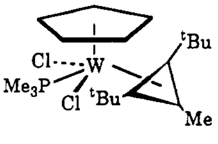

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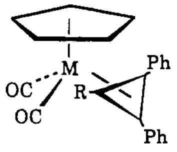
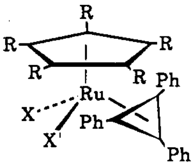


2 M = Mo; R = Ph

3 M = Mo; R = ^{t}Bu

4 M = W; R = ^{t}Bu



5 R = H; X = X′ = Cl

6 R = H; X = X′ = Br

7 R = H; X = X′ = I

8 R = H; X = Cl; X′ = Br

9 R = Me; X = X′ = Cl

and fractional atomic coordinates are presented in Table I. The cyclopropenyl ligand is η^3-bound to the ruthenium atom with the unique carbon C(6) directed away from the cyclopentadienyl ring. Like its Mo analogue **2**, but in contrast to the W complex **1**, the distance from Ru to the C_3 ring centroid [2.036 (8) Å] is significantly longer than that to the C_5 ring centroid [1.833 (8) Å], although both rings are closer to the metal than are their counterparts in **2** (vide supra). While the cyclopropenyl ring in **6** is held more closely to the metal than that in **2**, the phenyl rings in **6** (Figure 1) are bent back from the plane of the cyclopropenyl ring significantly less than those in **2**. Thus there is no direct correlation between closeness of binding (as measured by metal–ring centroid distances) and substituent bend-back angle.[3a,4b]

Spectroscopic analysis of **6** and its relatives indicated that the solid-state structure is maintained in solution.[7] In contrast to their fluxional relatives **2**–**4**, the presence of two ^{13}C resonances for the cyclopropenyl ring carbon atoms, and resonances due to two different phenyl groups, for complexes **5**, **6**, **7**, and **9** indicates a conformationally static structure in solution.[10] The observation of three cyclopropenyl ring carbon resonances for the mixed halo complex **8** is also consistent with conformational rigidity. That this increased rotational barrier is not due to steric interactions due to more closely bound cyclopentadienyl and cyclopropenyl rings is indicated by the free rotation of the cyclopentadienyl and pentamethylcyclopentadienyl rings, as evidenced by a single environment for all atoms in the ^{1}H and ^{13}C NMR spectra of **5**–**9**.

In summary, even though the cyclopropenyl ring is less closely bound to the metal center than is the cyclopentadienyl ring, the rotational barrier for the three-membered ring appears to exceed significantly that for the five-membered ring. The origin of the relatively high barriers in **1** and **5**–**9**, as compared to the low barriers in **2**-**4**,[10] must be related to the intimate details of orbital interactions between the respective metal fragments and the cyclopropenyl ring. It is hoped that molecular orbital calculations on the isoelectronic complexes **2** and **6** will allow further elucidation of these differences.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of our research. A generous loan of ruthenium trichloride from Johnson-Matthey Inc. is also gratefully acknowledged. We thank Dr. Paul Eagan for a preprint of ref 8a.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (4 pages); a listing of observed vs calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[10] The smallest separation between cyclopropenyl carbon peaks ($\Delta\nu$) is 30 Hz for the mixed halide complex **8**. Since the coalescence temperature is clearly >298 K, a *minimum* $\Delta G^* \geq 62$ kJ mol^{-1} for cyclopropenyl rotation can be calculated for this complex. Estimation of a value for **2** requires an estimate of $\Delta\nu$ at the slow exchange limit, which has not been reached at −80 °C.[3a] Assuming that $\Delta\nu$ for **2** is 3000 Hz (the value obtained for **6**) and that the coalescence temperature is clearly <193 K leads to a *maximum* $\Delta G^* \leq 32$ kJ mol^{-1} for cyclopropenyl rotation in **2**. It seems reasonable to conclude that the barriers for triphenylcyclopropenyl rotation in the Ru(IV) complexes are at least 30 kJ mol^{-1} greater than that in their isoelectronic molybdenum analogue.

Organobimetallic Complexes with $Hg(CH_2P(S)Ph_2)_2$. Syntheses and Characterization of Two Structural Isomers of $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ and the Hg Precursor

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Summary: The ylide complex $Hg(CH_2P(S)Ph_2)_2$ (**1a**) has been synthesized. **1a** reacts readily with Au(THT)Cl (THT = tetrahydrothiophene) in CH_2Cl_2 in the presence of $TlPF_6$ to yield a new bimetallic compound with HgC_2 and AuS_2 bonding, $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ (**2a**). This compound is isostructural with an isomer having AuSC and HgSC bonding, **3a**, obtained from the reaction of PPN$[Au(CH_2P(S)Ph_2)_2]$ with $HgCl_2$ in the presence of $TlPF_6$. The structures of **1a**, **2a**, and **3a** were determined by single-crystal X-ray diffraction. **2a** and **3a** do not interconvert upon heating in THF.

Recently, we have reported the synthesis and structure of the (methylenethiophosphinate)gold(I) complex PPN-$[Au(CH_2P(S)Ph_2)_2]$ and its use as a synthetic precursor for heterobimetallic methylenethiophosphinate complexes.[1-3] The complexes $Au_2Pt(CH_2P(S)Ph_2)_4$, $AuTl(CH_2P(S)Ph_2)_2$, and $Au_2Pb(CH_2P(S)Ph_2)_4$ were obtained. These heterobimetallic complexes display unique structural features and very interesting physical and chemical properties. The scarceness of Hg^{II}–Au^{I} bimetallic complexes and the chemical similarities of Au^{I} and Hg^{II} ions have promoted us to synthesize mercury–gold containing ylide bimetallic

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0276-7333/88/2307-2415$01.50/0

Table I. ^{1}H and ^{31}P NMR Data

compound	^{1}H NMR chem. shifts of $-CH_2$, δ	^{1}H NMR $^2J_{P-H}$, Hz	^{1}H NMR $^2J_{Hg-H}$, Hz	^{31}P NMR chem. shifts, ppm	^{31}P NMR $^2J_{Hg-P}$, Hz	^{31}P NMR $^4J_{P-P}$, Hz
1a, $CDCl_3$	2.32	12	135	44.78	148	
2a, $CDCl_3$	2.41	12	155	50.10	46	
3a, CD_2Cl_2	2.30	11		49.89		6
	2.91	12	210	54.36		6
$HgMe_2$ CD_2Cl_2	1.16		102			

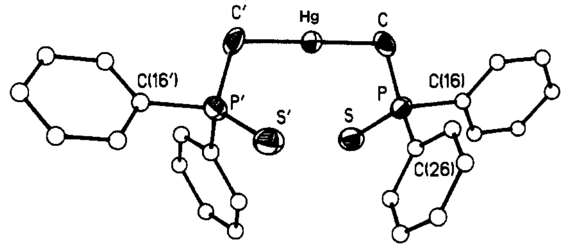


Figure 1. The molecular structure of **1a** showing 50% thermal ellipsoid. Selected bond lengths (Å) and angles (deg): Hg–C = 2.12 (2), P–S = 1.954 (7), P–C = 1.77 (2); C–Hg–C′ = 17993 (2), Hg–C–P = 113 (1).

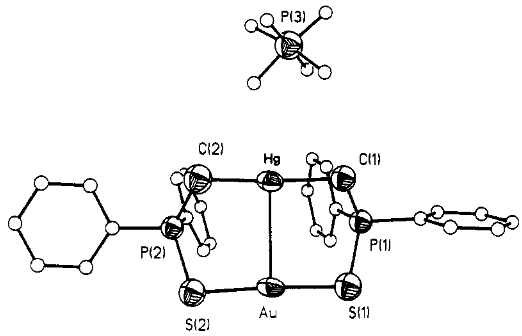


Figure 2. The molecular structure of **2a** showing 50% thermal ellipsoid. Selected bond lengths (Å) and angles (deg): Hg–Au = 3.088 (1), Hg–C(1) = 2.13 (2), Hg–C(2) = 2.14 (2), Au–S(1) = 2.299 (6), Au–S(2) = 2.313 (6), P(1)–C(1) = 1.82 (2), P(1)–S(1) = 2.033 (6), P(2)–C(2) = 1.82 (2), P(2)–S(2) = 2.034 (6); C(1)–Hg–C(2) = 175.0 (7), S(1)–Au–S(2) = 175.0 (2), Hg–C(1)–P(1) = 109.1 (7), Hg–C(2)–P(2) = 110.7 (9), Au–S(1)–P(1) = 102.9 (2), Au–S(2)–P(2) = 102.2 (2)°.

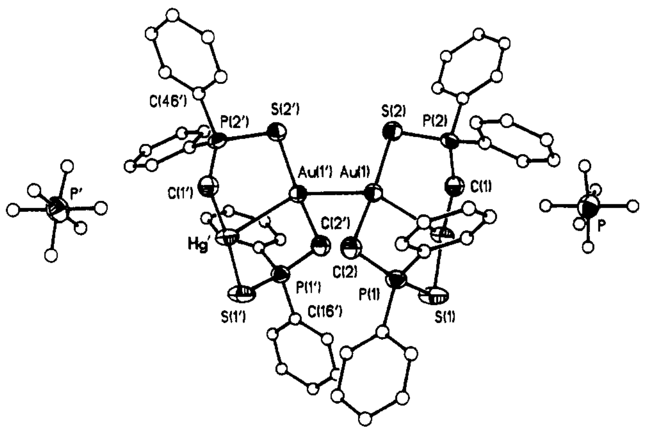
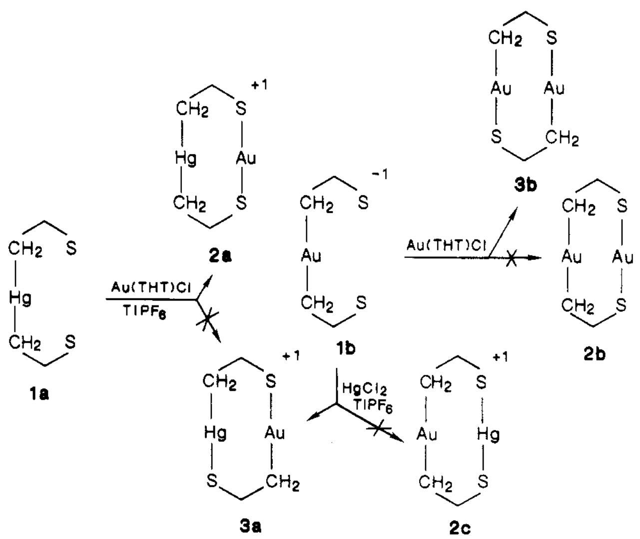


Figure 3. The dimeric structure of **3a** showing 50% thermal ellipsoid. Selected bond lengths (Å) and angles (deg): Hg–Au(1) = 2.989 (1), Au(1)–Au(1)′ = 3.150 (2), Hg–C(1) = 2.09 (2), Hg–S(1) = 2.335 (5), Au(1)–C(2) = 2.10 (2), Au(1)–S(2) = 2.337 (5), P(1)–S(1) = 2.04 (8), P(1)–C(2) = 1.82 (2), P(2)–S(2) = 2.03 (1), P(2)–C(1) = 1.81 (2); Hg–Au(1)–Au(1)′ = 111.1 (1), C(1)–Hg–S(1) = 174.8 (7), Hg–S(1)–P(1) = 105.4 (3)°, Hg–C(1)–P(2) = 107.4 (8), C(2)–Au(1)–S(2) = 175.2 (7)°, Au(1)–S(2)–P(2) = 104.3 (3)°, Au(1)–C(2)–P(1) = 108 (1).

Scheme I



complexes. We report here the synthesis and structural characterization of two structural isomers of $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ and the precursor complex $Hg(CH_2P(S)Ph_2)_2$.

Addition of 0.5 equiv of $HgCl_2$ to a THF solution of[4] $Li(CH_2P(S)Ph_2)_2$ results in the formation of the colorless compound $Hg(CH_2P(S)Ph_2)_2$ (**1a**) in greater than 50% yield.[5] The ^{1}H NMR spectrum shows only one type of CH_2 group bonded to Hg as indicated by the satellites of coupling to the ^{199}Hg nucleus with $^2J_{Hg-H}$ = 135 Hz (compare with[6] $HgMe_2$, Table I). The structure of **1a** was confirmed by a single-crystal X-ray diffraction analysis[7] as shown in Figure 1. The geometry of **1a** resembles that of the $[Au(CH_2P(S)Ph_2)_2]^-$ anion **1b**. Two carbon atoms coordinate linearly to the Hg(II) center with bond lengths and angles similar to those found in[8a] $Hg(CH_2Ph)_2$ and[8b]

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(5) Elemental Anal. Calcd for **1a**: C, 47.09; H, 3.65. For **2a** and **3a**: C, 31.07; H, 2.41. Found for **1a**: C, 46.37; H, 3.43. For **2a**: C, 30.78; H, 2.36. For **3a**: C, 32.14; H, 2.48. Preparation of **1a**: Li(MTP) (960 mg, 4.0 mmol in 20 mL of THF) was prepared according to the literature.[4] $HgCl_2$ (500 mg, 1.8 mmol) was added to this solution at −78 °C. After the solution was warmed to 0 °C, the white solid, **1a**, precipitated. After being stirred for 1 h, the solution was filtered and washed with THF and ether. **1a** (780 mg) was obtained (yield 65%). Preparation of **2a**: 20 mg of **1a** (0.03 mmol) and 10 mg of Au(THT)Cl (0.03 mmol) were dissolved in 5 mL of CH_2Cl_2. $TlPF_6$ (11 mg, 0.03 mmol) was added. After being stirred for 4 h, the solution was filtered and concentrated to 1 mL. Ether (5 mL) was added. Light yellow crystals of **2a** (18 mg) was obtained (yield 60%). Preparation of **3a**: 80 mg of **1b** (0.07 mmol) and 18 mg of $HgCl_2$ (0.07 mmol) were dissolved in CH_2Cl_2. $TlPF_6$ (48 mg, 0.14 mmol) was added. After being stirred for 4 h, the solution was filtered and concentrated to 3 mL. Ether (10 mL) was added. The $PPNPF_6$ cocrystallized with **3a** was washed out with MeOH. Light yellow crystals of **3a** (46 mg) was obtained (yield 69%). These new compounds are air-stable.

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(7) Crystal data. **1a**: $C_{26}H_{24}HgAuS_2P_2$; space group *C*2/*c*; *a* = 25.090 (8) Å, *b* = 10.886 (5) Å, *c* = 9.189 (4) Å; β = 91.83 (3)°; *V* = 2508 (2) Å^3; *Z* = 4. Convergence to the final *R* values of *R* = 5.38% and R_w = 6.89% was achieved by using 1200 reflections ($F_o^2 \geq 3\sigma(F_o^2)$) and 118 least-squares parameters. **2a**: $C_{26}H_{24}HgAuS_2P_3F_6$; space group *C*2/*c*; *a* = 30.356 (6) Å, *b* = 14.028 (5) Å, *c* = 16.491 (5) Å; β = 121.48 (2)°; *V* = 5988 (3) Å^3; *Z* = 8. Convergence to the final *R* values of *R* = 4.05% and R_w = 3.44% was achieved by using 2039 reflections ($F_o^2 \geq 3\sigma(F_o^2)$) and 174 least-squares parameters. **3a**: $C_{26}H_{24}HgAuS_2P_3F_6$; space group *C*2/*c*; *a* = 29.761 (7) Å, *b* = 8.824 (3) Å, *c* = 27.413 (5) Å; β = 125.39 (2)°; *V* = 5868 (3) Å^3; *Z* = 8. Convergence to the final *R* values of *R* = 5.27% and R_w = 6.30% was achieved by using 2699 reflections ($F_o^2 \geq 3\sigma(F_o^2)$) and 174 least-squares parameters. Data were collected on a Nicolet R3m/E diffractometer and processed on a Data General S140 computer using SHELXTL software (version 5.1). All the structures were solved by direct methods.

$[Hg(CH_2CH_2OCH_2CH_2)]_2$. The Hg atoms in **1a** lie on the *c* axis in the lattice with a Hg–Hg separation of 4.59 Å and with weak intermolecular Hg–S contacts, 3.20 and 3.16 Å, respectively. We believe that **1a** is the first structurally characterized two-coordinate ylide Hg^{II} complex. A linear two-coordinate geometry was suggested for the cations $[Hg(CH_2PR_3)_2]^{2+}$ (R = Ph, Me) reported previously by Seyferth[9] and Schmidbaur et al.[9]

As found for **1b**, **1a** is an excellent synthetic precursor for bimetallic complexes. For example, **1b** reacts readily with Au(THT)Cl (THT = tetrahydrothiophene) in CH_2Cl_2 to product[1,10] $Au_2(CH_2P(S)Ph_2)_2$ (**3b**),[1,10] while **1a** also reacts readily with Au(THT)Cl in the presence of $TlPF_6$ to yield the new bimetallic compound $[HgAu(CH_2P(S)Ph_2)_2]PF_6$ (**2a**) in 60% yield.[5] However, unlike **1b** which shows a rearrangement of the Au–C bond to form **3b**, **1a** yields **2a** without the rearrangement of Hg–C bonds (Scheme I). **2a** was fully characterized by ^1H NMR, ^{31}P NMR, elemental,[5] and X-ray diffraction analyses.[7] The molecular structure of **2a** is shown in Figure 2. As found in **1a**, the Hg^{II} center is linearly coordinated to two carbon atoms. This result is consistent with the ^1H NMR spectrum of **2a** which shows only one methylene signal and ^{199}Hg coupling satellites (Table I). The Au^I center in **2a** is bonded linearly to two sulfur atoms with normal Au–S bond distances. The Au–Hg separation is 3.088 Å, similar to the sum of metallic radii of Au and[11] Hg, 3.009 Å. The fact that **2a** is the only product from the reaction of **1a** with Au(THT)Cl and **3b** the only product from **1b** with Au(THT)Cl suggests that the Au–C bonds in **1b** are more labile than the Hg–C bonds in **1a**. This lability of Au–C bonds in **1b** is further demonstrated by the specific synthesis of compound **3a**, $[HgAu(CH_2P(S)Ph_2)_2]PF_6$, from **1b**.

Compound **3a** was obtained as the only product from the reaction of **1b** with $HgCl_2$ in the presence of $TlPF_6$ in CH_2Cl_2 in 69% yield.[5] **3a** is isomeric with **2a** and similar to **3b** in structure. A drawing of its structure is shown in Figure 3. Each metal atom in **3a** is bonded linearly to a methylene group and a sulfur atom with similar M–S and M–C bond lengths. This bonding mode agrees with the ^1H NMR spectrum of **3a** in solution in which two strikingly different chemical shifts of methylene groups are observed. Only one methylene group is coupled to the ^{199}Hg nucleus (Table I). The Hg–Au distance, 2.989 (1) Å, is shorter than that found in **2a** or the sum of metallic radii of Hg and Au atoms. Interestingly, **3a** dimerizes in the solid and forms a tetranuclear species. One-half of the dimer is related to the other half by a 2-fold symmetry axis. Hg and Au atoms are experimentally crystallographically indistinguishable. The intermolecular metal–metal distance of 3.150 (2) Å is similar to the intermolecular Au–Au separations in[1,3] $Au_2Pt(CH_2P(S)Ph_2)_4$, $Au_2Pb(CH_2P(S)Ph_2)_4$, and[10] $Au_2(CH_2PnS)Ph_2)_2$. On the basis of the fact that Au^I complexes tend to form short intermolecular Au–Au contacts in the solid[12] and that Hg atoms in **3a** are in a higher oxidation state (+2) than the Au atoms (+1) and therefore they would prefer to be further apart, the intermolecular M–M distance was assigned to a Au^I–Au^I distance.

2a and **3a** are the first examples of organometallic complexes containing both of Au and Hg atoms with $5d^{10}$ electronic configurations. These two compounds do not interconvert under reflux in THF.

The chemical reactivity of these new compounds and syntheses of other new bimetallic complexes using $Hg(CH_2P(S)Ph_2)_2$ as a precursor are currently under investigation in our laboratory.

Acknowledgment. We thank the Welch Foundation and the National Science Foundation (CHE 8708625) for financial support. The available fund of Texas A&M University has supported the crystallographic studies. We thank a referee for suggesting **1a** be refined in the space group *C*2/*c*.

Supplementary Material Available: Tables of positional and thermal parameters, bond lengths and angles, and crystallographic data for **1a**–**3a** (13 pages); listings of structure factors for **1a**–**3a** (57 pages). Ordering information is given on any current masthead page.

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Reaction of Primary Silanes with a Binuclear Rhodium Complex. Formation of μ-Silylene Complexes and Rapid Si–H/Rh–H Exchange

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Summary: The primary silanes $PhSiH_3$ and $EtSiH_3$ react with the binuclear complex $Rh_2H_2(CO)_2(dppm)_2$ to produce in sequence the μ-SiRH dihydride species $Rh_2(\mu\text{-}SiRH)H_2(CO)_2(dppm)_2$ and the bis μ-SiRH complex $Rh_2(\mu\text{-}SiRH)_2(CO)_2(dppm)_2$. The latter for R = Ph has been found by a single-crystal structure determination [$P\bar{1}$; a = 12.927 (5) Å, b = 15.165 (2) Å, c = 18.280 (8) Å; α = 93.8 (5)°, β = 103.6 (3)°, γ = 107.8 (9)°; Z = 2; d_{calcd} = 1.42 g/cm^3; R = 0.047, R_w = 0.059] to have a cradlelike structure with μ-SiPhH bridges of 2.35 (1) Å average Rh–Si distance and a Rh–Rh single bond of 2.813 (1) Å. The complexes $Rh_2(\mu\text{-}SiRH)H_2(CO)_2(dppm)_2$ are fluxional with Si–H and Rh–H protons undergoing rapid exchange, indicating the relative reactivity of the coordinated Si–H bond in these systems. For R = Ph, $\Delta G^{\ddagger}$ for the fluxional process is 12 ± 1 kcal/mol.

The reactivity of Si–H bonds with transition-metal complexes[1] has stimulated interest in dehydrogenative coupling of primary and secondary silanes, R_nSiH_{4-n} (n = 1, 2; R = alkyl, aryl), as a reaction path to the formation of Si–Si bonds. Recently, Harrod and co-workers have employed this approach using $Cp_2TiR'_2$ (R′ = Me, CH_2Ph) to obtain $(RSiH)_x$ with x = ~10.[2] In the course of this work, they obtained binuclear intermediates having μ-$SiRH_2$ groups (R = Ph) and observed Si–H/hydride ex-

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