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Synthesis of a New Tetrakis(hydrosulfido) Diiridium Complex and Its Conversion into Homo- and Heterometallic Sulfido−Hydrosulfido Clusters

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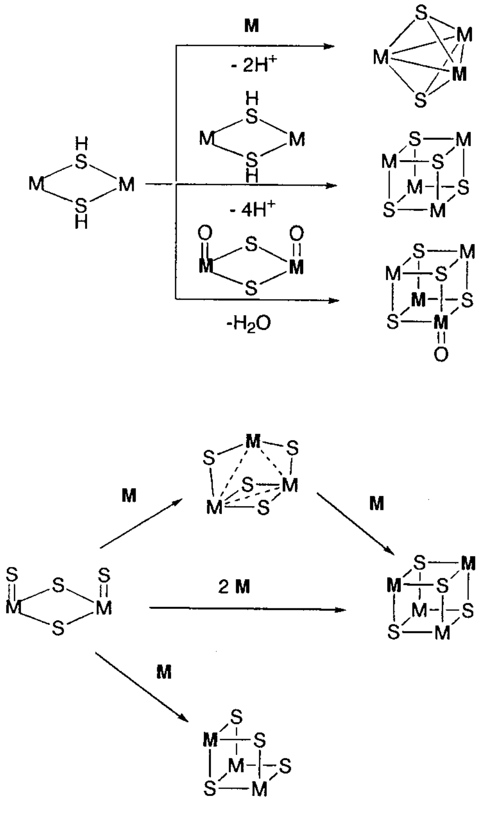
The diiridium tris(hydrosulfido) complex [Cp*Ir(μ_2-SH)$_3$IrCp*]Cl (**2**; Cp* = η^5-C$_5$Me$_5$) reacted with [NEt$_4$][SH] at room temperature for 3 h to afford the tetrakis(hydrosulfido) complex [Cp*Ir(SH)(μ_2-SH)$_2$IrCp*(SH)] (**3**). Complex **3** dissolved in benzene is thermally unstable and was converted into the triiridium sulfido−hydrosulfido cluster [(Cp*Ir)$_3$(μ_3-S)(μ_2-S)(μ_2-SH)$_2$] (**4**) at 50 °C. The related triiridium cluster [(Cp*Ir)$_3$(μ_3-S)(μ_2-SH)$_3$]Cl (**6**) was obtained from either the reaction of **3** with 0.5 equiv of [(Cp*IrCl)$_2$(μ_2-H)$_2$] or treatment of **2** with an equimolar amount of NEt$_3$. Furthermore, reaction of **3** with 2 equiv of [Pd(PPh$_3$)$_4$] or a [Pd(dba)$_2$]−PPh$_3$ (dba = dibenzalacetone) mixture gave the Ir$_2$Pd$_2$ mixed-metal sulfido−hydrosulfido cluster [(Cp*Ir)$_2$(SH)(μ_3-S)$_2${Pd(PPh$_3$)}$_2$(μ_2-SH)] (**8**). X-ray analyses were undertaken to determine the detailed structures of **3**, **4**, **6**, and **8**.

Introduction

Metal sulfido clusters are currently attracting significant attention,[1] and our recent studies have focused on the exploitation of rational synthetic routes for construction of the desired metal−sulfido cluster cores in high yields.[2] Thus, we have shown recently that hydrosulfido-bridged dinuclear complexes such as [Cp*MCl(μ_2-SH)$_2$MCp*Cl] (M = Ru, Rh, Ir (**1**); Cp* = η^5-C$_5$Me$_5$), [CymRuCl(μ_2-SH)$_2$RuCymCl] (Cym = *p*-MeC$_6$H$_4$Pr^i), and [Cp$_2$Ti(μ_2-SH)$_2$RuCp*Cl] (Cp = η^5-C$_5$H$_5$) can serve as remarkably promising precursors for synthesizing numerous homo- and heterometallic sulfido clusters containing, for example, M$_3$(μ_3-S)$_2$ and M$_4$(μ_3-S)$_4$ cores through reactions with other mono- or dinuclear metal species (Scheme 1).[3−5] The other versatile precursors used in our studies are the tetrakis(sulfido) dimolybdenum and ditungsten complexes [{MS(S$_2$CNEt$_2$)}$_2$(μ_2-S)$_2$] (M = Mo, W), whose reactions with a range of noble-metal complexes have resulted in the formation of clusters with M$_3$(μ_2-S)$_4$, M$_3$(μ_3-S)(μ_2-S)$_3$, and M$_4$(μ_3-S)$_4$ cores,[6] as shown in Scheme 1.

Scheme 1



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Our pursuit of new precursors to synthesize another series of metal−sulfur clusters has now led to the finding of a novel diiridium complex containing the two terminal and two bridging hydrosulfido ligands [Cp*Ir(SH)(μ_2-SH)$_2$IrCp*(SH)] (**3**). Subsequent studies on its reactivities have revealed that **3** is a potential compound which is readily convertible into new homo- and heterometallic sulfido−hydrosulfido clusters.

Results and Discussion

Synthesis and Characterization of [Cp*Ir(SH)(μ_2-SH)$_2$IrCp*(SH)] (3). We have reported previously that treatment of [Cp*IrCl(μ_2-Cl)$_2$IrCp*Cl] with excess H_2S gas in CH_2Cl_2 at room temperature for 5 min gives the bis(hydrosulfido) diiridium complex **1**, while that for the longer period, e.g. 15 h, affords the tris(hydrosulfido) complex [Cp*Ir(μ_2-SH)$_3$IrCp*]Cl (**2**) exclusively.[7] Now, it has been found that an acetonitrile solution of **2** can be treated further with [NEt$_4$][SH] at room temperature for 3 h to form a yellow-brown suspension, from which the tetrakis(hydrosulfido) diiridium complex **3** is obtained as a yellow solid in 76% yield (eq 1). The structure of **3** has been determined by an X-ray analysis using a single crystal grown from benzene−hexane, although the SH hydrogens could not be located. It is noteworthy that **3** contains both terminal and bridging SH ligands. Hydrosulfido complexes of this type are quite rare,[8] and to our knowledge, the only well-defined example is [Ru(PMe$_2$Ph)$_2$(SH)(μ_2-SH)$_3$Ru(PMe$_2$Ph)$_3$].[9]

(1)

2 **3**

For **3**, an ORTEP drawing as well as the important interatomic distances and angles are shown in Figure 1. Complex **3** consists of two 18-electron Ir centers connected with two bridging SH groups. There are no Ir−Ir bonding interactions. The planar Ir(μ_2-SH)$_2$Ir core observed in **3** is quite comparable to that in **1**. Thus, in **3** the Ir−Ir, Ir−S(1), and Ir−S(1*) distances associated with the Ir(μ_2-SH)$_2$Ir core are 3.655(1), 2.386(4), and 2.383(4) Å, while the corresponding distances in **1** are 3.654(1), 2.385(2), and 2.385(2) Å, respectively. The S(1)−Ir−S(1*) angle in **3** (79.9(1)°) is also in good agreement with that in **1** (80.00(7)°). These Ir−μ-SH bond lengths are slightly shorter than those in [{IrH(PPh$_3$)$_2$}$_2$(μ_2-SH)$_2$(μ_2-H)][BF$_4$] (average 2.438(4) Å).[10] In comparison to the related μ-sulfido complexes, the Ir−μ-SH bond distances in **3** are nearly the same as the Ir−μ-S bond distances in [{Cp*Ir(CN-*t*-Bu)}$_2$(μ_2-S)$_2$] at 2.376(3) and 2.367(2) Å and significantly or slightly longer than those in [Cp*Ir(PMe$_3$)(μ_2-S)$_2$IrCp*] (Cp*Ir−S = 2.273(5) and 2.262(5) Å; Cp*(PMe$_3$)Ir−S = 2.317(4) and 2.363(5) Å).[11]

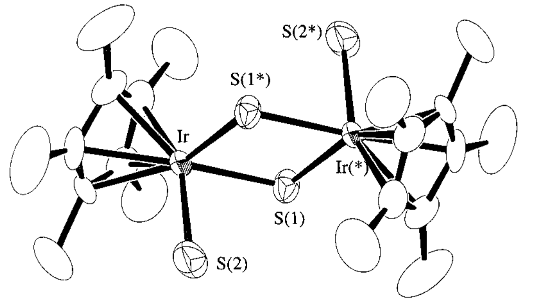

Figure 1. Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Important interatomic distances (Å) and angles (deg) are as follows: Ir−S(1), 2.386(4); Ir−S(1*), 2.383(4); Ir−S(2), 2.380(4); Ir···Ir*, 3.655(1); S(1)−Ir−S(1*), 79.9(1); S(1)−Ir−S(2), 88.3(1); S(1*)−Ir−S(2), 87.7(2); Ir−S(1)−Ir*, 100.1(1).

The Ir−S bond distance observed for the terminal SH ligands in **3** (2.380(4) Å) is essentially the same as that for the bridging SH ligands in **3** and is comparable to those in [Cp*Ir(PMe$_3$)(SH)$_2$] (average 2.375(2) Å)[12] but slightly longer and shorter than those in [IrHCl(SH)(CO)(PPh$_3$)$_2$] at 2.336(4) Å[13] and [IrH(SH)(PMe$_3$)$_4$][PF$_6$] at 2.427(1) Å,[14] respectively. A notable difference in the Ir−S bond lengths between the last two complexes is apparently ascribable to the trans influence, which is much weaker for the CO ligand than for the PMe$_3$ ligand.

The IR spectrum of **3** shows characteristic ν(S−H) bands at 2536 and 2462 cm^{-1}, which are not exceptional if compared with the ν(S−H) values previously reported for the terminal and bridging hydrosulfido ligands in the Ir complexes (2680−2478 cm^{-1}). The ^{1}H NMR spectrum of a C_6D_6 solution of **3** at room temperature may be interpreted in terms of the presence of syn and anti isomers in a molar ratio of ca. 1:1 with respect to the orientation of the two bridging S−H moieties. Such features of the hydrosulfido-bridged complexes have already been demonstrated for related complexes such as **1** (syn:anti = 3:2), its Rh analogue [Cp*RhCl(μ_2-SH)$_2$RhCp*Cl] (syn:anti = 3:2),[7] and [Cp*RuCl(μ_2-SH)$_2$RuCp*Cl] (syn:anti = 1:1).[15] It might also be noteworthy that the hydrosulfido protons of the bridging SH groups resonate at lower field than those of the terminal SH ligands for both isomers of **3** (see Experimental Section). Intensities of all these SH resonances gradually decreased upon addition of D_2O to the sample solution for ^{1}H NMR spectroscopy.

Formation of Triiridium Sulfido−Hydrosulfido Clusters. When the mixture of **2** and [NEt$_4$][SH] shown above was stirred for 24 h at room temperature, a small amount of the new trinuclear incomplete-cubane type cluster [(Cp*Ir)$_3$(μ_3-S)(μ_2-S)(μ_2-SH)$_2$] (**4**) was isolated from the reaction mixture together with **3** and the

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Scheme 2

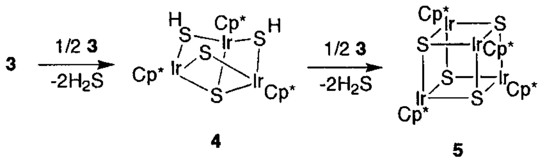


Table 1. Selected Interatomic Distances and Angles in 4 and 6

	4	6
(a) Interatomic Distances (Å)		
Ir(1)···Ir(2)	3.6145(8)	3.6339(6)
Ir(2)···Ir(2*)	3.6155(9)	3.6006(6)
Ir(1)−S(1)	2.382(5)	2.385(3)
Ir(1)−S(2)	2.366(4)	2.376(2)
Ir(2)−S(1)	2.381(3)	2.390(2)
Ir(2)−S(2)	2.364(4)	2.375(2)
Ir(2)−S(3)	2.361(3)	2.376(2)
(b) Interatomic Angles (deg)		
S(1)−Ir(1)−S(2)	80.6(1)	80.57(7)
S(2)−Ir(1)−S(2*)	91.0(2)	94.1(1)
S(1)−Ir(2)−S(2)	80.7(1)	80.48(9)
S(1)−Ir(2)−S(3)	80.5(1)	81.61(8)
S(2)−Ir(2)−S(3)	91.2(2)	91.77(9)
Ir(1)−S(1)−Ir(2)	98.74(9)	99.11(8)
Ir(2)−S(1)−Ir(2*)	98.8(2)	97.7(1)
Ir(1)−S(2)−Ir(2)	99.7(1)	99.78(8)
Ir(2)−S(3)−Ir(2*)	99.9(2)	98.5(1)

known cubane-type cluster [(Cp*Ir)$_4$(μ_3-S)$_4$] (**5**).[11] Clusters **4** and **5** are presumed to be produced from **3** with successive losses of H_2S, according to the stoichiometry shown in Scheme 2. Indeed, **3** dissolved in benzene is thermally unstable and slowly converted into **4** at room temperature. At 50 °C, this transformation of **3** into **4** was significantly enhanced and the formation of **5** was also observed; from the reaction mixture after 2 h, **4** was isolated as pure red crystals by fractional crystallization, although the yield was low. Cluster **4** has been characterized by an X-ray diffraction study, whose results are shown in Table 1 and Figure 2.

As shown in Figure 2a, the molecule of **4** has a crystallographically imposed mirror plane consisting of Ir(1), S(1), and S(3) atoms. The Ir−Ir distances in the incomplete-cubane type Ir$_3$(μ_3-S)(μ_2-S)$_3$ core are 3.6145(8) and 3.6155(9) Å, indicating the absence of Ir−Ir bonds. Each Ir atom has a three-legged piano-stool geometry, where the μ_2-S−Ir−μ_2-S angles are wider by ca. 10° than the μ_3-S−Ir−μ_2-S angles. Assignment of the S(2), S(2*), and S(3) atoms as either the sulfido sulfur or the hydrosulfido sulfur was unsuccessful, since the hydrosulfido hydrogens could not be located in the final Fourier map and, furthermore, no significant differences were observed between the bonding parameters associated with S(2) and S(3). The Ir−μ_3-S bond lengths (2.382(5) and 2.381(3) Å) are only slightly longer than the Ir−μ_2-S bond lengths (2.361(3)−2.366(4) Å).

Cluster **4** in the crystal exists as an aggregate of two molecules, which are mutually oriented in a staggered geometry with respect to the bridging S atoms (Figure 2b). The observed intermolecular S···S separations are either 3.874(5) Å for S(2)···{S(2*)}* or 3.905(4) Å for S(2)···{S(3)}* and S(3)···{S(2*)}*. These S···S distances might suggest that the four SH protons presumably exist between these six S atoms to form intermolecular hydrogen bonds, which is supported by the IR spectrum of **4** (KBr method), showing a strong broad ν(S−H) band

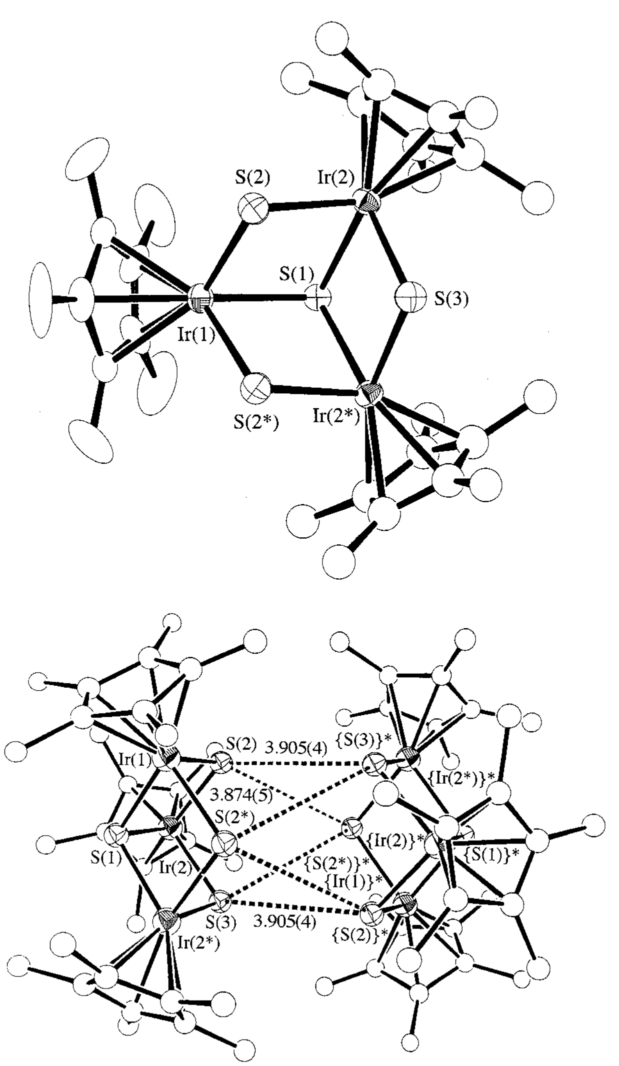
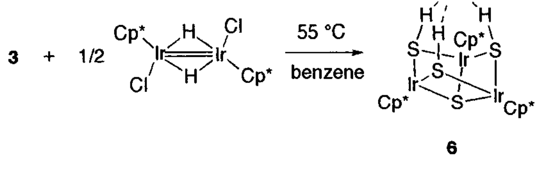


Figure 2. (a, top) Molecular structure of **4**. Hydrogen atoms and solvating benzene molecule are omitted for clarity. (b, bottom) Perspective view of two molecules of **4** aggregating in the crystal. Distances are in Å.

centered at ca. 2200 cm^{-1}. This significantly lower value as compared to that of the common ν(S−H) band and the broad feature are characteristic of SH groups with a hydrogen-bonding interaction. The ^{1}H NMR spectrum of the toluene-d_8 solution recorded at 30 °C exhibits only one broad singlet due to the Cp* protons at δ 1.77, which separates into two singlets at low temperatures with the intensity ratio 1:2 (e.g., δ 1.65 and 1.85 at −50 °C). However, the SH resonances could not be assigned.

Synthesis of incomplete cubane type cores is a subject of particular interest to us. Several attempts to construct the Ir$_3$S$_4$ core more cleanly have led to the finding that treatment of **3** with 0.5 equiv of [(Cp*IrCl)$_2$(μ-H)$_2$] yields the new triiridium sulfido−hydrosulfido cluster [(Cp*Ir)$_3$(μ_3-S)(μ_2-SH)$_3$]Cl (**6**) (eq 2), which is isolable in



(2)

50% yield as orange crystals after crystallization of the

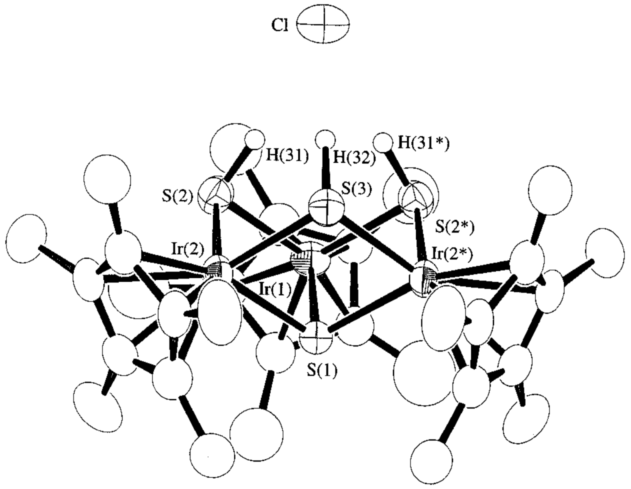


Figure 3. Molecular structure of **6**. For clarity, only one of the two disordered Cp* ligands attached to Ir(1) with the same occupancies is shown. The Cp* hydrogens are omitted.

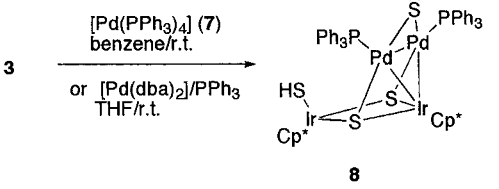
product from $ClCH_2CH_2Cl$−hexane. Cluster **6** was also isolable in 12% yield from the acetonitrile solution of **2**, to which NEt_3 was added to facilitate the removal of HCl (eq 3).

$$\frac{3}{2}\,\mathbf{2} \xrightarrow[\text{MeCN/-50 °C—r.t.}]{NEt_3} \mathbf{6} \tag{3}$$

The structure of **6** has also been clarified by an X-ray analysis. Figure 3 depicts the molecular structure of **6**, which has a crystallographically imposed mirror plane including the Ir(1), S(1), S(3), and Cl atoms, except for the Cp* ligand attached to Ir(1). As shown in Table 1, bonding parameters associated with the Ir_3S_4 core and the Ir⋯Ir distances are in good agreement with those in **4**. The hydrosulfido protons were located in the Fourier map, whose distances from the Cl anion at 2.43 and 2.32 Å indicate clearly the presence of a hydrogen-bonding interaction between the SH hydrogens and the Cl anion.

The IR spectrum, showing a broad ν(S−H) band at as low as 2330 cm^{-1}, is consistent with the hydrogen-bonded SH ligands, while the ^1H NMR spectrum exhibiting one singlet at δ 1.37 suggests the equivalence of the three Cp*Ir units. The SH resonances were unassignable.

Formation of an Ir_2Pd_2 Mixed-Metal Sulfido−Hydrosulfido Cluster. As reported already, **1** reacts with $[Pd(PPh_3)_4]$ (**7**) in THF at room temperature to afford $[(Cp^*Ir)_2(\mu_3\text{-}S)_2PdCl(PPh_3)]Cl$.[3a,f] Now, treatment of **3** with 2 equiv of **7** has been found to afford $[(Cp^*Ir)_2(SH)(\mu_3\text{-}S)_2\{Pd(PPh_3)\}_2(\mu_2\text{-}SH)]$ (**8**) in 22% yield (eq 4).



8 (4)

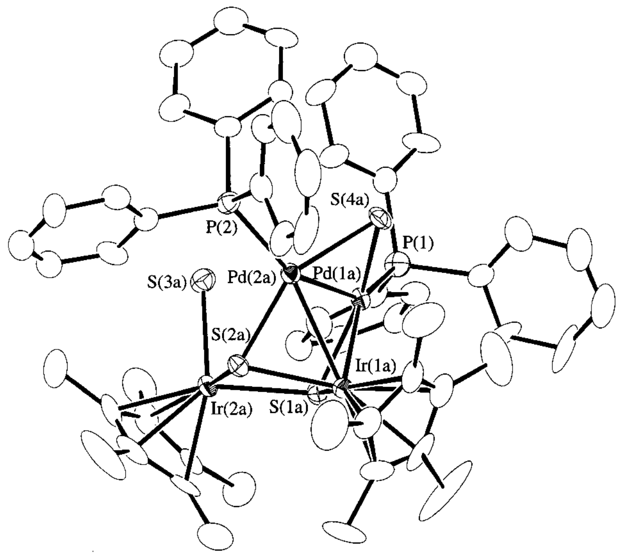


Figure 4. Molecular structure of **8**. The major component with ca. 91% occupancy is shown. Solvating THF and all hydrogen atoms are omitted for clarity.

Table 2. Selected Interatomic Distances and Angles in 8

(a) Interatomic Distances (Å)			
Ir(1a)⋯Ir(2a)	3.546(1)	Ir(1a)−Pd(1a)	2.742(2)
Ir(1a)−Pd(2a)	2.745(2)	Ir(2a)⋯Pd(1a)	3.818(2)
Ir(2a)⋯Pd(2a)	3.820(2)	Pd(1a)−Pd(2a)	2.726(2)
Ir(1a)−S(1a)	2.294(5)	Ir(1a)−S(2a)	2.320(6)
Ir(2a)−S(1a)	2.372(5)	Ir(2a)−S(2a)	2.385(6)
Ir(2a)−S(3a)	2.382(6)	Pd(1a)−S(1a)	2.289(5)
Pd(1a)−S(4a)	2.369(5)	Pd(2a)−S(2a)	2.303(6)
Pd(2a)−S(4a)	2.370(5)	Pd(1a)−P(1)	2.237(4)
Pd(2a)−P(2)	2.269(5)		
(b) Interatomic Angles (deg)			
Pd(1a)−Ir(1a)−Pd(2a)	59.59(5)	Ir(1a)−Pd(1a)−Pd(2a)	60.27(5)
Ir(1a)−Pd(2a)−Pd(1a)	60.15(5)		
Pd(1a)−Ir(1a)−S(1a)	53.2(1)	Pd(1a)−Ir(1a)−S(2a)	93.5(1)
Pd(2a)−Ir(1a)−S(1a)	93.1(1)	Pd(2a)−Ir(1a)−S(2a)	53.3(1)
S(1a)−Ir(1a)−S(2a)	82.6(2)	S(1a)−Ir(2a)−S(2a)	79.6(2)
S(1a)−Ir(2a)−S(3a)	94.7(2)	S(2a)−Ir(2a)−S(3a)	94.5(2)
Ir(1a)−Pd(1a)−S(1a)	53.3(1)	Ir(1a)−Pd(1a)−S(4a)	95.6(1)
Ir(1a)−Pd(1a)−P(1)	153.0(1)	Pd(2a)−Pd(1a)−S(1a)	93.7(1)
Pd(2a)−Pd(1a)−S(4a)	54.9(1)	Pd(2a)−Pd(1a)−P(1)	146.6(1)
S(1a)−Pd(1a)−S(4a)	146.0(2)	S(1a)−Pd(1a)−P(1)	109.1(2)
S(4a)−Pd(1a)−P(1)	104.8(2)	Ir(1a)−Pd(2a)−S(2a)	53.9(1)
Ir(1a)−Pd(2a)−S(4a)	95.5(1)	Ir(1a)−Pd(2a)−P(2)	154.7(1)
Pd(1a)−Pd(2a)−S(2a)	94.3(1)	Pd(1a)−Pd(2a)−S(4a)	54.9(1)
Pd(1a)−Pd(2a)−P(2)	144.8(1)	S(2a)−Pd(2a)−S(4a)	146.6(2)
S(2a)−Pd(2a)−P(2)	108.1(2)	S(4a)−Pd(2a)−P(2)	105.1(2)
Ir(1a)−S(1a)−Ir(2a)	98.9(2)	Ir(1a)−S(1a)−Pd(1a)	73.5(2)
Ir(2a)−S(1a)−Pd(1a)	110.0(2)	Ir(1a)−S(2a)−Ir(2a)	97.8(2)
Ir(1a)−S(2a)−Pd(2a)	72.9(2)	Ir(2a)−S(2a)−Pd(2a)	109.1(2)
Pd(1a)−S(4a)−Pd(2a)	70.2(1)		

The reaction of **3** and **7** in a molar ratio of 1:1 also resulted in the formation of this tetranuclear Ir_2Pd_2 cluster **8** in 17% yield as the only characterizable bimetallic product. A major byproduct was $[Cp^*Ir(PPh_3)(SH)_2]$ (**9**),[11] which is inferred to be formed from **3** and excess PPh_3 liberated from **7**. As expected, when **3** was treated with 2 equiv of a $[Pd(dba)_2]/PPh_3$ 1:1 mixture (dba = dibenzalacetone) in THF at room temperature, the yield of **8** was improved to 65% and the formation of **9** was not observed.

The structure of **8** has been determined by an X-ray analysis, whose results are shown in Figure 4 and Table 2. The formal $Ir^{III}{}_2Pd^{I}{}_2$ cluster **8** consists of an $IrPd_2$ triangular core, for which the Ir(1a)−Pd(1a), Ir(1a)−Pd(2a), and Pd(1a)−Pd(2a) distances at 2.742(2), 2.745(2), and 2.726(2) Å are all diagnostic of the presence of metal−metal bonding interactions. Two Ir−Pd edges are bridged by the sulfido ligands, which further bind to the second Ir atom Ir(2a) as μ_3-sulfides, whereas the remaining Pd−Pd edge has a bridging SH ligand that had migrated from Ir(1a) during the reaction. The separations of Ir(2a) from Ir(1a), Pd(1a), and Pd(2a) are 3.546(1), 3.818(2), and 3.820(2) Å, respectively, indicating the absence of bonding interactions between Ir(2a) and the other three metals. The structure of **8** has a pseudo mirror plane defined by the two Ir atoms and the two hydrosulfido S atoms. The Ir_2S_2 ring is slightly puckered, the dihedral angle around the S(1a)−S(2a) vector being 169°. Two Pd atoms as well as the S(1a) and S(2a) atoms are coplanar, and the dihedral angles between this Pd_2S_2 plane and the Ir(1a)−S(1a)−S(2a), Ir(2a)−S(1a)−S(2a), and Pd(1a)−Pd(2a)−S(4a) planes are 71, 120, and 166°, respectively.

With respect to the M−μ_3-S bonds in **8**, the Ir(2a)−μ_3-S distances at 2.372(5) and 2.385(6) Å are significantly longer than those of the Ir(1a)−μ_3-S (2.294(5) and 2.320(6) Å) and Pd−μ_3-S bonds (2.289(5) and 2.303(6) Å) but are almost comparable to the Ir−μ_3-S bond lengths in **4** and **6** (2.381(3)−2.390(2) Å), the cubane-type cluster **5** (2.367(3)−2.380(3) Å),[11] and the incomplete cubane-type cluster $[Ir(PPh_3)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{W(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (2.382(7) Å).[6a] The Pd−μ_3-S bonds in **8** are considerably shorter than those in a series of cubane-type $PdMo_3(\mu_3\text{-}S)_4$ clusters (2.356(3)−2.378(4) Å).[16] In the Ir_2Pd cluster cited above, $[(Cp^*Ir)_2(\mu_3\text{-}S)_2PdCl(PPh_3)]Cl$, the Ir−S bond lengths are 2.295(3) and 2.279(3) Å, with Pd−S bond distances at 2.362(4) and 2.293(4) Å.[3a,f]

For the SH ligand in **8**, the Ir(2a)−S(3a) distance at 2.382(6) Å is similar to the Ir−S bond length of the terminal SH group in **3** (2.380(4) Å). With respect to the $Pd_2(\mu_2\text{-}SH)$ moiety, the Pd−S bond lengths are 2.369(5) and 2.370(5) Å. It is noteworthy that the well-defined hydrosulfido complexes of Pd are quite limited; Pd−SH bond lengths have been reported only for terminal hydrosulfido complexes such as *trans*-$[Pd(SH)_2(P\text{-}i\text{-}Bu_3)_2]$ (2.305(1) Å)[17] and [Na(15-crown-5)][Pd(SH)(L)] (L = 1,3-imidazolidinyl-*N*,*N'*-bis(2-benzenethiolato)) (2.374(2) Å).[18]

In the IR spectrum, two ν(S−H) bands appeared at 2520 and 2402 cm^{-1}. The ^1H NMR spectrum showed two signals arising from the SH protons at δ −0.32 and 3.18. Since the latter observed at much lower field is a triplet coupled with the two ^{31}P nuclei, it is unambiguously assignable to the SH group which symmetrically bridges the Pd−Pd bond. Appearance of the bridging SH signal at lower field as compared to the terminal SH resonance has also been observed in the ^1H NMR spectrum of **3** (vide supra). Interestingly, only the signal at δ −0.32 disappears smoothly upon treatment with D_2O, indicating that deuterium exchange takes place much more rapidly for the terminal SH ligand on the Ir atom than for the bridging SH ligand bound to two Pd atoms.

We are currently investigating the syntheses of a wide range of mixed-metal clusters with the sulfido and hydrosulfido ligands by using the dinuclear hydrosulfido complex **3** along with the tri- and tetranuclear sulfido−hydrosulfido clusters **4**, **6**, and **8**.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques. IR and NMR spectra were recorded on JASCO FT/IR-420 and JEOL AL-400 spectrometers, while elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer. Compounds **2**,[7] $[(Cp^*IrCl)_2(\mu_2\text{-}H)_2]$,[19] **7**,[20] $[Pd(dba)_2]$,[21] and $[NEt_4][SH]$[22] were prepared by literature methods.

Synthesis of 3. Complex **2** (407 mg, 0.514 mmol) and $[NEt_4][SH]$ (252 mg, 1.54 mmol) were dissolved in acetonitrile (20 mL), and the solution was stirred at room temperature. The color changed immediately from yellow to red-brown. After 3 h, a yellow-brown suspension was obtained, which was filtered off, washed with acetonitrile, and then dried in vacuo (309 mg, 76% yield). IR (KBr): ν(S−H) 2536, 2462 cm^{-1}. ^1H NMR (C_6D_6 solution): δ −1.40, −1.09 (s, 1H each, terminal SH of syn isomer), −1.15 (s, 2H, ternimal SH of anti isomer), 0.37 (s, 2H, bridging SH), 0.42 (s, 2H, bridging SH), 1.40, 1.59 (s, 15H each, Cp* of syn isomer), 1.50 (s, 30H, Cp* of anti isomer); syn:anti = 1:1. Assignment of two bridging SH resonances to either a syn isomer or an anti isomer was uncertain. Anal. Calcd for $C_{20}H_{34}S_4Ir_2$: C, 30.52; H, 4.35. Found: C, 30.59; H, 4.30.

Synthesis of 4. A benzene solution (5 mL) of **3** (79 mg, 0.10 mmol) was heated at 50 °C for 2 h with stirring. The resulting red-brown mixture was filtered, and hexane was added to the concentrated filtrate, yielding a small amount of **4**·$0.5C_6H_6$ as red crystals, which were separated manually. The yield was unable to be determined. IR (KBr): ν(S−H) ca. 2200 (s, br) cm^{-1}. ^1H NMR ($C_6D_5CD_3$ solution): 30 °C, δ 1.77 (s, 45H, Cp*); −50 °C, δ 1.65 (s, 15H, Cp*), 1.84 (s, 30H, Cp*). The resonances coalesce at ca. +10 °C. The SH protons could not be assigned. Anal. Calcd for $C_{33}H_{50}S_4Ir_3$: C, 34.42; H, 4.38. Found: C, 34.36; H, 4.31.

Synthesis of 6. (a) Complex **3** (68 mg, 0.086 mmol) and $[(Cp^*IrCl)_2(\mu\text{-}H)_2]$ (31 mg, 0.043 mmol) dissolved in benzene (5 mL) were reacted for 5 h at 55 °C. A yellow solid precipitated, which was separated from the dark purple solution by filtration and crystallized from $ClCH_2CH_2Cl$/hexane (49 mg, 50% yield). Single crystals suitable for X-ray diffraction were obtained by recrystallization of this product from benzene/hexane.

(b) To a suspension of **2** (79 mg, 0.10 mmol) in acetonitrile (10 mL) was added NEt_3 (14 μL, 0.10 mmol) at −50 °C with stirring. The mixture was gradually warmed to room temperature, and the deposited solid of **5** was removed by filtration. The filtrate was evaporated, and the residue was extracted with benzene. The extract was evaporated again and the residue crystallized from $ClCH_2CH_2Cl$/hexane to give orange crystals of **6** (9.3 mg, 12% yield). A similar reaction in the presence of anhydrous Na_2S (31 mg, 0.40 mmol) gave 17 mg of **6** (22% yield) after an analogous workup of the reaction mixture.

IR (KBr): ν(S−H), 2330 (br) cm^{-1}. ^1H NMR (C_6D_6 solution): δ 1.36 (s, 45H, Cp*). The SH resonances were unassignable. Anal. Calcd for $C_{30}H_{48}S_4ClIr_3$: C, 31.36; H, 4.21. Found: C, 31.15; H, 4.58.

Synthesis of 8. A benzene solution (10 mL) containing **3** (49 mg, 0.062 mmol) and **7** (143 mg, 0.124 mmol) was stirred at room temperature for 24 h, and the resultant red-brown mixture was filtered. Addition of hexane to the concentrated filtrate gave black crystals of **8**·$0.5C_6H_6$ (22 mg, 22% yield).

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Table 3. Crystal Data for 3, 4·0.5C$_6$H$_6$, 6, and 8·THF

	3	**4**·0.5C$_6$H$_6$	**6**	**8**·THF
formula	$C_{20}H_{34}S_4Ir_2$	$C_{33}H_{50}S_4Ir_3$	$C_{30}H_{48}S_4ClIr_3$	$C_{60}H_{70}OP_2S_4Pd_2Ir_2$
fw	787.17	1151.66	1149.06	1594.71
space group	$P2_1/n$ (No. 14)	$C2/m$ (No. 12)	$Pbcm$ (No. 57)	$P2_1/n$ (No. 14)
a, Å	8.588(1)	17.522(2)	9.894(2)	12.867(2)
b, Å	9.3975(9)	19.011(2)	19.736(3)	11.171(3)
c, Å	15.728(1)	12.912(1)	18.098(2)	41.674(5)
β, °	104.125(8)	122.465(7)	90	92.71(2)
V, Å^3	1231.0(2)	3628.8(7)	3533(1)	5983(1)
Z	2	4	4	4
ρ_{calcd}, g cm^{-3}	2.124	2.108	2.160	1.768
μ(Mo Kα), cm^{-1}	111.72	112.56	116.31	52.70
cryst size, mm^3	0.4 × 0.15 × 0.10	0.5 × 0.3 × 0.15	0.6 × 0.2 × 0.1	0.5 × 0.15 × 0.02
no. of unique rflns	2163	4295	4181	13731
no. of data used	1828 ($I > 2\sigma(I)$)	3101 ($I > 3\sigma(I)$)	2718 ($I > 3\sigma(I)$)	6160 ($I > 3\sigma(I)$)
no. of variables	124	143	174	692
transmissn factor	0.2593−0.9995	0.2759−0.9946	0.6115−0.9971	0.2914−0.9984
R^a	0.059	0.048	0.033	0.060
$R_w{}^b$ or wR2^c	0.167^c	0.059^b	0.034^b	0.061^b

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o{}^2]^{-1}$). [c] wR2 $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Similar treatment of a THF solution (10 mL) of **3** (41 mg, 0.052 mmol), Pd(dba)$_2$ (60 mg, 0.10 mmol), and PPh$_3$ (27 mg, 0.10 mmol) afforded **8**·THF in 64% yield (53 mg). IR (KBr): ν(S−H), 2520 (vw), 2402 (vw) cm^{-1}. ^{1}H NMR (C$_6$D$_6$ solution): δ −0.32 (s, 1H, IrSH), 1.57, 1.85 (s, 15H each, Cp*), 3.18 (t, J_{P-H} = 4 Hz, 1H, μ-SH), 7.04−8.03 (m, 30H, Ph). Anal. Calcd for $C_{60}H_{70}OP_2S_4Ir_2Pd_2$: C, 45.19; H, 4.42. Found: C, 45.11; H, 4.28.

X-ray Crystallography. All diffraction studies were carried out at room temperature by using a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo Kα source (λ = 0.710 69 Å). Structure solution and refinements were carried out by using the teXsan program package,[23] whereby the positions of the non-hydrogen atoms were determined by Patterson methods (DIRDIF PATTY).[24] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at the calculated positions and included at the final stages of refinements with fixed parameters. Only for **3** were refinements carried out by SHELXL97.[25] Details for **3**, **4**·0.5C$_6$H$_6$, **6**, and **8**·THF are summarized in Table 3. For **3**, **4**, and **8**, the SH hydrogens could not be found and the structure refinements were done without these hydrogens. In **4**·0.5C$_6$H$_6$, the Cp* ligand attached to Ir(1) is oriented in two disordered positions with occupancies of 70 and 30%, while that bound to Ir(2) is found in three positions with occupancies of 35, 30, and 35%. The C atoms in the latter have only been refined isotropically. For **6**, the Cp* ligand on Ir(1) is present over two disordered positions, which are mutually related by inversion with respect to the mirror plane in the Ir$_3$S$_4$ core. In the crystal of **8**·THF, the molecule of **8** was located in two positions with 91 and 9% occupancies. For the minor component, only the positions of the Ir, Pd, and S atoms could be determined and refined anisotropically, where the Ir$_2$Pd$_2$S$_4$ core in the minor component is identical with that in the major component but directed in the opposite direction, being related to each other with the mirror plane vertical to the Ir−Ir vector. The P atoms are presumed to be overlapping for both components, while the C atoms in the minor component could not be located.

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Supporting Information Available: Listings of atomic coordinates, anisotropic thermal parameters, and extensive bond lengths and angles for **3**, **4**·0.5C$_6$H$_6$, **6**, and **8**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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