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Mixed-Metal Sulfido Clusters Containing Noble Metals and Group 15 Metals. Stepwise Construction of Bimetallic and Trimetallic Ru_2MS_2 (M = Sb, Bi), Ru_2PdSbS_2, and $Ru_2Pd_2SbS_2$ Cores

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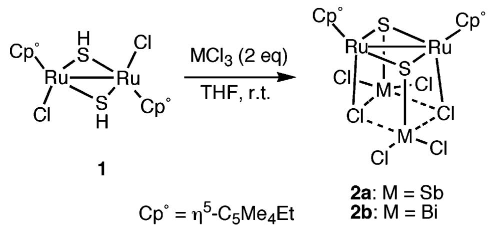
By starting from a diruthenium bis(μ-hydrosulfido) complex $[(Cp^\circ RuCl)_2(\mu\text{-}SH)_2]$ (**1**; Cp° = η^5-C_5Me_4Et), a series of new mixed-metal sulfur clusters containing both noble metals and group 15 metals have been synthesized. Thus, **1** was allowed to react with 1 equiv of MCl_3 (M = Sb, Bi) to give the trinuclear Ru_2M clusters $[(Cp^\circ RuCl)_2(\mu\text{-}SMCl_2)(\mu\text{-}SH)]$ (**3a**, M = Sb; **3b**, M = Bi) containing bridging SH and $SMCl_2$ ligands. Treatment of **3a** with 1 equiv of $[Pd(PPh_3)_4]$ at room temperature gave a mixture of the Ru−Pd−Sb clusters $[(Cp^\circ Ru)(Cp^\circ RuCl)(\mu\text{-}SSbCl_2)\{PdCl(PPh_3)\}(\mu_3\text{-}S)(\mu\text{-}H)]$ (**4**), $[(Cp^\circ Ru)_2(SbCl_2)\{Pd(PPh_3)\}_2(\mu_3\text{-}S)_2(\mu\text{-}Cl)]$ (**5**), and $[(Cp^\circ Ru)(Cp^\circ RuCl)\{PdCl(PPh_3)\}(SbCl)(\mu_3\text{-}S)_2]$ (**6**). An analogous reaction carried out at −5 °C gave **4** as the major product. By contrast, isolation of the Bi analogues from the reaction of **3b** and $[Pd(PPh_3)_4]$ was unsuccessful. It was also confirmed that the isolated **4** was treated with 1 equiv of $[Pd(PPh_3)_4]$ in THF either at 50 °C or at room temperature in the presence of triethylamine to give **5**, while **4** was converted to **6** upon either warming to 50 °C or dehydrochlorination by the use of triethylamine in THF. Cluster **6** was readily transformed into **5** by treatment with $[Pd(PPh_3)_4]$ in THF at room temperaure. Structures of the new clusters **3a**, **3b**, **4**, **5**, and **6** have been determined by single-crystal X-ray analysis.

Introduction

We reported previously the syntheses of hydrosulfido- and hydroselenido-bridged dinuclear complexes of noble metals having $M'(\mu\text{-}EH)_2M'$ cores such as $[(Cp^*M'Cl)_2(\mu\text{-}EH)_2]$ (M′ = Ir, Rh; E = S, Se; Cp* = η^5-C_5Me_5) and $[(Cp^{R5}RuCl)_2(\mu\text{-}SH)_2]$ (Cp^{R5} = Cp*, Cp° (**1**); Cp° = η^5-C_5EtMe_4) together with their reactivities toward various transition metal species to give the mixed-metal chalcogenido clusters with nuclearities ranging from 3 to 5.[1] More recently, it has turned out that these μ-hydrochalcogenido complexes also react with 2 equiv of group 15 metal chlorides MCl_3 (M = Sb, Bi), affording a series of cubane-type bimetallic chalcogenido clusters $[(Cp^*M'Cl)_2(\mu\text{-}EMCl_2)_2]$ and $[(Cp^\circ RuCl)_2(\mu\text{-}SMCl_2)_2]$ (**2**), respectively,[2] through dehydrochlorination from the μ-EH ligand and MCl_3. Formation of **2** from **1** is shown in eq 1. This finding demonstrates that these dinuclear Ir, Rh, and Ru μ-hydrochalcogenido complexes can serve as good precursors to the mixed-metal chalcogenido clusters containing not only the numerous d-block transition metals as reported previously[1] but also the main group metals in addition to these noble metals. It is to be noted that the syntheses and reactivities of chalcogenido clusters containing both transition metals and the heavier group 15 elements[3] are less investigated than those of clusters consisting of only transition metals, although such clusters are attracting much attention not only because of their importance in structural chemistry in their own right but also due to their relevance to the active sites of certain heterogeneous metal catalysts containing main group elements as promoters.[4]



(1)

We have found now that treatment of **1** with 1 equiv of MCl_3 results in the incorporation of only one MCl_2 fragment to the Ru_2S_2 core to afford $[(Cp^\circ RuCl)_2(\mu\text{-}SMCl_2)(\mu\text{-}SH)]$ (**3a**, M = Sb; **3b**, M = Bi). Furthermore, among these bimetallic trinuclear clusters **3** containing one μ-SH ligand, **3a** has proved to be converted into the novel trimetallic sulfido clusters with Ru_2PdSbS_2 and $Ru_2Pd_2SbS_2$ cores. In this paper, we describe the

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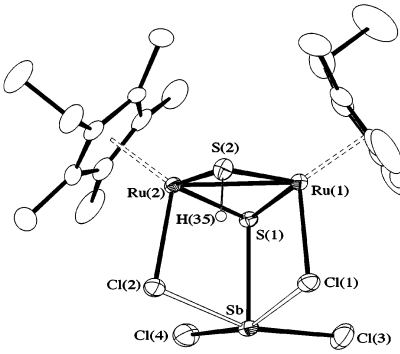
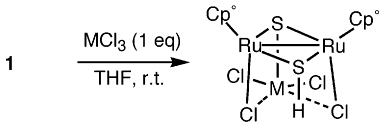


Figure 1. ORTEP drawing for **3a** at the 30% probability level. Hydrogen atoms are omitted for clarity except for the hydrosulfido hydrogen H(35). Cluster **3b**, containing Bi in place of Sb, has the same atom-connecting scheme.

details of the syntheses and structures of these new bi- and trimetallic sulfido clusters.

Results and Discussion

Preparation of Clusters 3 Containing Incomplete Cubane-Type $Ru_2MS_2Cl_2$ Cores. All reactions of $[(Cp^*M'Cl)_2(\mu\text{-}EH)_2]$ (M′ = Ir, Rh; E = S, Se) with 1 equiv of MCl_3 (M = Sb, Bi) in THF conducted at room temperature or upon cooling resulted in the formation of 1:1 mixtures of the known tetranuclear clusters $[(Cp^*M'Cl)_2(\mu\text{-}EMCl_2)_2]$ and unreacted $[(Cp^*M'Cl)_2(\mu\text{-}EH)_2]$. In contrast, when the Ru^{III} complex **1** was treated with an equimolar amount of MCl_3 in THF at room temperature, the desired trinuclear clusters containing only one M atom, **3a** and **3b**, were obtained in 74 and 83% yields, respectively (eq 2).



(2)

3a: M = Sb
3b: M = Bi

At present, it is not clear why the mono(pnictogeno) complexes can be derivatized from **1** but not from $[(Cp^*M'Cl)_2(\mu\text{-}EH)_2]$. Both clusters **3a** and **3b** were characterized by X-ray analysis; an ORTEP drawing of **3a** is shown in Figure 1, while selected interatomic distances and angles in **3a** and **3b** are listed in Table 1.

Table 1. Selected Interatomic Distances and Angles in 3

	3a (M = Sb)	**3b** (M = Bi)
(a) Distances (Å)		
Ru(1)−Ru(2)	2.8462(5)	2.8525(5)
Ru(1)−S(1)	2.318(1)	2.311(1)
Ru(1)−S(2)	2.308(1)	2.311(1)
Ru(2)−S(1)	2.3188(9)	2.312(1)
Ru(2)−S(2)	2.314(1)	2.313(2)
Ru(1)−Cl(1)	2.418(1)	2.442(1)
Ru(2)−Cl(2)	2.439(1)	2.448(1)
M−S(1)	2.492(1)	2.590(1)
M−Cl(3)	2.454(1)	2.582(1)
M−Cl(4)	2.445(1)	2.564(2)
M···Cl(1)	2.811(1)	2.854(2)
M···Cl(2)	2.825(1)	2.898(1)
(b) Angles (deg)		
S(1)−Ru(1)−S(2)	102.80(4)	102.73(5)
S(1)−Ru(1)−Cl(1)	87.12(4)	88.87(5)
S(2)−Ru(1)−Cl(1)	88.30(4)	88.11(5)
S(1)−Ru(2)−S(2)	102.58(4)	102.66(4)
S(1)−Ru(2)−Cl(2)	87.64(4)	89.44(5)
S(2)−Ru(2)−Cl(2)	90.48(5)	89.09(5)
S(1)-M−Cl(3)	89.77(4)	84.61(4)
S(1)−M−Cl(4)	86.68(4)	88.84(6)
Cl(3)−M−Cl(4)	92.81(5)	94.16(6)
Ru(1)−S(1)−Ru(2)	75.75(4)	76.19(4)
Ru(1)−S(1)−M	104.25(4)	103.14(4)
Ru(2)−S(1)−M	104.05(4)	103.60(4)
Ru(1)−S(2)−Ru(2)	76.03(3)	76.17(4)

Clusters **3** consist of two Cp°RuCl fragments connected by the μ-SH and μ-$SMCl_2$ ligands. The structures of **3** are analogous to those of correspnding **2** except for the presence of the H atom on S(2) in **3** in place of the MCl_2 moiety in **2**. The Ru−Ru distances at 2.8462(5) and 2.8525(5) Å in **3a** and **3b**, respectively, are indicative of the presence of a Ru−Ru single bond, which is consistent with the diamagnetic nature of **3** containing two Ru^{III} centers. These as well as the Ru−S, Ru−Cl, M−S, and M−Cl bond distances listed in Table 1 are comparable to those in **2** reported previously.[2] Two Cl ligands bound to Ru are mutually cis, and the separations of these Cl atoms from M (M = Sb, 2.811(1) and 2.825(1) Å; M = Bi, 2.854(2) and 2.898(1) Å) are longer than the sum of the covalent radii (Sb−Cl, 2.40 Å; Bi−Cl, 2.51 Å) but apparently shorter than the sum of the van der Waals radii (Sb, 2.2 Å; Bi, 2.4 Å; Cl, 1.8 Å), suggesting the presence of secondary bonding interactions between M and Cl.[5] Taking these weak M···Cl(1) and M···Cl(2) bonds into account, the structures of **3** may be considered as the incomplete cubane-type. It is to be noted that these M···Cl bonds in **3** are significantly shorter than the corresponding M···Cl bonds in the cubane-type **2** (Sb···Cl, 2.944(5)−3.000(4) Å; Bi···Cl, 2.934(5)−3.002(5) Å).

For both **3a** and **3b**, the H atom in the μ-SH ligand was able to be located unambiguously by the X-ray analysis, the orientation of which is syn with respect to the MCl_2 moiety of the μ-$SMCl_2$ ligand. These hydrosulfido protons were observed in their ^1H NMR spectra as singlets at δ 5.38 and 5.60 for **3a** and **3b**, respectively. For comparison, complex **1**, which is present as a 1:1 mixture of syn and anti forms with respect to two SH ligands in solution, shows the hydrosulfido protons in its ^1H NMR spectrum at δ 5.14 and 5.16.[6] The presence of the S−H ligand was also confirmed by their IR spectra (KBr), exhibiting characteristic ν(S−H) bands at 2434 and 2425 cm^{-1} for **3a** and **3b**.

Reactions of 3 with $[Pd(PPh_3)_4]$ Affording Ru_2PdSbS_2 and $Ru_2Pd_2SbS_2$ Clusters. Clusters **3** still consist of one μ-SH ligand, which may be expected to show high reactivity toward transition metal complexes as demonstrated already in this laboratory for **1** as well as related Rh and Ir μ-SH complexes. Hence, reactions of **3** with a range of late transition metal complexes have been attempted, and it has been found that treatment of **3a** with 1 equiv of $[Pd(PPh_3)_4]$ in THF at room temperature gives a mixture of trimetallic clusters $[(Cp°Ru)(Cp°RuCl)(\mu\text{-}SSbCl_2)\{PdCl(PPh_3)\}(\mu_3\text{-}S)(\mu\text{-}H)]$ (**4**), $[(Cp°Ru)_2(SbCl_2)\{Pd(PPh_3)\}_2(\mu_3\text{-}S)_2(\mu\text{-}Cl)]$ (**5**), and $[(Cp°Ru)(Cp°RuCl)\{PdCl(PPh_3)\}(SbCl)(\mu_3\text{-}S)_2]$ (**6**), as indicated by the ^1H NMR spectra of the evaporated reaction mixture residue (eq 3). Formation of a small amount of **2a** was also observed. Incorporation of one $\{Pd(PPh_3)\}$ fragment into **3a**, accompanied by the oxidative addition of the S−H bond to the Pd^0 center, affords **4**, containing the core assigned formally as $Ru^{III}{}_2Pd^{II}Sb^{III}$, while that of two $\{Pd(PPh_3)\}$ moieties with concurrent loss of HCl leads to **5**, consisting of the $\{Ru_2Pd_2Sb\}^{9+}$ core.

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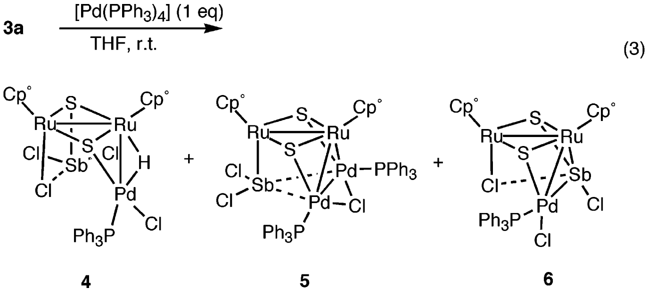
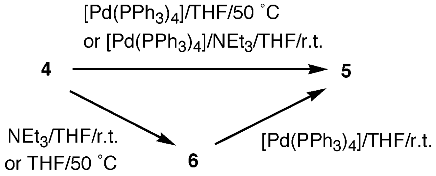


(3)

When the reaction of **3a** with 1 equiv of $[Pd(PPh_3)_4]$ was conducted under the milder conditions, viz., at −5 °C, the yield of **4** increased significantly.

It has been confirmed that isolated **4** was treated with 1 equiv of $[Pd(PPh_3)_4]$ in THF to be converted into **5** gradually at room temperature and much faster at 50 °C. This reaction proceeded more rapidly and cleanly even at room temperature, when conducted in the presence of triethylamine (Scheme 1). It has also been demonstrated that by treatment of **4** with triethylamine in THF at room temperature **6** was obtained in moderate yield. By warming the solution of **4** in THF at 50 °C, transformation of **4** into **6** also took place, as indicated by the NMR spectroscopy. Isolated **6** was converted further into **5** upon reaction with 1 equiv of $[Pd(PPh_3)_4]$ in THF at room temperature (Scheme 1).

Scheme 1



In contrast, reactions of the Bi complex **3b** with 1 equiv of $[Pd(PPh_3)_4]$ at room temperature and at −5 °C were both elusive, and isolation of the characterizable products from the reaction mixtures was unsuccessful; although the reaction at room temperature once afforded the Bi analogue of **5**, $[(Cp^{\circ}Ru)_2(BiCl_2)\{Pd(PPh_3)\}_2(\mu_3\text{-}S)_2(\mu\text{-}Cl)]$, to be characterized by the X-ray analysis, we could not reproduce this result again.

X-ray Structures of 4, 5, and 6. New clusters **4**, **5**, and **6** were isolable as single crystals, and their structures were fully characterized by X-ray diffraction as shown in Figures 2, 3, and 4, while selected bond distances and angles therein are listed in Tables 2−4, respectively.

Table 2. Selected Interatomic Distances and Angles in 4

Distances (Å)			
Ru(1)−Ru(2)	2.827(2)	Ru(1)−Pd	2.810(1)
Ru(1)−S(1)	2.318(3)	Ru(1)−S(2)	2.261(3)
Ru(2)−S(1)	2.316(3)	Ru(2)−S(2)	2.315(3)
Ru(2)−Cl(1)	2.452(3)	Pd−S(2)	2.243(3)
Pd−Cl(4)	2.362(4)	Pd−P	2.275(3)
Sb−S(1)	2.442(2)	Sb−Cl(3)	2.428(5)
Sb−Cl(4)	2.421(4)	Sb⋯Cl(2)	2.798(3)
Angles (deg)			
Ru(2)−Ru(1)−Pd	80.19(5)	Pd−Ru(1)−S(1)	103.41(8)
Pd−Ru(1)−S(2)	51.12(6)	S(1)−Ru(1)−S(2)	103.6(1)
S(1)−Ru(2)−S(2)	101.9(1)	S(1)−Ru(2)−Cl(2)	86.6(1)
S(2)−Ru(2)−Cl(2)	91.5(1)	S(2)−Pd−Cl(1)	161.3(1)
S(2)−Pd−P	97.2(1)	Cl(1)−Pd−P	98.0(1)
S(1)−Sb−Cl(3)	88.4(1)	S(1)−Sb−Cl(4)	96.8(1)
Cl(3)−Sb−Cl(4)	91.6(1)	Ru(1)−S(1)−Ru(2)	75.4(2)
Ru(1)−S(1)−Sb	97.7(1)	Ru(2)−S(1)−Sb	104.1(1)
Ru(1)−S(2)−Ru(2)	76.31(8)	Ru(1)−S(2)−Pd	77.20(9)
Ru(2)−S(2)−Pd	105.6(1)		

Table 3. Selected Interatomic Distances and Angles in 5

(a) Distances (Å)			
Ru(1)−Ru(2)	2.8272(7)	Ru(1)−Pd(1)	2.7845(7)
Ru(1)−Pd(2)	2.8060(7)	Pd(1)−Pd(2)	2.7755(6)
Ru(2)−Sb	2.6004(7)	Pd(1)−Sb	2.8690(6)
Pd(2)−Sb	2.8803(7)	Ru(1)−S(1)	2.226(2)
Ru(1)−S(2)	2.220(1)	Ru(2)−S(1)	2.300(2)
Ru(2)−S(2)	2.287(2)	Pd(1)−S(1)	2.267(2)
Pd(1)−Cl(1)	2.443(2)	Pd(1)−P(1)	2.284(2)
Pd(2)−S(2)	2.225(2)	Pd(2)−Cl(1)	2.450(2)
Pd(2)−P(2)	2.290(2)	Sb−Cl(2)	2.484(2)
Sb−Cl(3)	2.462(2)		
(b) Angles (deg)			
Ru(2)−Ru(1)−Pd(1)	82.29(2)	Ru(2)−Ru(1)−Pd(2)	81.46(2)
Pd(1)−Ru(1)−Pd(2)	59.53(2)	Ru(1)−Ru(2)−Sb	91.69(2)
Ru(1)−Pd(1)−Pd(2)	60.62(2)	Ru(1)−Pd(1)−Sb	87.14(2)
Pd(2)−Pd(1)−Sb	61.34(2)	Ru(1)−Pd(2)−Pd(1)	59.85(2)
Ru(1)−Pd(2)−Sb	86.52(2)	Pd(1)−Pd(2)−Sb	60.93(2)
Ru(2)−Sb−Pd(1)	84.77(2)	Ru(2)−Sb−Pd(2)	84.07(2)
Pd(1)−Sb−Pd(2)	57.73(2)	S(1)−Ru(1)−S(2)	101.38(6)
S(1)−Ru(2)−S(2)	97.17(6)	S(1)−Pd(1)−Cl(1)	151.38(6)
S(1)−Pd(1)−P(1)	106.36(7)	Cl(1)−Pd(1)−P(1)	102.22(7)
S(2)−Pd(2)−Cl(1)	150.46(6)	S(2)−Pd(2)−P(2)	105.75(6)
Cl(1)−Pd(2)−P(2)	103.67(7)	Cl(2)−Sb−Cl(3)	95.08(7)

Table 4. Selected Interatomic Distances and Angles in 6

(a) Distances (Å)			
Ru(1)−Ru(2)	2.8453(5)	Ru(1)−Pd	2.7997(6)
Ru(1)−Sb	2.7414(5)	Pd−Sb	2.8274(4)
Ru(1)−S(1)	2.339(1)	Ru(1)−S(2)	2.256(1)
Ru(2)−S(1)	2.342(1)	Ru(2)−S(2)	2.310(1)
Ru(2)−Cl(2)	2.424(2)	Pd−S(2)	2.259(1)
Pd−Cl(1)	2.411(1)	Pd−P	2.298(1)
Sb−S(1)	2.454(1)	Sb−Cl(3)	2.506(1)
Sb⋯Cl(2)	2.903(1)		
(b) Angles (deg)			
Ru(2)−Ru(1)−Pd	84.06(2)	Ru(2)−Ru(1)−Sb	79.79(2)
Pd−Ru(1)−Sb	61.35(1)	Ru(1)−Pd−Sb	58.31(1)
Ru(1)−Sb−Pd	60.34(1)	S(1)−Ru(1)−S(2)	103.35(4)
S(1)−Ru(2)−S(2)	101.45(4)	S(1)−Ru(2)−Cl(2)	87.47(5)
S(2)−Ru(2)−Cl(1)	88.67(5)	S(2)−Pd−Cl(1)	158.39(5)
S(2)−Pd−P	106.34(4)	Cl(1)−Pd−P	92.87(5)
S(1)−Sb−Cl(3)	93.08(5)		

Figure 2 shows that in **4** two Ru and one Pd atom comprise an open triangle capped with one μ_3-sulfide, where the Ru−Ru and Ru(1)−Pd edges have single-bond distances of 2.827(2) and 2.810(1) Å, respectively. Two Ru atoms are further bridged by a $SSbCl_2$ ligand, and this Sb atom is connected weakly to the Cl atom on Ru(2) with the Sb⋯Cl distance of 2.798(3) Å. The other Cl atom originally bonded to Ru(1) in **3a** has migrated to the Pd site in **4**. In the ^1H NMR spectrum, the hydride proton was observed at δ −15.49 as a doublet with $J_{P-H} = 80$ Hz, which is indicative of the geometry around Pd with the hydride occupying the position nearly trans to the PPh_3 ligand. As expected, the hydride H(54) was found in the Fourier map to complete the distorted square-planar geometry around Pd together with S(2), P, and Cl(1) atoms. This hydride is also bonded to Ru(1) as the bridging ligand, the Pd−H(54) and Ru(1)−H(54) distances being 1.7 and 1.5 Å, respectively. For comparison, the hydride proton that bridges the Pd−Ru edge with a Pd−Ru single bond in $[(Cp^*Ru)\{Pd(PPh_3)_2\}(CpTiCl)(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ was reported to appear at δ −11.92 as a doublet of doublets with $J_{P(trans)-H}$ and $J_{P(cis)-H}$ of 114.7 and 4.9 Hz.[7]

Cluster **5** consists of a distorted Ru_2Pd_2 tetrahedral core, the lengths of one Ru−Ru, one Pd−Pd, and two Ru(1)−Pd edges of which are in the range of single-bond distances as listed in

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[7] Kuwata, S.; Kabashima, S.; Sugiyama, N.; Ishii, Y.; Hidai, M. *Inorg. Chem.* **2001**, *40*, 2034.

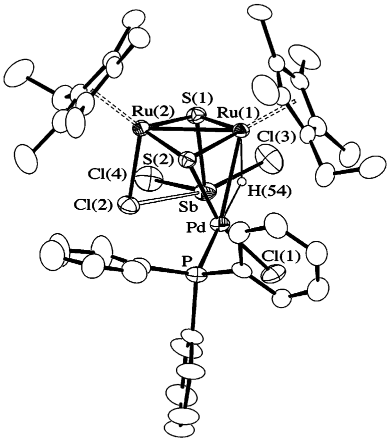

Figure 2. ORTEP drawing for **4** at the 30% probability level. All hydrogen atoms except for H(54) were omitted for clarity. For the two disordered Et groups in the Cp° ligands, only those with the larger occupancies are shown.

Table 3. Two Ru_2Pd faces of this tetrahedron are capped with the μ_3-sulfides. The Sb atom is bound directly to one Ru center with the Sb−Ru(2) bond distance at 2.6004(7) Å, which is considerably shorter than the Sb−Ru bond distances in monoruthenium complexes $[Cp^*(CO)_2RuSb(COPh)_2]$ (2.641(2) Å) and $[Cp^*(CO)_2RuSb(COPh)(SiMe_3)]$ (2.677(1) Å)[8] as well as the triruthenium complex having a four-membered Ru_3Sb ring $[Ph_2SbRu_3(COPh)(CO)_{10}]$ (2.6361(6)−2.6473(7) Å).[9] Weaker bonding interactions are also observed between the Sb atom and two Pd atoms, separations of which are 2.8690(6) and 2.8803(7) Å. The Pd−Pd edge is bridged by the Cl ligand, and two Pd atoms are each coordinated further by one PPh_3 ligand. Two P atoms are almost coplanar with the nearly planar S_2Pd_2Cl ring. The hydrosulfido proton in **3a** is lost in **5** probably as HCl, whereas the remaining Cl atom originally bonded to Ru is now bridging two Pd atoms.

A related, almost symmetrical Ru_2Pd_2 core with two capped μ_3-S ligands on the Ru_2Pd faces as well as the μ_2-Cl ligand on the Pd−Pd edge has been reported previously for $[(Cp^*Ru)_2\{Pd(PPh_3)\}_2(\mu_3\text{-}S)_2(\mu_2\text{-}Cl)]Cl$ (**7**).[10] By incorporation of the $\{SbCl_2\}$ fragment on the $Ru(2)Pd_2$ face with the Ru(2)−Sb single bond and the weaker Pd−Sb interactions, the metrical parameters with respect to the Ru_2Pd_2 core in **5** differ significantly from those in **7**. Thus, in **5** two Ru(2)−Pd bonds of the $Ru(2)Pd_2$ face are cleaved and the Ru−Ru bond is much elongated by ca. 0.2 Å, while two Ru(1)−Pd bonds are both shortened by ca. 0.1 Å (average), as compared to those in **7**.

An ORTEP drawing for **6** is depicted in Figure 4, and selected bond distances and angles therein are summarized in Table 4. Cluster **6** has a Ru_2PdSb core with metal−metal bonds between two Ru atoms (2.8453(5) Å), between Ru(1) and Pd (2.7997(6) Å), between Ru(1) and Sb (2.7414(5) Å), and between Pd and Sb (2.8274(4) Å). This core may result from the elimination of the bridging hydride and one Cl atom bonded to the Sb atom in **4**, followed by the binding of the Sb atom to the Ru−Pd edge in place of the hydride. The Pd−Sb distance in **6** as well as that in **5** shown above are somewhat longer than those in the Pd_4Sb_4 cubane cluster $[\{Pd(PPh_2Me)_2\}_4Sb_4][Ph_2SbCl_2]_2$ (2.6273(9)−2.8245(10) Å)[11] and much longer than those in the $Pd-SbPh_3$ complexes such as $[Pd_2(OAc)_4(SbPh_3)_2]$ (2.508(4) and 2.509(4) Å) and $[Pd_3(OAc)_4Ph_2(SbPh_3)_2]$ (2.473(4) Å).[12] The Ru_2Pd and Ru_2Sb faces are capped with μ_3-S ligands. The Sb−S bond length at 2.454(1) Å is shorter than that at 2.492(1) Å in **3a** but comparable to those in **4** (2.442(2) Å) and $[\{Cp^*Mo(CO)_2\}_2(\mu\text{-}SSb)]$ (2.436(1) Å).[13] The Cl atom on Ru(2) is interacting weakly with the Sb atom (Cl(2)···Sb, 2.903(1) Å).

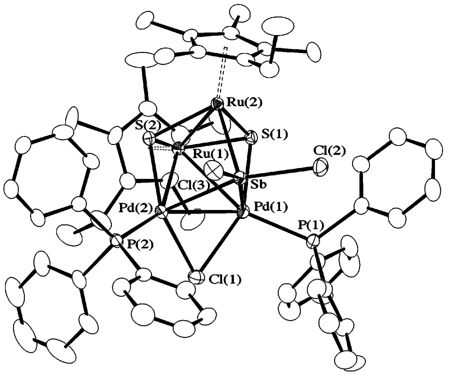

Figure 3. ORTEP drawing for **5** at the 30% probability level. Hydrogen atoms are omitted for clarity.

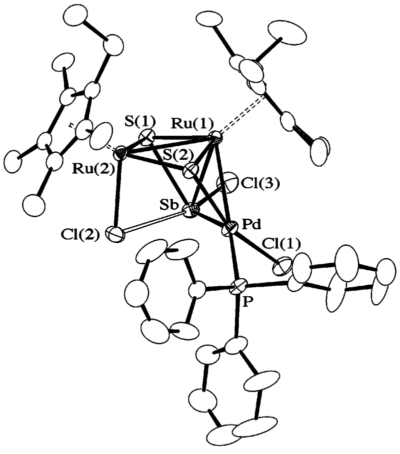

Figure 4. ORTEP drawing for **6** at the 30% probability level. Hydrogen atoms are omitted for clarity.

In conclusion, a convenient route to synthesize mixed-metal sulfido-hydrosulfido clusters **3** containing both the noble metals and group 15 metals has been demonstrated by using the diruthenium bis(μ-hydrosulfido) complex, and further treatment of the Sb cluster **3a** with $[Pd(PPh_3)_4]$ has proved to give three new trimetallic sulfido clusters.

Experimental Section

General Considerations. All manipulations were carried out under N_2 using standard Schlenk techniques. Solvents were dried by common methods and distilled under N_2 before use. Complex **1** was prepared in the same manner as that described for its Cp* analogue,[6] while $[Pd(PPh_3)_4]$ was obtained by the literature method.[14] Other chemicals were obtained commercially and used as received.

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Table 5. Crystal Data for 3a, 3b, 4, 5, and 6·0.5THF

	3a	**3b**	4	**5**	**6·0**.5THF
formula	$C_{22}H_{35}Cl_4S_2Ru_2Sb$	$C_{22}H_{35}BiCl_4S_2Ru_2$	$C_{40}H_{50}Cl_4PPdS_2Ru_2Sb$	$C_{58}H_{64}Cl_3P_2Pd_2S_2$-$Ru_2Sb$	$C_{42}H_{53}Cl_3O_{0.5}P$-PdS_2Ru_2Sb
fw	829.34	916.57	1198.03	1530.26	1197.62
space group	$P2_1/a$ (No. 14)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a, Å	17.805(4)	10.454(2)	24.475(9)	25.40(3)	9.739(4)
b, Å	8.603(2)	23.873(4)	9.905(3)	12.198(12)	11.704(4)
c, Å	19.694(4)	11.819(2)	18.476(7)	38.82(4)	21.644(8)
α, deg	90	90	90	90	89.36(2)
β, deg	108.0696(7)	97.8019(7)	90	106.638(3)	89.00(2)
γ, deg	90	90	90	90	66.400(11)
V, Å^3	2868(1)	2922.4(9)	4479(3)	11522(20)	2261(2)
Z	4	4	4	8	2
μ, cm^{-1}	25.02	75.35	20.48	18.91	19.72
ρ_{calcd}, g cm^{-3}	1.921	2.083	1.777	1.764	1.759
cryst size, mm^3	0.70 × 0.40 × 0.05	0.50 × 0.30 × 0.10	0.30 × 0.15 × 0.03	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.10
no. of unique reflns	6809	6940	9989	12 406	10 577
no. of data obsd	4778 ($I > 2\sigma(I)$)	5005 ($I > 2\sigma(I)$)	4662 ($I > 2\sigma(I)$)	8593 ($I > 2\sigma(I)$)	7262 ($I > 2\sigma(I)$)
no. of variables	318	318	527	695	589
transmn factor	0.527−0.882	0.220−0.471	0.657−0.940	0.464−0.685	0.627−0.821
R_1[a]	0.032	0.028	0.043	0.050	0.035
wR_2[b]	0.108	0.098	0.140	0.159	0.113
GOF[c]	1.000	1.000	1.010	1.004	1.006

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ ($I > 2\sigma(I)$). [b] $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$ (all data). [c] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/\{(\text{no. observed}) - (\text{no. variables})\}]^{1/2}$.

NMR and IR spectra were measured on a JEOL alpha-400 or a JASCO FT/IR-420 spectrometer at room temperature. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of 3a. A THF solution (50 mL) of **1** (1.89 g, 2.95 mmol) and $SbCl_3$ (0.672 g, 2.95 mmol) was stirred at room temperature overnight, and the resultant red-brown suspension was dried in vacuo. The residue was washed with THF (5 mL) and then extracted twice with CH_2Cl_2 (10 mL). Addition of hexane (200 mL) to the combined extract afforded **3a** as red-brown crystals (1.83 g, 74% yield). ^{1}H NMR ($CDCl_3$): δ 1.12 (t, J = 7.6 Hz, 6H, CH_2CH_3), 1.68, 1.69 1.71, 1.74 (s, 6H each, CCH_3), 2.08 (q, J = 7.6 Hz, 4H, CH_2CH_3), 5.38 (s, 1H, SH). IR (KBr): ν(S−H), 2434 cm^{-1}. Anal. Calcd for $C_{22}H_{35}S_2Cl_4Ru_2Sb$: C, 31.86; H, 4.25. Found: C, 32.01; H, 4.18.

Preparation of 3b. This complex was prepared similarly from **1** (331 mg, 0.519 mmol) and $BiCl_3$ (163 mg, 0.517 mmol). The yield of **3b** as red-brown crystals was 394 mg (83%). ^{1}H NMR ($CDCl_3$): δ 1.13 (t, J = 7.6 Hz, 6H, CH_2CH_3), 1.66, 1.67, 1.70, 1.74 (s, 6H each, CCH_3), 2.08 (q, J = 7.6 Hz, 4H, CH_2CH_3), 5.60 (s, 1H, SH). IR (KBr): ν(S−H), 2425 cm^{-1}. Anal. Calcd for $C_{22}H_{35}S_2Cl_4Ru_2Bi$: C, 28.83; H, 3.85. Found: C, 28.90; H, 3.87.

Reaction of 3a with [Pd(PPh$_3$)$_4$]. (1) A mixture of **3a** (41 mg, 0.049 mmol) and [Pd(PPh$_3$)$_4$] (57 mg, 0.049 mmol) in THF (3 mL) was stirred overnight at room temperature in the dark for 23 h. The resultant dark red solution was dried in vacuo, and its ^{1}H NMR spectrum showed the presence of compounds **4**, **5**, **6**, **3a**, and **2a** in the molar ratio 41:21:12:21:5. The residue was first extracted with ether (17.5 mL). The extract was dried again and the residue was crystallized from THF−hexane (1 mL/12 mL), affording **5** as red-brown crystals (5 mg, 7% yield). The reaction mixture residue extracted by ether was extracted again by THF (3 mL) and the extract was dried. The residue was crystallized from CH_2Cl_2−hexane (2 mL/12 mL), yielding a mixture of **4** and **6** in a molar ratio 78:22 as determined by ^{1}H NMR (14 mg, 24% combined yield). **5**: ^{1}H NMR ($CDCl_3$): δ 0.91, 0.93 (t, J = 7.6 Hz, 3H each, CH_2CH_3), 1.75, 1.81, 1.91, 1.92 (s, 6H each, CCH_3), 2.24, 2.32 (q, J = 7.6 Hz, 2H each, CH_2CH_3), 7.3−7.4, 7.6−7.7 (m, total 30H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 7.3 (s). Anal. Calcd for $C_{58}H_{64}P_2S_2Cl_3Ru_2Pd_2Sb$: C, 45.52; H, 4.22. Found: C, 45.14; H, 4.25.

(2) Complex **3a** (167 mg, 0.201 mmol) was added to a solution of [Pd(PPh$_3$)$_4$] (232 mg, 0.201 mmol) in THF (10 mL), and the mixture was stirred at −5 °C in the dark for 17 h. The resultant mixture was dried in vacuo, and its ^{1}H NMR spectrum showed the presence of compounds **4**, **5**, **6**, **3a**, and **2a** in the molar ratio 74:11:5:5:5. The residue was first extracted with ether (25 mL). The extract was dried again and crystallized from THF−hexane (1 mL/10 mL), affording **5**. The evaporated reaction mixture residue was extracted again with THF (8 mL), and the addition of hexane (16 mL) to the concentrated extract (3 mL) gave a mixture of **4** and **6** (83:17; total 150 mg, 62% yield) together with an additional amount of **5**. The combined yield of **5** was 33 mg (11% yield). The yield of **6** suggests that the amount of this product presumably increased during workup of the reaction mixture. Crystallization of a mixture of **4** and **6** from CH_2Cl_2−hexane at −20 °C gave red-brown single crystals of **4** for the X-ray diffraction study. **4**: ^{1}H NMR ($CDCl_3$): δ −15.49 (d, J_{P-H} = 80 Hz, RuHPd), 0.96, 1.04 (t, J = 7.6 Hz, 3H each, CH_2CH_3), 1.37, 1.40, 1.41, 1.46, 2.00, 2.03, 2.06, 2.12 (s, 3H each, CCH_3), 1.65−1.75 (m, 2H, CH_2CH_3), 2.40, 2.51 (dq, J = 15 and 7.6 Hz, 1H each, CH_2CH_3), 7.3−7.4, 7.6−7.7 (m, total 15H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.1 (s). Anal. Calcd for $C_{40}H_{50}PS_2Cl_4Ru_2PdSb$: C, 40.10; H, 4.21. Found: C, 39.94; H, 4.26.

Reaction of 4 with [Pd(PPh$_3$)$_4$] to Give 5. (1) Reaction of **4** (22 mg, 0.018 mmol) with [Pd(PPh$_3$)$_4$] (23 mg, 0.020 mmol) in THF was monitored by the ^{1}H NMR spectra of the reaction mixture residues, which showed that the reaction at room temperature for 25 h gave **5** together with the unreacted **4** and uncharacterizable byproducts (**5**:**4** = 2), while that at 50 °C converted almost all **4** into **5** together with a small amount of one uncharacterized byproduct.

(2) Into a THF solution (3 mL) of **4** (30 mg, 0.025 mmol) and [Pd(PPh$_3$)$_4$] (28 mg, 0.024 mmol) was added triethylamine (4 μL, 0.03 mmol), and the solution was stirred at room temperature. After 3 h, the NMR spectrum showed the absence of **4** in the reaction mixture. The mixture was dried in vacuo and the residue was extracted with benzene (5 mL). The extract was dried again and the residue was crystallized from THF−hexane, affording **5** as crystals (21 mg, 55% yield).

Reaction of 4 with Triethylamine to Give 6. (1) Into a THF (12.5 mL) solution of **4** (54 mg, 0.045 mmol) was added triethylamine (7.8 μL, 0.055 mmol), and the mixture was stirred at room tempearture overnight. The resultant mixture was dried in vacuo and the residue was extracted with benzene (10 mL × 2). The extract was concentrated to ca. 4 mL and then CH_2Cl_2 (2 mL) was added. After stirring this mixture, hexane (30 mL) was added slowly to give **6** as red-brown crystals (39 mg, 74% yield). ^{1}H NMR ($CDCl_3$): δ 0.97, 1.00 (t, J = 7.2 Hz, 3H each, CH_2CH_3), 1.40, 1.41, 1.42, 1.43, 2.04, 2.08, 2.13, 2.17 (s, 3H each, CCH_3), 1.69 (br q, $J = 7.2$ Hz, 2H, CH_2CH_3), 2.54, 2.66 (dq, $J = 15.2$ and 7.2 Hz, 1H each, CH_2CH_3), 7.3−7.4, 7.6−7.7 (m, total 15H, Ph). ^{31}P-{^1H} NMR ($CDCl_3$): δ 22.4 (s). Single crystals for the X-ray diffraction were obtained by recrystallization from THF−hexane as **6**·0.5THF. Anal. Calcd for $C_{42}H_{53}O_{0.5}PS_2Cl_3Ru_2PdSb$: C, 42.12; H, 4.46. Found: C, 42.35; H, 4.57.

(2) A THF solution (2 mL) of **4** (9 mg, 0.008 mmol) was stirred at 50 °C for 10 h. The NMR spectrum of the reaction mixture showed about 50% conversion of **4** into **6**.

Reaction of 6 with [Pd(PPh$_3$)$_4$]. A THF solution (2 mL) of **6**·0.5THF (6.7 mg, 0.0056 mmol) and [Pd(PPh$_3$)$_4$] (6.5 mg, 0.0056 mmol) was stirred at room temperature for 16 h. The NMR spectrum of the reaction mixture showed that almost all **6** was converted to **5**.

X-ray Crystallography. Single crystals of **3a**, **3b**, **4**, **5**, and **6**·0.5THF were sealed in glass capillaries under argon and mounted on a Rigaku Mercury-CCD diffractometer equipped with a graphite-monochromatized Mo Kα source. All diffraction studies were done at 23 °C, the details of which are listed in Table 5.

Structure solution and refinements were carried out by using the CrystalStructure program package.[15] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[16] and subsequent Fourier synthesis (DIRDIF 99).[17] These were refined with anisotropic thermal parameters by full-matrix least-squares techniques. Hydrosulfido protons H(35) in **3a** and H(35) in **3b** were found in the Fourier maps and refined isotropically, whereas the hydride H(54) in **4** found in the Fourier map was not refined but included with fixed parameters in the refinements. All other hydrogen atoms were placed at the calculated positions and included in the refinements. Two Cp° ligands in **4** are both occupying two disordered positions with respect to the orientations of the Et groups in the ratios 55:45 and 60:40. Only one C atom of the Et group in the Cp° ligand with less occupancy was refined isotropically. The absolute structure of **4** was determined by refinement of the Flack parameter ($\chi = 0.42(4)$).

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Supporting Information Available: Detailed crystallographic data and extensive interatomic distances and angles for **3a**, **3b**, **4**, **5**, and **6**·0.5THF in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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