL-200 spectrometer at 200 MHz. Elemental analyses were done by Desert Analytics Co., Tucson, AZ.

Synthesis of $Hg^{II}(MTP)_2(Au^ICl)_2$ (2). $Hg(MTP)_2$ (1; 20 mg, 0.030 mmol) was placed in a Schlenk tube containing 3 mL of CH_2Cl_2. Au(THT)Cl (20 mg, 0.062 mmol) was added to the solution. The white suspension of 1 dissolved immediately, and the solution became clear. After the mixture was stirred for 2 h, white solid precipitated from the solution. Diethyl ether (5 mL) was added to complete the precipitation of the product. The solution was decanted. The white solid was washed with diethyl ether several times and dried under vacuum. The colorless solid of 2 (mp 178-180 °C) was obtained in 88% yield (30 mg, 0.027 mmol). Anal. Calcd for $C_{26}H_{24}Cl_2P_2S_2Au_2Hg$: C, 27.68; H, 2.13. Found: C, 27.85; H, 1.91. ^{1}H NMR ($CDCl_3$, δ): 2.46 (d, 4 H, $^2J_{P-H}$ = 12 Hz, $^2J_{Hg-H}$ = 166 Hz); 7.30-7.60 (m, 12 H); 7.65-7.90 (m, 8 H).

Synthesis of $Hg^{II}Au^I(MTP)_2Au^{III}Cl_4$ (3). 2 (32 mg, 0.028 mmol) was placed in a Schlenk tube containing 4 mL of CH_2Cl_2. $C_6H_5ICl_2$ (9 mg, 0.033 mmol) was added to the solution. The white solid of 2 disappeared rapidly and the solution turned yellow. After the mixture was stirred for 1.5 h, excess diethyl ether was added to precipitate the product. The yellow solid was isolated by centrifugation and washed with diethyl ether. Recrystallization of the raw product from CH_2Cl_2/diethyl ether at 0 °C produced orange crystals of 3 (mp 165 °C) in 68% yield (23 mg, 0.019 mmol). Anal. Calcd for $C_{26}H_{24}Cl_4P_2S_2Au_2Hg$: C, 26.04; H, 2.00. Found: C, 26.19; H, 1.94. ^{1}H NMR (CD_2Cl_2, δ): 2.51 (d, 4 H, $^2J_{P-H}$ = 12 Hz, $^2J_{Hg-H}$ = 152 Hz); 7.40-7.90 (m, 20 H).

Crystal Structure Determinations by X-ray Diffraction. Colorless crystals of 2 for X-ray diffraction analysis were grown by diffusion of pentane into the CH_2Cl_2 solution of 2 at 22 °C. Orange needles of 3 suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into CH_2Cl_2 at 0 °C.

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Table I. Crystallographic Data for 2 and 3

	2	**3**
formula	$C_{26}H_{24}HgAu_2Cl_2S_2P_2\cdot{}^1/_2C_5H_{12}$	$C_{26}H_{24}HgAu_2Cl_4S_2P_2\cdot CH_2Cl_2$
fw	1163.96	1283.65
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.930 (4)	10.199 (6)
b, Å	13.452 (4)	12.340 (3)
c, Å	10.516 (4)	15.064 (4)
α, deg	108.44 (2)	74.17 (2)
β, deg	90.61 (3)	82.76 (3)
γ, deg	81.06 (2)	82.27 (3)
V, Å^3	1580.1 (8)	1799 (1)
Z	2	2
d_{calc}, g cm^{-3}	2.44	2.37
cryst siz, mm	0.20 × 0.20 × 0.20	0.08 × 0.10 × 0.40
F(000), e	1070	1180
μ(Mo Kα), cm^{-1}	148.5	133.4
radiation (Mo Kα), Å	0.71069	
temp, °C	22	
scan method	Wyckoff	
range, 2θ, deg	4–45	4–40
no. of rflns measd	4403	3152
no. of rflns, $F_o^2 \geq 3\sigma(F_o^2)$	2744	1680
no. of params refined	154	178
transmissn factors; max, min	0.981, 0.525	not applied
R^a	0.0432	0.0505
$R_w{}^b$	0.0489	0.0501
largest shift/esd, final cycle	0.004	0.007
largest peak, e Å^{-3}	1.97	1.26
goodness-of-fit indicator^c	1.256	1.498

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + |g|F_o^2]$. $g = 0.00049$ for **2**; $g = 0.00029$ for **3**. ^{c}Goodness to fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

Crystals were mounted on glass fibers and sealed with epoxy. Unit cell constants were determined from 25 machine-centered reflections. Data were collected with graphite-monochromated Mo Kα radiation at ambient temperature with a Nicolet R3m/E diffractometer controlled by a Data General Nova 4 minicomputer. Data in the range of 4° ≤ 2θ ≤ 45° ($|h| \leq 13$, $|k| \leq 15$, $l \leq 12$) were collected for **2**. Data in the range of 4° ≤ 2θ ≤ 40° ($h \leq 10$, $|k| \leq 12$, $|l| \leq 15$) were collected for **3**. At the end of data collection (4–40°) for **3** the crystal had decayed by about 40%. Therefore, high-angle reflections and azimuthal data for empirical absorption corrections were not collected. All data were corrected for decay, Lorentz, and polarization effects. Empirical absorption corrections were applied for **2**. Data processing was performed on a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic software (version 5.1). Scattering factors, including terms for anomalous dispersion, were taken from ref 7.

The crystals of **2** and **3** belong to the triclinic crystal system. Crystals of **2** were solvated by pentane molecules (0.5 pentane/molecule of **2**). In the lattice the pentane molecule is disordered. Crystals of **3** were solvated by CH_2Cl_2 molecules (1 CH_2Cl_2/molecule of **3**). These solvent molecules were refined successfully. The positions of metal atoms in **2** and **3** were determined by heavy-atom methods. All non-hydrogen atoms were located by subsequent difference Fourier syntheses. Metal, S, P, and Cl atoms were refined anisotropically. Phenyl rings were refined as rigid bodies with fixed C–C distances 1.395 Å, and C–C–C angles, 120°. The positions of hydrogen atoms on phenyl rings were calculated by using fixed C–H bond lengths, 0.96 Å. Their contributions were included in the structure factor calculations. The largest peak in the final difference map of **2**, 1.97 e/Å^3, is 1.19 Å from the Au(2) atom. The largest peak in the final difference Fourier map of **3**, 1.26 e/Å^3, is 1.16 Å from the Hg atom. C(4), C(5), and C(6) atoms of the disordered pentane molecule were refined with fixed 50% occupancies, while C(3) was refined with fixed 100% occupancy. The data from crystallographic analyses are given in Table I.

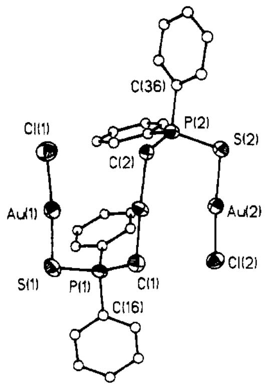
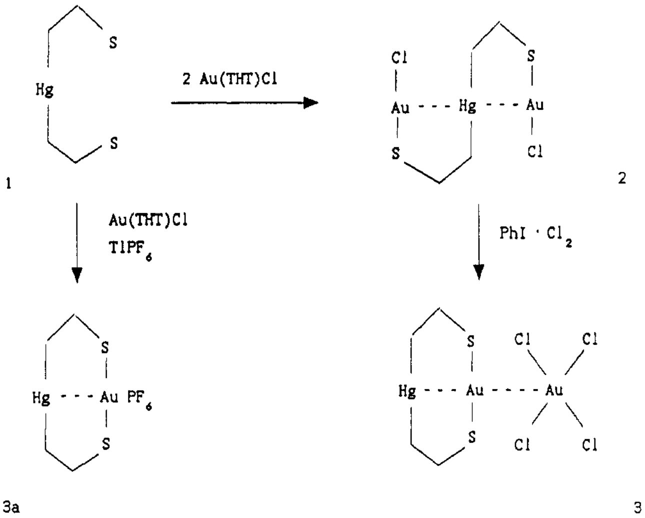


Figure 1. Molecular structure of **2** (50% thermal ellipsoids) with the labeling scheme.

Scheme I



Results and Discussion

Synthesis and Crystal Structure of $Hg^{II}(MTP)_2(Au^ICl)_2$ (2). We reported[5] previously that the reaction of $Hg^{II}(MTP)_2$ with 1 equiv of Au(THT)Cl in the presence of $TlPF_6$ in CH_2Cl_2 solution yields the dinuclear complex $HgAu(MTP)_2PF_6$ (**3a**). If, however, 2 equiv of Au(THT)Cl reacts with $Hg^{II}(MTP)_2$ (**1**) in the absence of $TlPF_6$, the new trinuclear complex $Hg^{II}(MTP)_2(Au^ICl)_2$ (**2**) is obtained quantitatively (Scheme I). Compound **2** is colorless and air-stable. It is only slightly soluble in warm $CHCl_3$ or CH_2Cl_2. The ^1H NMR spectrum of **2** resembles that of **3a** except that the $^2J_{Hg-H}$ constant is larger than that observed for **3a**. The crystal structure of **2** was determined by single-crystal X-ray diffraction analysis.

Atomic coordinates and thermal parameters for **2** are given in Table II. Bond lengths and angles are listed in parts a and b, respectively, of Table III. The molecular structure of **2** is shown in Figure 1. As found in **3a**, the Hg atom is linearly coordinated to two carbon atoms with typical Hg–C bond distances: Hg–C(1) = 2.13 (2) Å, Hg–C(2) = 2.16 (2) Å, C(1)–Hg–C(2) = 178.1 (8)°. The two Au^I atoms are linearly coordinated to one chlorine atom and one sulfur atom with bond lengths and angles similar to those found in $Au^I(S(CH_2Ph)_2)Cl$[8a] and Au^I(trithia-

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for Compound 2

atom	x	y	z	U_{iso}[b]
Au(1)	1530 (1)	745 (1)	10823 (1)	40 (1)*
Au(2)	1578 (1)	27 (1)	4442 (1)	40 (1)*
Hg	897 (1)	292 (1)	7638 (1)	36 (1)*
Cl(1)	1639 (4)	−993 (4)	10676 (6)	56 (2)*
Cl(2)	1538 (4)	1787 (4)	4687 (5)	49 (2)*
S(1)	1387 (5)	2516 (4)	11181 (5)	54 (2)*
S(2)	1705 (4)	−1746 (4)	3989 (5)	44 (2)*
P(1)	1704 (4)	2562 (4)	9312 (5)	35 (2)*
P(2)	2083 (4)	−2037 (4)	5743 (5)	34 (2)*
C(1)	721 (15)	1969 (15)	8096 (20)	45 (5)
C(2)	1062 (14)	−1415 (13)	7105 (17)	31 (4)
C(11)	1713 (11)	4733 (11)	10646 (11)	66 (7)
C(12)	1714 (11)	5778 (11)	10680 (11)	72 (7)
C(13)	1561 (11)	6050 (11)	9508 (11)	64 (6)
C(14)	1406 (11)	5276 (11)	8301 (11)	83 (8)
C(15)	1405 (11)	4231 (11)	8267 (11)	53 (6)
C(16)	1559 (11)	3960 (11)	9440 (11)	42 (5)
C(21)	3448 (5)	1385 (8)	7406 (10)	50 (5)
C(22)	4590 (5)	1050 (8)	6992 (10)	57 (6)
C(23)	5434 (5)	1339 (8)	7901 (10)	58 (6)
C(24)	5137 (5)	1964 (8)	9224 (10)	69 (7)
C(25)	3995 (5)	2299 (8)	9639 (10)	61 (6)
C(26)	3150 (5)	2010 (8)	8730 (10)	33 (4)
C(31)	3103 (10)	−4090 (13)	5600 (14)	79 (8)
C(32)	3152 (10)	−5189 (13)	5218 (14)	110 (10)
C(33)	2251 (10)	−5653 (13)	4560 (14)	83 (8)
C(34)	1300 (10)	−5020 (13)	4284 (14)	62 (6)
C(35)	1250 (10)	−3922 (13)	4667 (14)	50 (5)
C(36)	2152 (10)	−3457 (13)	5324 (14)	48 (5)
C(41)	4355 (10)	−2072 (10)	5295 (9)	48 (5)
C(42)	5455 (10)	−1932 (10)	5690 (9)	51 (6)
C(43)	5661 (10)	−1481 (10)	7043 (9)	60 (6)
C(44)	4767 (10)	−1170 (10)	8001 (9)	54 (6)
C(45)	3667 (10)	−1310 (10)	7606 (9)	54 (6)
C(46)	3461 (10)	−1761 (10)	6253 (9)	39 (5)
C(3)	5187 (26)	5049 (26)	733 (29)	114 (11)
C(4)	4455 (34)	4506 (33)	2632 (43)	56 (12)
C(5)	4694 (34)	5045 (33)	1931 (42)	57 (12)
C(6)	5337 (33)	5864 (33)	1743 (41)	54 (12)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic U is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å) and Angles (deg)[a] for 2

(a) Bond Lengths			
Au(1)–Hg	3.310 (1)	Au(1)–Cl(1)	2.278 (6)
Au(1)–S(1)	2.270 (6)	Au(2)–Hg	3.361 (1)
Au(2)–Cl(2)	2.292 (5)	Au(2)–S(2)	2.260 (5)
Hg–C(1)	2.130 (20)	Hg–C(2)	2.161 (17)
S(1)–P(1)	2.027 (8)	S(2)–P(2)	2.036 (8)
P(1)–C(1)	1.805 (19)	P(1)–C(16)	1.823 (16)
P(1)–C(26)	1.800 (8)	P(2)–C(2)	1.788 (16)
P(2)–C(36)	1.807 (17)	P(2)–C(46)	1.782 (13)
C(3)–C(5)	1.397 (57)	C(3)–C(6)	1.297 (46)
C(3)–C(3)′	1.571 (62)	C(4)–C(5)	1.248 (73)
C(5)–C(6)	1.498 (69)		
(b) Bond Angles			
Hg–Au(1)–Cl(1)	93.0 (1)	Cl(2)–Au(2)–S(2)	174.1 (2)
Cl(1)–Au(1)–S(1)	174.6 (2)	Au(1)–Hg–C(1)	85.1 (6)
Hg–Au(2)–S(2)	87.6 (1)	Au(1)–Hg–C(2)	96.8 (5)
Au(1)–Hg–Au(2)	151.8	C(1)–Hg–C(2)	178.1 (8)
Au(2)–Hg–C(1)	88.8 (6)	Au(2)–S(2)–P(2)	106.1 (2)
Au(2)–Hg–C(2)	89.5 (5)	S(1)–P(1)–C(16)	106.6 (4)
Au(1)–S(1)–P(1)	101.9 (2)	S(1)–P(1)–C(26)	112.1 (5)
S(1)–P(1)–C(1)	113.7 (8)	C(16)–P(1)–C(26)	105.2 (6)
C(1)–P(1)–C(16)	107.6 (8)	S(2)–P(2)–C(36)	104.1 (5)
C(1)–P(1)–C(26)	111.0 (6)	S(2)–P(2)–C(46)	111.4 (5)
S(2)–P(2)–C(2)	116.1 (7)	C(36)–P(2)–C(46)	106.4 (6)
C(2)–P(2)–C(36)	107.7 (8)	Hg–C(2)–P(2)	110.1 (10)
C(2)–P(2)–C(46)	110.4 (6)	P(1)–C(16)–C(15)	118.3 (4)
Hg–C(1)–P(1)	113.2 (10)	P(1)–C(26)–C(25)	117.0 (3)
P(1)–C(16)–C(11)	121.4 (4)	P(2)–C(36)–C(35)	118.7 (4)
P(1)–C(26)–C(21)	122.8 (3)	P(2)–C(46)–C(45)	120.6 (3)
P(2)–C(36)–C(31)	121.2 (4)	C(5)–C(3)–C(3)′	137.6 (39)
P(2)–C(46)–C(41)	119.3 (3)	C(3)–C(5)–C(4)	147.1 (38)
C(5)–C(3)–C(6)	67.4 (31)	C(3)–C(5)–C(6)	53.1 (27)
C(6)–C(3)–C(3)′	131.6 (44)	C(3)–C(6)–C(5)	59.5 (29)
Hg–Au(1)–S(1)	92.0 (1)	C(4)–C(5)–C(6)	149.3 (42)
Hg–Au(2)–Cl(2)	98.2 (1)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

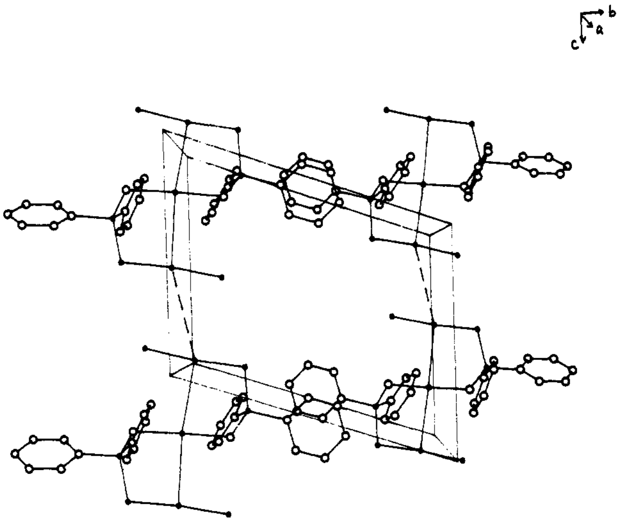

Figure 2. Unit cell packing diagram showing the one-dimensional structure of 2.

pentalene)Cl.[8b] The molecule of 2 has an approximate C_2 symmetry. The Au(1)–Hg–Au(2) unit is nonlinear with a angle of 151.8 (1)°. The Au–Hg distances (3.310 (1), 3.361 (1) Å) are much longer than those found in **3a** (3.088 (1) Å)[5] and $[HgAu(MTP)_2]_2[PF_6]_2$ (2.989 (1) Å). It seems that the double bridges made by the MTP ligand in **3a** and $[HgAu(MTP)_2]_2[PF_6]_2$ play an important role in shortening Hg–Au separations. In fact similar bridging effects have been also observed in $[Au(dppm)Cl]_2$[9a] (Au–Au = 3.351 (2) Å) and $[Au_2(dppm)_2]X_2$[9b,c] (X = BF_4, Au–Au = 2.931 (1) Å; X = NO_3, Au–Au = 2.988 (1) Å). The structure of 2 is similar to that of the known compound $[ClAu^I(dppm)Au^I(dppm)Au^ICl][Au^{III}Cl(C_6F_5)_3]$,[10] in which the arrangement of the three Au^I atoms is nonlinear with a very small Au–Au–Au angle of 72.3° and Au–Au distances of 3.067 (5) and 3.164 (5) Å. Solid 2 has a zigzag one-dimensional chain structure (Figure 2) with a intermolecular Au(1)–Au(2)′ distance of 4.210 Å, much longer than those observed in the one-dimensional chain compounds of[3b,4b] $Au_2Pt(MTP)_4$ and $Au_2Pb(MTP)_4$[3b,4b] and $Au_2(MTP)_2$ (3.15–3.23 Å).[11] Nevertheless, 2 is the first example of a trinuclear organometallic compound containing Au and Hg atoms. Compound 2 can be oxidized readily by 1 equiv of $C_6H_5ICl_2$ to generate the mixed-valence compound $HgAu^I(MTP)_2Au^{III}Cl_4$ (3).

Synthesis and Crystal Structure of $HgAu^I(MTP)_2Au^{III}Cl_4$ (3). The reaction of 2 with 1 equiv of $C_6H_5ICl_2$ in CH_2Cl_2 yields the new compound 3 quantitatively. 3 is an orange air-stable compound and is slightly

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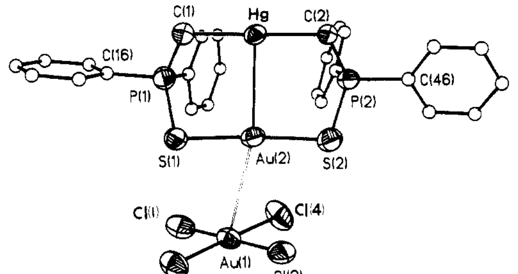

Figure 3. Molecular structure of 3 (50% thermal ellipsoids) with the labeling scheme.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for Compound 3

atom	x	y	z	U_{iso}[b]
Au(1)	1816 (1)	83 (1)	2730 (1)	50 (1)*
Au(2)	4686 (1)	63 (1)	3671 (1)	50 (1)*
Hg	7445 (1)	522 (1)	4022 (1)	44 (1)*
Cl(1)	1973 (10)	1280 (8)	1279 (6)	76 (5)*
Cl(2)	1618 (9)	−1121 (7)	4168 (6)	67 (5)*
Cl(3)	484 (9)	1441 (8)	3278 (6)	70 (5)*
Cl(4)	3113 (10)	−1293 (8)	2181 (6)	84 (5)*
Cl(5)	9316 (17)	4578 (13)	1976 (16)	231 (13)*
Cl(6)	11785 (22)	5171 (19)	1058 (15)	265 (15)*
S(1)	4042 (9)	1967 (7)	3085 (6)	56 (4)*
S(2)	5183 (9)	−1860 (7)	4295 (6)	61 (5)*
P(1)	5817 (10)	2517 (7)	2573 (6)	52 (4)*
P(2)	7154 (9)	−2111 (7)	4164 (5)	46 (4)*
C(1)	6950 (31)	2267 (24)	3408 (19)	48 (10)
C(2)	7971 (29)	−1229 (23)	4646 (17)	36 (8)
C(3)	10843 (69)	4084 (53)	1561 (40)	181 (24)
C(11)	4853 (23)	4646 (20)	2672 (11)	87 (13)
C(12)	4596 (23)	5817 (20)	2341 (11)	91 (13)
C(13)	5003 (23)	6349 (20)	1423 (11)	86 (13)
C(14)	5666 (23)	5709 (20)	838 (11)	97 (13)
C(15)	5923 (23)	4537 (20)	1169 (11)	82 (12)
C(16)	5516 (23)	4005 (20)	2086 (11)	54 (10)
C(21)	5732 (16)	1563 (16)	1120 (14)	60 (10)
C(22)	6287 (16)	1058 (16)	417 (14)	68 (11)
C(23)	7665 (16)	862 (16)	256 (14)	71 (11)
C(24)	8487 (16)	1172 (16)	798 (14)	95 (14)
C(25)	7932 (16)	1678 (16)	1501 (14)	66 (11)
C(26)	6555 (16)	1873 (16)	1662 (14)	41 (9)
C(31)	7009 (17)	−1933 (18)	2276 (16)	70 (11)
C(32)	7576 (17)	−1976 (18)	1392 (16)	82 (12)
C(33)	8955 (17)	−2100 (18)	1207 (16)	83 (12)
C(34)	9768 (17)	−2181 (18)	1906 (16)	90 (13)
C(35)	9201 (17)	−2139 (18)	2790 (16)	53 (10)
C(36)	7822 (17)	−2015 (18)	2975 (16)	50 (9)
C(41)	8397 (21)	−3858 (18)	5496 (16)	78 (12)
C(42)	8649 (21)	−4989 (18)	5984 (16)	77 (12)
C(43)	8058 (21)	−5826 (18)	5764 (16)	94 (13)
C(44)	7215 (21)	−5532 (18)	5055 (16)	95 (14)
C(45)	6964 (21)	−4401 (18)	4567 (16)	88 (13)
C(46)	7555 (21)	−3564 (18)	4788 (16)	64 (11)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic U is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table V. Bond Lengths (Å) and Angles (deg)[a] for 3

(a) Bond Lengths			
Au(1)–Cl(1)	2.280 (8)	Au(1)–Cl(2)	2.270 (8)
Au(1)–Cl(3)	2.279 (9)	Au(1)–Cl(4)	2.281 (10)
Au(2)–Hg	3.079 (2)	Au(2)–S(1)	2.308 (8)
Au(2)–S(2)	2.313 (8)	Hg–C(1)	2.119 (27)
Hg–C(2)	2.132 (25)	Cl(5)–C(3)	1.700 (68)
Cl(6)–C(3)	1.705 (70)	S(1)–P(1)	2.007 (13)
S(2)–P(2)	1.985 (13)	P(1)–C(1)	1.752 (33)
P(1)–C(16)	1.782 (24)	P(1)–C(26)	1.804 (24)
P(2)–C(2)	1.798 (34)	P(2)–C(36)	1.812 (24)
P(2)–C(46)	1.801 (21)		
(b) Bond Angles			
Cl(1)–Au(1)–Cl(2)	178.7 (4)	Cl(1)–Au(1)–Cl(3)	90.6 (3)
Cl(2)–Au(1)–Cl(3)	89.3 (3)	Cl(1)–Au(1)–Cl(4)	89.6 (3)
Cl(2)–Au(1)–Cl(4)	90.5 (3)	Cl(3)–Au(1)–Cl(4)	178.9 (4)
Hg–Au(2)–S(1)	92.4 (3)	Hg–Au(2)–S(2)	90.9 (3)
S(1)–Au(2)–S(2)	176.1 (3)	Au(2)–Hg–C(1)	89.1 (9)
Au(2)–Hg–C(2)	91.9 (8)	C(1)–Hg–C(2)	179.1 (9)
Au(2)–S(1)–P(1)	100.0 (4)	Au(2)–S(2)–P(2)	104.9 (5)
S(1)–P(1)–C(1)	113.8 (10)	S(1)–P(1)–C(16)	106.5 (9)
C(1)–P(1)–C(16)	108.9 (14)	S(1)–P(1)–C(26)	110.7 (8)
C(1)P(1)–C(26)	108.5 (12)	C(16)–P(1)–C(26)	108.3 (9)
S(2)–P(2)–C(2)	114.8 (10)	S(2)–P(2)–C(36)	112.3 (8)
C(2)–P(2)–C(36)	110.2 (12)	S(2)–P(2)–C(46)	105.2 (8)
C(2)–P(2)–C(46)	108.2 (12)	C(36)–P(2)–C(46)	105.7 (11)
Hg–C(1)–P(1)	113.0 (17)	Hg–C(2)–P(2)	111.2 (13)
Cl(5)–C(3)–Cl(6)	110.8 (36)	P(1)–C(16)–C(11)	116.9 (7)
P(1)–C(16)–C(15)	123.1 (7)	P(1)–C(26)–C(21)	119.3 (7)
P(1)–C(26)–C(25)	120.7 (7)	P(2)–C(36)–C(31)	122.1 (7)
P(2)–C(36)–C(35)	117.6 (7)	P(2)–C(46)–C(41)	121.7 (9)
P(2)–C(46)–C(45)	118.3 (9)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

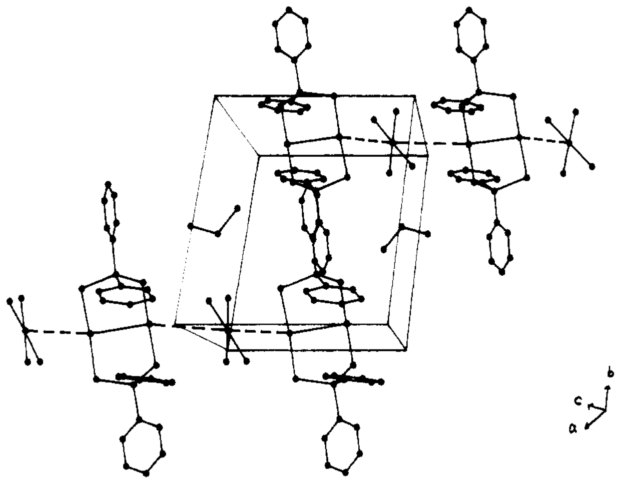

Figure 4. Unit cell packing diagram showing the one-dimensional structure of 3.

soluble in CH_2Cl_2. The ^1H NMR spectrum of 3 is very similar to that of the known compound **3a**. The crystal structure of 3 was determined by single-crystal X-ray diffraction analysis.

The molecular structure of 3 is shown in Figure 3. Atomic positional and thermal parameters are given in Table IV. Bond lengths and angles are listed in parts a and b, respectively, of Table V. Two of the metal atoms in 3, Hg and Au(2), are bridged by the MTP ligand. The Hg atom is linearly coordinated to two carbon atoms, typical for a Hg^{II} ion. The coordination of carbon atoms to the Hg center is consistent with the solution ^1H NMR data. The Au(2) atom is linearly coordinated to two sulfur atoms, typical for a Au^I center. The Au(2)–Hg distance of 3.079 (2) Å is much shorter than those in 2. The structure of the Hg–Au(2) portion of 3 is very similar to the structure[5] of the cation in $HgAu(MTP)_2PF_6$ (**3a**). The third metal atom Au(1) is coordinated by four chlorine atoms in a square-planar fashion, a common coordination geometry[12] for Au^{III}. The Au(1)–Cl bond lengths are similar to literature values reported for the $AuCl_4^-$ anion.[12] The $AuCl_4$ portion is planar with a maximum deviation of ±0.019 (1) Å from the plane for Au(1). The $AuCl_4$ plane is nearly perpendicular to the Hg–Au(2) axis. The dihedral angle between the $AuCl_4$ plane and the $HgAuS_2$ plane is 97.3°. The molecules of 3 form a one-dimensional chain

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structure in the solid as shown in Figure 4. The Au(1) atom is 3.404 (2) Å from Au(2). However, it is 4.658 Å from the Hg atom of the neighboring molecule. The preference of the Au^{III} center for a Au^{I} rather than a Hg^{II} center is apparent here. The Hg–Au(2)–Au(1) axis is nonlinear by about 16°.

The formation of mixed-valence compounds by oxidative addition of halogen to Au^{I} compounds has been observed previously.[2,3c,13] In some dinuclear gold complexes it has been established[13c–e] that mixed-valence Au^{I}–Au^{III} species are formed by the disproportionation of Au^{II}–Au^{II} intermediates. The mechanism of the formation of **3** is not yet understood.

We have found that the PF_6^- and $AuCl_4^-$ anions in **3** and **3a**, respectively, can be readily replaced by other dianionic metal complexes such as $Pt(i\text{-}MNT)_2^{2-}$ (i-MNT = 1,1-dicyano-2,2-dithioethene) to form new heteronuclear one-dimensional compounds. The structural characterizations of these new interesting materials are under way.

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Supplementary Material Available: Tables of anisotropic thermal parameters and positional and thermal parameters of hydrogen atoms for 2 and 3 (4 pages); listings of structure factors for 2 and 3 (42 pages). Ordering information is given on any current masthead page.

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Structural Studies on Cyclopentadienyl Compounds of Trivalent Cerium: Tetrameric $(MeC_5H_4)_3Ce$ and Monomeric $(Me_3SiC_5H_4)_3Ce$ and $[(Me_3Si)_2C_5H_3]_3Ce$ and Their Coordination Chemistry

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The coordinated tetrahydrofuran in $(MeC_5H_4)_3Ce(THF)$ can be removed by Me_3Al in a Lewis acid–base reaction or by the "toluene-reflux method" to give base-free $(MeC_5H_4)_3Ce$ which is a monomer in the gas phase though a tetramer in the solid state: monoclinic, $P2_1/a$, with a = 12.497 (5) Å, b = 26.002 (8) Å, c = 9.664 (3) Å, β = 97.33 (3)°; R = 0.041 for 2117 data, $F^2 > 2\sigma(F^2)$. The structure is made up of a cyclic tetramer in which two MeC_5H_4 rings are η^5-bonded to each cerium atom and one MeC_5H_4 ring is bridging two cerium atoms such that the MeC_5H_4 ring is η^5-bonded to one cerium and η^1-bonded to the other. With larger cyclopentadienyl groups, the binary metallocenes $(\eta^5\text{-}Me_3SiC_5H_4)_3Ce$, $(\eta^5\text{-}Me_3CC_5H_4)_3Ce$, and $[\eta^5\text{-}(Me_3Si)_2C_5H_3]_3Ce$ are monomeric in the gas phase and the solid state. The structure of the latter is based upon a trigonal-planar geometry; the crystals are monoclinic, $I2/c$, with a = 22.752 (5) Å, b = 11.386 (3) Å, c = 17.431 (4) Å, β = 105.70 (3)°, R = 0.046 for 2519 data, and $F^2 > 3\sigma(F^2)$. All of the binary metallocenes form 1:1 complexes with isocyanides and organocyanides, and the crystal structure of two of them have been determined; $(MeC_5H_4)_3Ce(CNCMe_3)$ is monoclinic, $P2_1/c$, with a = 14.259 (3) Å, b = 9.382 (2) Å, c = 17.652 (3) Å, β = 106.16 (3)°, R = 0.050 for 1501 data, and $F^2 > 3\sigma(F^2)$, and $[(Me_3Si)_2C_5H_3]_3Ce(CNCMe_3)$ is also monoclinic, $P2_1/c$, with a = 11.462 (3) Å, b = 17.146 (4) Å, c = 26.826 (6) Å, β = 112.93 (3)°, R = 0.047 for 2437 data, and $F^2 > 3\sigma(F^2)$.

The solid-state structures of the trivalent lanthanide (including scandium and its congeners) metallocenes, $(C_5H_5)_3M$, are unusual as only in a few cases are their crystal structures as expected, i.e., monomeric with each C_5H_5 group η^5-bonded to the metal so that the coordination number is nine (defining a C_5H_5 group as occupying three coordination sites) and the geometry about the metal atom as trigonal planar (defining the centroid of a C_5H_5 group as occupying one coordination site). The structures of the light lanthanide (praseodymium) and lanthanum tris(cyclopentadienyl) compounds are polymers with two terminal C_5H_5 groups η^5-bonded to the metal while a third C_5H_5 group is bridging two metal centers in a η^5 and a η^1 or η^2 fashion so as to form a zigzag polymer.[1a–c] The bridging cyclopentadienyl group allows the metal atom to increase its coordination number from nine in the monomer to either ten or eleven in the polymer. The structure of the middle lanthanide, samarium, appears to have a similar structure though the low quality of the data prevents any detailed conclusion.[1d] The heavier lanthanides (Er, Tm)

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