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Structures and Reactivities of Palladium−Ruthenium Mixed-Metal Sulfido Clusters Derived from Disulfido- or Hydrosulfido-Bridged Diruthenium Complexes

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The reaction of the disulfido-bridged diruthenium complex $[\mathrm{Cp^*Ru}(\mu_2\text{-}\mathrm{S_2})(\mu_2\text{-}\mathrm{SPr^i})_2\mathrm{RuCp^*}]$ (**1**; $\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) with 2 equiv of $[\mathrm{Pd(PPh_3)_4}]$ in boiling toluene resulted in the formation of the palladium−ruthenium mixed-metal sulfido cluster $[(\mathrm{Cp^*Ru})_2(\mu_3\text{-}\mathrm{S})_2\mathrm{Pd_2}(\mu_2\text{-}\mathrm{SPr^i})(\mathrm{SPr^i})(\mathrm{PPh_3})]$ (**2**). Upon treatment with benzyl bromide, stepwise substitution of the thiolato ligands in **2** by bromo ligands took place to afford the monobromo cluster $[(\mathrm{Cp^*Ru})_2(\mu_3\text{-}\mathrm{S})_2\mathrm{Pd_2}(\mu_2\text{-}\mathrm{SPr^i})\mathrm{Br}(\mathrm{PPh_3})]$ (**4**) and the dibromo cluster $[(\mathrm{Cp^*Ru})_2(\mu_3\text{-}\mathrm{S})_2\mathrm{Pd_2}(\mu_2\text{-}\mathrm{Br})\mathrm{Br}(\mathrm{PPh_3})]$ (**5**). On the other hand, the cationic palladium−ruthenium sulfido cluster $[(\mathrm{Cp^*Ru})_2(\mu_3\text{-}\mathrm{S})_2\mathrm{Pd_2}(\mu_2\text{-}\mathrm{Cl})(\mathrm{PPh_3})_2]\mathrm{Cl}$ (**7**) was obtained by the reaction of the hydrosulfido-bridged diruthenium complex $[\mathrm{Cp^*RuCl}(\mu_2\text{-}\mathrm{SH})_2\mathrm{RuClCp^*}]$ (**6**) with 2 equiv of $[\mathrm{Pd(PPh_3)_4}]$. The structural feature commonly observed for the 60e clusters **2**, **4**, **5**, and **7** is the presence of a distorted-tetrahedral $\mathrm{Pd_2Ru_2}$ core containing one Pd−Pd (2.780(1)−2.8130(8) Å) and one Ru−Ru bond (2.6231(7)−2.6386(9) Å) as well as four relatively long Pd−Ru contacts (2.831(1)−3.095(2) Å). Furthermore, **7** reacted with CO to afford the 64e carbonyl cluster $[\{\mathrm{Cp^*Ru(CO)}\}_2(\mu_3\text{-}\mathrm{S})_2\{\mathrm{PdCl(PPh_3)}\}_2]$ (**8**) with a boatlike $\mathrm{Pd_2Ru_2}(\mu_3\text{-}\mathrm{S})_2$ framework. The detailed structures of **2**, **4**, **5**, **7**, and **8** have been determined by X-ray crystallography.

Introduction

The disulfido $(\mathrm{M{-}S_2})$[2−9] and hydrosulfido (M−SH)[10,11] groups are attractive functionalities for metal−sulfur cluster synthesis because they have a potential to attach to other metal centers as inorganic mimics of organic disulfides and thiols. In the course of our investigations to realize the efficient substrate transformations on the polynuclear noble metal sites supported by the bridging sulfur ligands,[12,13] we have developed this methodology to build up such polynuclear frameworks by using the disulfido- or hydrosulfido-bridged dinuclear complexes

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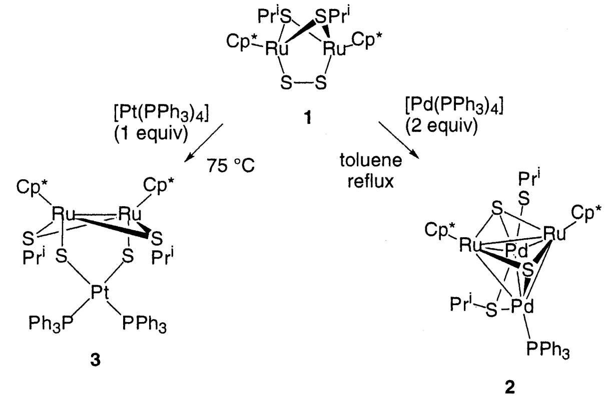
Scheme 1



of noble metals such as [Cp*Ru(μ_2-S$_2$)(μ_2-SPr^i)$_2$RuCp*] (**1**; Cp* = η^5-C$_5$Me$_5$)[14] and [Cp*MCl(μ_2-SH)$_2$MClCp*] (M = Ru (**6**),[15] Rh, Ir[16,17]). From these versatile precursors, substantial numbers of homometallic and, more importantly, heterometallic sulfido clusters have been synthesized in such a manner that the products contain the expected metal−sulfur compositions and core structures.

It is well-recognized that palladium and ruthenium exhibit various catalytic activities in their own right, and extensive studies have been undertaken on the chemistry of palladium and ruthenium complexes. However, the palladium−ruthenium mixed-metal complexes are somehow surprisingly scarce even in the vast candidates included in the low-valent metal carbonyl category.[18−24] As an application of our cluster synthesis based on the bridging disulfido and hydrosulfido functionalities, we report here the syntheses of the palladium−ruthenium mixed-metal sulfido clusters [(Cp*Ru)$_2$(μ_3-S)$_2$Pd$_2$(μ_2-SPr^i)(SPr^i)(PPh$_3$)] (**2**) and [(Cp*Ru)$_2$(μ_3-S)$_2$Pd$_2$(μ_2-Cl)(PPh$_3$)$_2$]Cl (**7**) from the diruthenium complexes **1** and **6**. Ligand substitution and core transformation reactions of these Pd$_2$Ru$_2$ clusters are also described. These new clusters reported here represent still rare examples of palladium−ruthenium mixed-metal clusters. Part of this work has appeared in a preliminary form.[25]

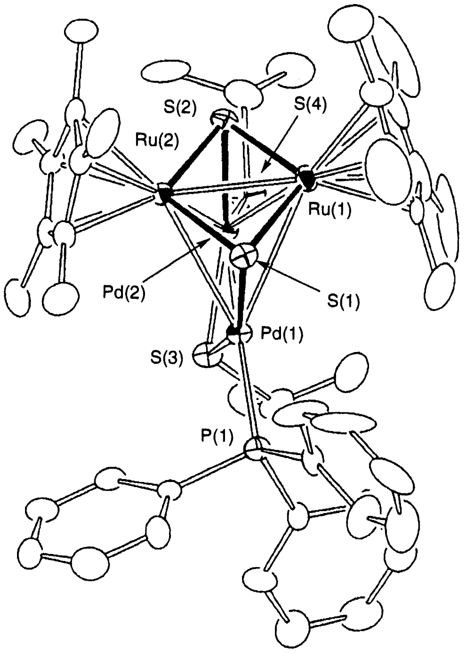


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

Results and Discussion

Preparation of the Pd$_2$Ru$_2$ Mixed-Metal Sulfido Cluster 2 from the Disulfido-Bridged Diruthenium Complex 1. We have already demonstrated that treatment of the disulfido-bridged diruthenium complex **1** with an equimolar amount of [Pt(PPh$_3$)$_4$] at 75 °C leads to insertion of the Pt atom into the S−S bond in **1**, giving the mixed-metal sulfido cluster [(Ph$_3$P)$_2$Pt(μ_2-S)$_2$(RuCp*)$_2$(μ_2-SPr^i)$_2$] (**3**; Scheme 1).[25] We thus treated **1** with [Pd(PPh$_3$)$_4$] in a similar manner. The reaction was found to require more forcing conditions (toluene reflux) and, interestingly, isolated from the reaction mixture was not a trinuclear cluster but the tetranuclear Pd$_2$Ru$_2$ sulfido cluster **2**, although the yield was low. The tetranuclear nature of **2** has unequivocally been established by X-ray crystallography (vide infra). As expected, the yield of **2** was increased to 47% when **1** was treated with 2 equiv of the palladium complex (Scheme 1). We could not detect any intermediary PdRu$_2$ species such as [(Ph$_3$P)$_2$Pd(μ_2-S)$_2$(RuCp*)$_2$(μ_2-SPr^i)$_2$], a Pd analogue of the PtRu$_2$ cluster **3**. During the formation of **2**, the two Pd atoms are formally oxidized from Pd^0 to Pd^I. To the best of our knowledge, **2** represents the first example of Pd−Ru bimetallic sulfido clusters.

Figure 1 depicts the molecular structure of **2** determined by an X-ray analysis; selected bond distances and angles are listed in Table 1. Cluster **2** has a distorted-tetrahedral Pd$_2$Ru$_2$ core in which each PdRu$_2$ face is capped by a μ_3-S ligand and the Pd−Pd edge is bridged by a μ_2-thiolato ligand. The Pd atoms are further ligated by a terminal thiolato or PPh$_3$ ligand. The molecule has a pseudo C_s symmetry with a mirror plane containing the Pd(1), Pd(2), S(1), S(2), and P(1) atoms, if the Pr^i group in the bridging thiolato ligand directed toward one side of this plane is ignored. In contrast to this solid-state structure, the ^{1}H NMR spectrum recorded for **2** in toluene-d_8 exhibits only one Cp* resonance throughout the variable-temperature measurements from −60 to +80 °C, as expected from the structure of C_s sym-

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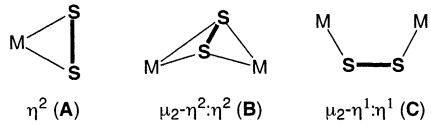
Table 1. Selected Bond Distances (Å) and Angles (deg) for 2, 4, 5·CH$_2$Cl$_2$, and 7

	2	**4**	**5**·CH$_2$Cl$_2$	**7**
Distances				
Pd(1)−Pd(2)	2.804(2)	2.780(1)	2.8130(8)	2.8044(7)
Pd(1)−Ru(1)	3.095(2)	3.076(1)	3.0112(9)	2.9970(7)
Pd(1)−Ru(2)	2.934(2)	2.947(1)	2.9359(9)	2.8778(7)
Pd(2)−Ru(1)	3.006(2)	2.975(1)	2.9266(9)	3.0385(7)
Pd(2)−Ru(2)	2.857(2)	2.831(1)	2.842(1)	2.8903(7)
Ru(1)−Ru(2)	2.632(2)	2.631(1)	2.6386(9)	2.6231(7)
Pd(1)−S(1)	2.273(4)	2.259(3)	2.237(2)	2.226(2)
Pd(2)−S(2)	2.243(4)	2.249(3)	2.214(2)	2.229(2)
Ru(1)−S(1)	2.264(4)	2.272(3)	2.254(2)	2.249(2)
Ru(1)−S(2)	2.277(4)	2.262(3)	2.254(2)	2.254(2)
Ru(2)−S(1)	2.265(4)	2.269(3)	2.263(2)	2.252(2)
Ru(2)−S(2)	2.267(4)	2.265(3)	2.249(2)	2.254(2)
Pd(1)−P(1)	2.289(4)	2.278(3)	2.287(2)	2.299(2)
Pd(1)−X$_b$[a]	2.332(4)	2.313(3)	2.508(1)	2.409(2)
Pd(2)−X$_b$[a]	2.309(4)	2.326(3)	2.540(1)	2.396(2)
Pd(2)−X$_t$[b]	2.326(4)	2.505(1)	2.504(1)	2.304(2)
Angles				
Pd(2)−Pd(1)−S(1)	98.9(1)	98.80(7)	98.59(6)	101.77(5)
Pd(2)−Pd(1)−P(1)	155.9(1)	159.66(8)	159.43(7)	157.42(5)
Pd(2)−Pd(1)−X$_b$[a]	52.47(10)	53.39(8)	56.68(3)	54.09(4)
S(1)−Pd(1)−P(1)	104.8(1)	101.5(1)	101.44(8)	100.35(6)
S(1)−Pd(1)−X$_b$[a]	149.2(1)	150.3(1)	154.92(6)	155.47(6)
P(1)−Pd(1)−X$_b$[a]	105.0(1)	106.7(1)	103.58(7)	104.10(6)
Pd(1)−Pd(2)−S(2)	103.8(1)	104.56(7)	103.31(6)	100.38(4)
Pd(1)−Pd(2)−X$_b$[a]	53.22(9)	52.97(7)	55.59(3)	54.50(4)
Pd(1)−Pd(2)−X$_t$[b]	149.6(1)	154.28(5)	157.47(4)	157.15(5)
S(2)−Pd(2)−X$_b$[a]	154.1(1)	155.5(1)	158.51(6)	154.66(6)
S(2)−Pd(2)−X$_t$[b]	102.8(1)	97.89(8)	98.52(6)	101.62(6)
X$_b$−Pd(2)−X$_t$[a,b]	102.6(1)	106.33(8)	102.90(4)	103.72(6)

[a] X$_b$ = S(3) (**2** and **4**), Br(1) (**5**·CH$_2$Cl$_2$), Cl(1) (**7**). [b] X$_t$ = S(4) (**2**), Br(1) (**4**), Br(2) (**5**·CH$_2$Cl$_2$), P(2) (**7**).

Chart 1



metry. The two diastereotopic methyl groups in the bridging SPr^i ligand give rise to only one doublet, which suggests that the structure is not rigid in solution and a rapid sulfur inversion process is present for this ligand. The equivalence of the two Cp* ligands on the ^{1}H NMR time scale is explained by this fluxional feature of the bridging SPr^i ligand. Two septets resonating at largely separated positions (δ 4.93 and 3.08) can be assigned to the methine protons in the terminal and bridging thiolato ligands, respectively, by comparison with the spectrum of the bromo−thiolato cluster **4** (vide infra).

Oxidative addition of disulfido ligands to low-valent metal complexes is now a practical method to prepare sulfido complexes with higher nuclearity. Among the coordination modes of disulfido ligands used in this synthetic approach, η^2 (side on; **A**)[4] and μ_2-η^2:η^2 (**B**)[5−8] are common (Chart 1). On the other hand, nuclearity expansion reactions using μ_2-η^1:η^1-disulfido complexes (**C**) are limited to those of [Cp′V(μ_2-S)$_2$(μ_2-η^1:η^1-S$_2$)VCp′] (Cp′ = η^5-C$_5$H$_4$Me)[9] and [Cp*M(μ_2-η^2:η^2-S$_2$)(μ_2-η^1:η^1-S$_2$)MCp*] (M = Fe, Ru),[3] which also bear μ_2-η^2:η^2-S$_2$ or μ_2-S ligands as glue to the incoming metals. The double-bond character of the S−S bond often associated with the coordination mode **C**[26] may retard the metal insertion into these types of disulfido ligands. Transformations of the disulfido complex **1** into the Pd$_2$Ru$_2$ and PtRu$_2$ clusters **2** and **3** are the first unambiguous metal-insertion reactions into the μ_2-η^1:η^1-disulfido ligand.[27]

Metal−Metal Interactions in 2. According to the effective atomic number (EAN) rule, the 60e cluster **2** should have six metal−metal bonds. The Pd(1)−Pd(2) distance of 2.804(2) Å is comparable to that in the related Pd$^{I}_2$Ir$^{III}_2$ cluster [(Cp*Ir)$_2$(SH)(μ_3-S)$_2${Pd(PPh$_3$)}$_2$(μ_2-SH)] (2.726(2) Å)[28] and other Pd^I−Pd^I distances reported so far.[29,30] The Ru(1)−Ru(2) distance at 2.632(2) Å is also consistent with the presence of an Ru^{III}−Ru^{III} single bond.[31] In contrast, the four Pd−Ru distances (2.857(2)−3.095(2) Å) are somewhat longer than those in [ClPd(μ_2-Ph$_2$Ppy)$_2$RuCl(CO)$_2$] (2.660(1) Å; Ph$_2$Ppy = 2-Ph$_2$PC$_5$H$_4$N),[18] [Et$_4$N]$_2$[Pd$_6$Ru$_6$(CO)$_{24}$] (2.680(1)−2.804(1) Å),[20] [PPN]$_2$[Pd$_2$Ru$_{12}$C$_2$(CO)$_{30}$] (2.722(1)−2.848(1) Å; PPN = (Ph$_3$P)$_2$N$^+$),[21] and [{Pd(PBu$^t_3$)}$_2$Ru$_2$(CO)$_9$] (2.7694(6)−2.8207(7) Å),[22] suggesting weaker Pd−Ru interactions. The distorted-tetrahedral Pd$_2$Ru$_2$ core structure described above may be explained by the tendency for palladium to adopt the 16-electron configuration, which allows palladium clusters to have an electron count smaller than that expected from the EAN rule.[32] For example, the 58e cluster [CpMo(μ_3-CO)(μ_2-CO)$_2$Pd(PEt$_3$)]$_2$ (Cp = η^5-C$_5$H$_5$), containing two 16e Pd and two 18e Mo centers, has a planar-butterfly core,[33] for which a 62e count is expected according to the EAN rule. Assuming that the Pd atoms take the 16e configuration, the 60e cluster **2** is "electron-rich"[34] by 4e (2e from each Pd atom) for a tetrahedral core with six metal−metal bonds. The elongation of the four Pd−Ru bonds in **2** is thus ascribed to the occupation of delocalized metal−metal antibonding orbitals by the extra 4e. Similar elongation of metal−metal bonds is observed in, for example, the 64e butterfly cluster [Os$_4$(μ_3-S)$_2$(CO)$_{12}$], which contains three normal Os−Os bonds and two relatively long Os−Os contacts against the EAN rule.[35]

Conversion of Thiolato Cluster 2 into Bromo Clusters 4 and 5. When the bis(thiolato) cluster **2** was treated with benzyl bromide, stepwise substitution of two thiolato ligands in **2** by bromo ligands took place, depending upon the amount of benzyl bromide and the reaction time; both the monobromo cluster [(Cp*Ru)$_2$(μ_3-S)$_2$Pd$_2$(μ_2-SPr^i)Br(PPh$_3$)] (**4**) and dibromo cluster [(Cp*Ru)$_2$(μ_3-S)$_2$Pd$_2$(μ_2-Br)Br(PPh$_3$)] (**5**) were success-

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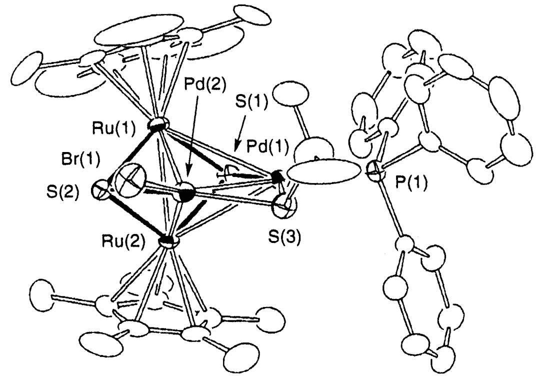
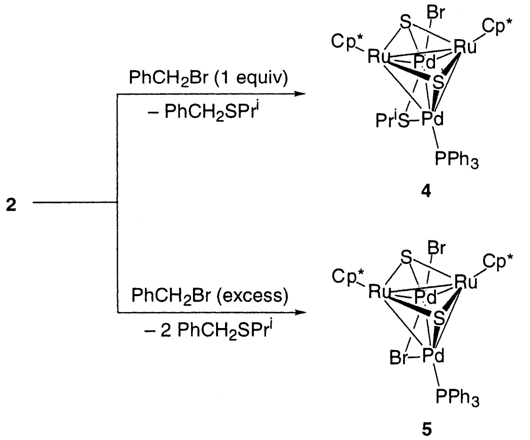


Figure 2. Molecular structure of **4**. Hydrogen atoms are omitted for clarity.

Scheme 2



fully isolated (Scheme 2). Quantitative formation of $PhCH_2SPr^i$ (96% based on **2**) was observed in the former reaction, whereas the amount of the thioether detected in the latter reaction was considerably smaller than 2 equiv with respect to **2** (128%), probably because the thioether that formed was further converted into a sulfonium salt by the excess of benzyl bromide.

The ^1H NMR spectrum of **4** exhibits only one set of resonances ascribed to the SPr^i ligand at δ 3.14 and 1.65 with intensities of 1H and 6H, respectively. On the other hand, the ^1H NMR spectrum of **5** indicates the absence of thiolato ligands. The Cp* resonance of both **4** and **5** appears as one singlet, suggesting that the thiolato sulfur inversion in **4** is again faster than the NMR time scale. The detailed structures of the monobromo and dibromo clusters **4** and **5** have been determined by X-ray crystallography (Figures 2 and 3, Table 1). The $Pd_2Ru_2(\mu_3\text{-}S)_2$ frameworks in **4** and **5** are almost superimposable on that in the starting bis(thiolato) cluster **2**. In both **4** and **5**, a Br atom is bound to the Pd(2) atom as a terminal ligand instead of the thiolato ligand in **2**. The $Pd(2)-Br_{terminal}$ distances in **4** and **5** are very close to each other. The Pd(1)−Pd(2) edge is bridged by a thiolato ligand (in **4**) or the second bromo ligand (in **5**). The $Pd-(\mu_2\text{-}Br)$ distances in **5** (2.524 Å (mean)) are slightly longer than those in the related dipalladium(I) complex $[Pd_2(\mu_2\text{-}Br)_2(PBu^t_3)_2]$ (2.457 Å (mean)).[30]

Preparation of the Pd_2Ru_2 Mixed-Metal Sulfido Cluster 7 from the Hydrosulfido-Bridged Diruthenium Complex 6. For the rational synthesis of palladium−ruthenium mixed-metal sulfido clusters, we have another versatile diruthenium metallo-ligand,

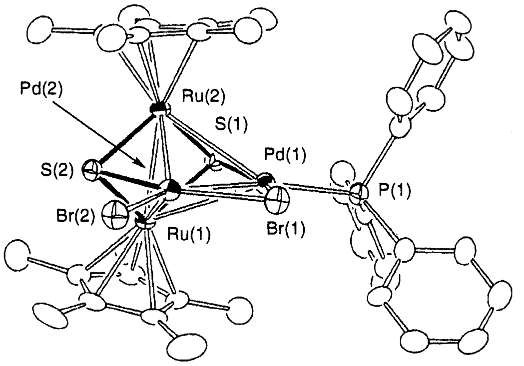
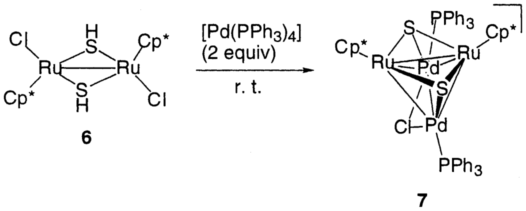


Figure 3. Molecular structure of **5**·CH_2Cl_2. Hydrogen atoms and the solvating CH_2Cl_2 molecule are omitted for clarity.

namely, the hydrosulfido complex **6**. Treatment of **6** with 2 equiv of $[Pd(PPh_3)_4]$ resulted in the formation of the cationic tetranuclear Pd_2Ru_2 sulfido cluster **7** in 64% yield (eq 1). Concurrent evolution of H_2 has been



(1)

confirmed by GLC analysis. As in the reaction of the disulfido complex **1** and $[Pd(PPh_3)_4]$, no intermediary $PdRu_2$ species could be observed even when 1 equiv of the palladium complex was used. This is in marked contrast with our previous results of the reactions of **6** and metal complexes, which lead to the formation of $M_2M'(\mu_3\text{-}S)_2$ triangular clusters exclusively. For example, **6** reacts with $[RhCl(PPh_3)_3]$ and $[RuH_2(PPh_3)_4]$ to give the Ru_2Rh and Ru_3 trinuclear clusters $[(\mu_2\text{-}H)(Cp^*Ru)_2(\mu_3\text{-}S)_2RhCl_2(PPh_3)]$[15] and $[(Cp^*Ru)_2(\mu_3\text{-}S)_2(\mu_2\text{-}H)RuCl(PPh_3)_2]$,[36] respectively. The reaction of $[Pd(PPh_3)_4]$ with the hydrosulfido-bridged diiridium complex $[Cp^*IrCl(\mu_2\text{-}SH)_2IrClCp^*]$ also affords the Ir_2Pd trinuclear cluster $[(Cp^*Ir)_2(\mu_3\text{-}S)_2PdCl(PPh_3)]Cl$.[13,16] Formation of the $Pd_2Ru_2(\mu_3\text{-}S)_2$ framework from both the disulfido complex **1** and hydrosulfido complex **6** implies that the tetranuclear core is thermodynamically preferred. As related reactions, we have reported incorporation of two Pd atoms into the dinuclear chalcogen-bridged complexes $[Cp^*Ir(SH)(\mu_2\text{-}SH)_2Ir(SH)Cp^*]$,[28] $[Cp^*Ir(\mu_2\text{-}Se_4)_2IrCp^*]$,[37] and $[Mo_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2]$,[38] although these dinuclear metallo-ligands have more than two chalcogen atoms to bridge the metal atoms. Curtis and co-workers have revealed that the sulfur-deficient tetranuclear mixed-metal cluster $[(Cp'Mo)_2\{Co(CO)_2\}_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)]$ reacts with thiophene to afford the cubane-type cluster $[(Cp'Mo)_2\{Co(CO)\}_2(\mu_3\text{-}S)_4]$ along with desulfurized hydrocarbons.[39] In this context, we

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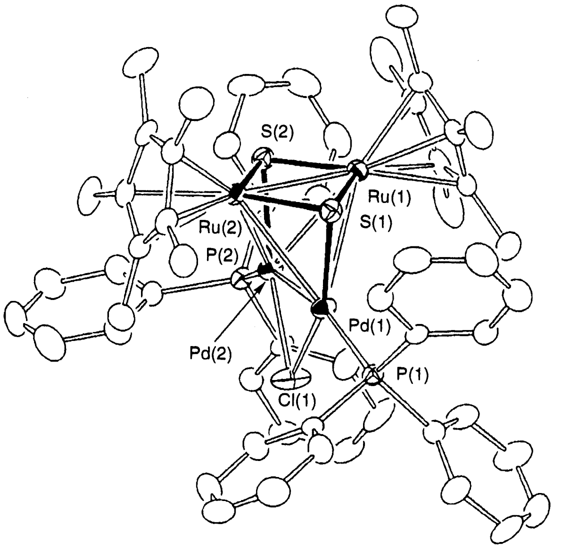
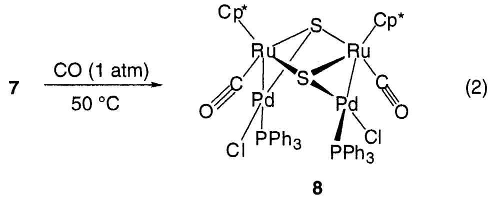


Figure 4. Structure of the cationic part of **7**. Hydrogen atoms are omitted for clarity.

are currently investigating the reactivities of the sulfur-deficient Pd$_2$Ru$_2$(μ_3-S)$_2$ tetranuclear clusters synthesized here as well as the related Pd$_2$Ir$_2$(μ_3-E)$_2$ (E = S,[28] Se[37]) clusters toward organosulfur compounds in anticipation of their possible activity as hydrodesulfurization catalysts.

In accordance with the structure shown in eq 1, the ^{1}H and ^{31}P{^{1}H} NMR spectra of **7** exhibit only one singlet for the Cp* protons and phosphorus nuclei, respectively. The tetranuclear structure of **7** has finally been established by an X-ray analysis (Figure 4, Table 1). The cation has an approximate C_{2v} symmetry with a 2-fold axis bisecting the Ru−Ru and Pd−Pd vectors. The Pd$_2$Ru$_2$(μ_3-S)$_2$ framework in **7** is essentially the same as those in the isoelectronic clusters **2**, **4**, and **5**. A chloro ligand bridges the two Pd atoms with the Pd−Cl distances of 2.403 Å (mean), which are comparable to those in the related dipalladium(I) complex [Pd$_2$(μ_2-C$_3$H$_3$)(μ_2-Cl)(PPh$_3$)$_2$] (2.401 Å (mean)).[40]

Core Transformation of 7 Induced by CO To Give 8. When the cationic cluster **7** was allowed to react with CO at 50 °C, the 64e carbonyl cluster [{Cp*Ru(CO)}$_2$(μ_3-S)$_2${PdCl(PPh$_3$)}$_2$] (**8**) was obtained (eq 2). The



8

(2)

structure of **8** with a boatlike Pd$_2$Ru$_2$(μ_3-S)$_2$ framework has unambiguously been determined by an X-ray diffraction study (Figure 5, Table 2). Cluster **8** has a crystallographically imposed C_2 symmetry with a 2-fold axis through the Ru$_2$S$_2$ face. This face is slightly puckered with a dihedral angle of 161.0(1)° around the Ru−Ru vector. The structure of **8** may be related to the thiolato-bridged diruthenium dicarbonyl complex [Cp*Ru(CO)(μ_2-SBu^t)$_2$Ru(CO)Cp*],[41] in which each S atom is bound to a *tert*-butyl group in place of the PdCl(PPh$_3$) moiety in **8**. The long Ru−Ru distance (3.626(1) Å) precludes any direct metal−metal bonding interaction, whereas the Pd−Ru distances (2.7340(7) Å) are significantly shortened from those of the parent cluster **7** (2.951 Å (mean)) and are in line with the presence of Pd^{I}−Ru^{III} bonds. The Ru$_2$S$_2$ face is not equilateral (Ru−S, 2.341(2) Å; Ru−S*, 2.410(2) Å), and these Ru−S distances are elongated from those in the parent cluster **7** (2.252 Å (mean)). The Pd−Cl, Pd−P, and Pd−S distances are essentially invariant from those in **7**. Consistent with the solid-state structure, the Cp* and PPh$_3$ resonances appear as one singlet in the ^{1}H and ^{31}P{^{1}H} NMR spectra. The IR spectrum exhibits the ν(CO) bands at 1948 and 1935 cm^{-1}.

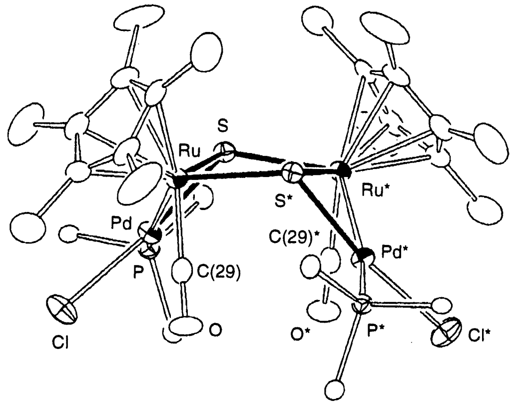


Figure 5. Molecular structure of **8**. Hydrogen atoms and the phenyl groups, except for the ipso carbon atoms, are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 8

Distances			
Pd−Ru	2.7340(7)	Pd−Cl	2.378(2)
Ru−Ru*	3.626(1)	Ru−S	2.341(2)
Pd−S	2.241(2)	Ru−S*	2.410(2)
Pd−P	2.273(2)		
Angles			
Ru−Pd−S	55.06(4)	Cl−Pd−P	91.60(7)
Ru−Pd−Cl	107.05(5)	Pd−Ru−S	51.71(5)
Ru−Pd−P	160.84(5)	Pd−Ru−S*	115.61(4)
S−Pd−Cl	161.93(6)	S−Ru−S*	79.17(6)
S−Pd−P	106.07(6)		

During the formation of **8**, the Ru−Ru and Pd−Pd bonds as well as the four relatively weak Pd−Ru interactions in **7** were cleaved, whereas two Pd−Ru bonds were formed. In total, four-electron addition to the valence electron count led to the cleavage of the four weak metal−metal interactions in **7**. The resultant cluster **8** has two 16e Pd and two 18e Ru centers and is electron-precise if the high-lying atomic p$_z$-type orbitals of Pd atoms do not contribute to the metal−metal bonding. As a related reaction, the "electron-rich" 64e butterfly cluster [Os$_4$(μ_3-S)$_2$(CO)$_{12}$] (vide supra) reacts with CO to give the electron-precise 66e cluster [Os$_4$(μ_3-S)$_2$(CO)$_{13}$] with three Os−Os bonds.[35] In this transformation, the two weak Os−Os interactions in the former cluster have been lost in the latter upon increase of the electron count by 2.

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Table 3. X-ray Crystallographic Data for 2, 4, $5\cdot CH_2Cl_2$, 7, and 8

	2	**4**	**5**·CH_2Cl_2	**7**	**8**
formula	$C_{44}H_{59}PPd_2Ru_2S_4$	$C_{41}H_{52}BrPPd_2Ru_2S_3$	$C_{39}H_{47}Br_2Cl_2PPd_2Ru_2S_2$	$C_{56}H_{60}Cl_2P_2Pd_2Ru_2S_2$	$C_{58}H_{60}Cl_2O_2P_2Pd_2Ru_2S_2$
fw	1162.10	1166.86	1256.55	1345.00	1401.02
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$R\bar{3}c$ (No. 167)
cryst color	dark brown	dark brown	dark brown	black	dark brown
cryst dimens, mm^3	0.2 × 0.3 × 0.4	0.4 × 0.4 × 0.5	0.2 × 0.3 × 0.4	0.2 × 0.4 × 0.6	0.2 × 0.3 × 0.4
a, Å	13.084(1)	12.561(2)	15.777(1)	16.409(2)	25.552(5)
b, Å	17.184(3)	17.610(2)	12.136(3)	15.248(2)	25.552(5)
c, Å	21.537(2)	11.170(2)	23.816(1)	21.954(1)	44.490(5)
α, deg	90	97.41(1)	90	90	90
β, deg	102.036(9)	115.43(1)	101.944(6)	90.096(6)	90
γ, deg	90	82.08(1)	90	90	120
V, Å^3	4735.8(9)	2203.5(7)	4461(1)	5493.0(8)	25155(9)
Z	4	2	4	4	18
D_c, g cm^{-3}	1.630	1.759	1.871	1.626	1.665
μ(Mo Kα), cm^{-1}	16.12	25.91	35.31	14.51	14.32
rflns measd	$+h, +k, \pm l$	$+h, \pm k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$\pm h, +k, +l;$ $-h+k+l=3n$
no. of unique rflns	11 231	10 137	10 724	13 093	4942
transmission factors	0.8652−0.9974	0.7312−1.0000	0.6248−1.0000	0.7080−1.0000	0.8457−0.9999
no. of data used ($I > 3\sigma(I)$)	3883	4859	5461	6994	2859
no. of variables	479	452	452	595	316
R_{int}	0.150	0.034	0.040	0.033	0.045
R^a	0.056	0.066	0.043	0.043	0.038
$R_w{}^a$	0.050	0.095	0.042	0.027	0.023

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$; $w = [\sigma_c{}^2(F_o) + p^2F_o{}^2/4]^{-1}$ (p = 0.030 (**2**), 0.020 (**5**·CH_2Cl_2), 0.002 (**7** and **8**)) or $w = 1/\sigma_c{}^2(F_o{}^2)$ (**4**) with $\sigma_c(F_o)$ and $\sigma_c(F_o{}^2)$ from counting statistics.

Unlike the cationic cluster **7**, the bis(thiolato) cluster **2** reacted with CO at 50 °C to afford a mixture containing the mononuclear ruthenium thiolato complex $[Cp^*Ru(SPr^i)(CO)_2]$,[42] whereas the dibromo cluster **5** did not react with CO under the same conditions. Although clusters **2**, **4**, **5**, and **7** have the same tetrahedral Pd_2Ru_2 core in common, their stability is apparently perturbed by the ancillary ligands and the charge of the clusters.

To summarize, we have synthesized the palladium−ruthenium mixed-metal sulfido clusters **2** and **7** from the disulfido- or hydrosulfido-bridged diruthenium complexes **1** and **6**. Unexpectedly, two Pd atoms have been incorporated into the dinuclear centers in these reactions, in contrast to our previous work using **1** and **6** as dinuclear metallo-ligands. The resultant clusters **2** and **7** feature a $Pd_2Ru_2(\mu_3\text{-}S)_2$ core containing Pd−Pd and Ru−Ru bonds along with four weaker Pd−Ru interactions. Cluster **2** further undergoes stepwise substitution of thiolato ligands by bromo ligands to afford the monobromo and dibromo clusters **4** and **5** with retention of the Pd_2Ru_2 tetrahedral core. On the other hand, addition of two 2e donors, CO, to the Pd_2Ru_2 tetrahedral core in **7** opened up the tetrahedron to give the boatlike $Pd_2Ru_2(\mu_3\text{-}S)_2$ framework in **8**.

Experimental Section

General Comments. All manipulations were performed under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were dried by refluxing over Na/benzophenone ketyl (THF, toluene, diethyl ether, and hexanes) or P_2O_5 (dichloromethane) and distilled just before use. Complexes **1**[14] and **6**[15] were prepared according to the literature. IR spectra were recorded on a Shimadzu 8100M spectrometer, whereas ^1H (270 MHz) and $^{31}P\{^1H\}$ (109 MHz) NMR spectra were obtained on a JEOL EX-270 spectrometer. Hydrogen gas evolution was determined by GLC analysis using a Shimadzu GC-8A gas chromatograph equipped with a molecular sieve 13X column, whereas $PhCH_2SPr^i$ was determined on a Shimadzu GC-14A gas chromatograph equipped with a CBP-10 capillary column by using *n*-pentadecane as an internal standard. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer.

Preparation of $[(Cp^*Ru)_2(\mu_3\text{-}S)_2Pd_2(\mu_2\text{-}SPr^i)(SPr^i)(PPh_3)]$ (2). To a solution of **1** (110.9 mg, 0.1614 mmol) in toluene (5 mL) was added $[Pd(PPh_3)_4]$ (374.0 mg, 0.3236 mmol), and the mixture was refluxed for 8 h. The resultant dark brown solution was reduced to 2 mL. Addition of hexanes (5 mL) yielded dark brown crystals, which were recrystallized from THF−hexanes (2 mL/5 mL). Dark brown crystals that formed were filtered off, washed with hexanes (3 mL), and dried in vacuo. Crystals were further obtained by cooling the filtrate; the combined yield was 88.0 mg (47%). ^1H NMR (C_6D_6): δ 7.10−7.93 (m, 15H, Ph), 4.93 (sep, 1H, terminal $SCHMe_2$), 3.08 (sep, 1H, bridging $SCHMe_2$), 2.24 (d, 6H, terminal $SCHMe_2$), 1.74 (s, 30H, C_5Me_5), 1.55 (d, 6H, bridging $SCHMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.0 (s). Anal. Calcd for $C_{44}H_{59}PPd_2Ru_2S_4$: C, 45.47; H, 5.12. Found: C, 45.20; H, 5.14.

Preparation of $[(Cp^*Ru)_2(\mu_3\text{-}S)_2Pd_2(\mu_2\text{-}SPr^i)Br(PPh_3)]$ (4). To a solution of **2** (35.6 mg, 0.0306 mmol) in toluene (3 mL) was added benzyl bromide (3.6 μL, 0.030 mmol), and the mixture was stirred in the dark for 8 h at room temperature. The resultant dark brown solution was reduced to 1.5 mL, and hexanes (3 mL) were layered on the solution. The dark brown crystals that formed were filtered off and dried in vacuo (25.6 mg, 72%). ^1H NMR (C_6D_6): δ 7.10−7.89 (m, 15H, Ph), 3.14 (sep, 1H, J = 6.6 Hz, $SCHMe_2$), 1.69 (s, 30H, C_5Me_5), 1.65 (d, 6H, J = 6.6 Hz, $SCHMe_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.3 (s). Anal. Calcd for $C_{41}H_{52}BrPPd_2Ru_2S_3$: C, 42.40; H, 4.49. Found: C, 42.23; H, 4.50.

Preparation of $[(Cp^*Ru)_2(\mu_3\text{-}S)_2Pd_2(\mu_2\text{-}Br)Br(PPh_3)]\cdot CH_2Cl_2$ ($5\cdot CH_2Cl_2$). To a solution of **2** (64.8 mg, 0.0558 mmol) in toluene (6 mL) was added benzyl bromide (64 μL, 0.54 mmol), and the mixture was stirred in the dark for 26 h at room temperature. After removal of the solvent in vacuo, the resultant dark brown oil was crystallized from dichloromethane−hexanes (2 mL/10 mL). The dark brown crystals that formed were filtered off, washed with hexanes (2 mL × 2), and dried in vacuo (39.9 mg, 57%). ^1H NMR ($CDCl_3$): δ 7.40−7.69 (m, 15H, Ph), 1.79 (s, 30H, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.1 (s). Anal. Calcd for $C_{39}H_{47}Br_2Cl_2PPd_2Ru_2S_2$: C, 37.28; H, 3.77. Found: C, 37.33; H, 3.86.

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Preparation of [$(Cp^*Ru)_2(\mu_3\text{-}S)_2Pd_2(\mu_2\text{-}Cl)(PPh_3)_2$]Cl (7). To a suspension of **6** (49.2 mg, 0.0807 mmol) in THF (10 mL) was added [$Pd(PPh_3)_4$] (186.5 mg, 0.161 mmol), and the mixture was stirred for 18 h. After removal of the solvent, the resultant dark brown oil was extracted with 10 mL of dichloromethane. Addition of diethyl ether to the concentrated extract afforded **7** as dark brown crystals (65.4 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 7.59−7.47 (m, 30H, PPh_3), 1.61 (s, 30H, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.2 (s). Anal. Calcd for $C_{56}H_{60}Cl_2P_2Pd_2Ru_2S_2$: C, 50.01; H, 4.50. Found: C, 49.61; H, 4.63.

Preparation of [$\{Cp^*Ru(CO)\}_2(\mu_3\text{-}S)_2\{PdCl(PPh_3)\}_2$] (8). Through a suspension of **7** (62.0 mg, 0.0461 mmol) in THF (8 mL) was bubbled CO for 5 min, and the mixture was stirred for 8 h at 50 °C under CO. The resultant dark reddish brown solution was evaporated to dryness, and the residue was recrystallized from dichloromethane−hexanes (2 mL/8 mL). The dark brown crystals that formed were filtered off and dried in vacuo (51.5 mg, 80%). IR (KBr): 1948, 1935 cm^{-1} (s, ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 7.71−7.36 (m, 30H, PPh_3), 1.58 (s, 30H, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.8 (s). Anal. Calcd for $C_{58}H_{60}Cl_2O_2P_2Pd_2Ru_2S_2$: C, 49.72; H, 4.32. Found: C, 49.38; H, 4.37.

X-ray Diffraction Studies. Single crystals suitable for X-ray analyses were sealed in glass capillaries under an inert atmosphere and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromated Mo Kα source (λ = 0.710 69 Å). Orientation matrixes and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections with $25° < 2\theta < 40°$. The data collection was performed at room temperature using the ω scan (for **5**·CH_2Cl_2) or $\omega-2\theta$ scan technique (except for **5**·CH_2Cl_2) at a rate of 32° min^{-1} to a maximum 2θ value of 50° (for **8**) or 55° (except for **8**). The intensities of 3 check reflections were monitored every 150 reflections, which showed no significant decay during data collections. Intensity data were corrected for Lorentz−polarization effects and for absorption (ψ scans). Details of crystal and data collection parameters are summarized in Table 3.

Structure solution and refinement were carried out by using the teXsan program package.[43] The heavy-atom positions were determined by a Patterson method program (DIRDIF-PATTY;[44] for **2**, **4**, and **7**) or a direct methods program (SIR92;[45] for **5**·CH_2Cl_2 and **8**), and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 (for **4**) or F (except for **4**). All other hydrogen atoms were placed at calculated positions, and these were included in the final stages of refinements with fixed parameters. The atomic scattering factors were taken from ref 46, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 47.

Acknowledgment. This work was financially supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, and all bond lengths and angles for **2**, **4**, **5**·CH_2Cl_2, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020627L

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