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The Hydrosulfido-Bridged Diiridium and Dirhodium Complexes [Cp*MCl(μ_2-SH)$_2$MCp*Cl] (M = Ir, Rh; Cp* = η^5-C$_5$Me$_5$) as Versatile Precursors for Tri- and Tetranuclear Sulfido Clusters

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*Summary: The hydrosulfido-bridged diiridium and dirhodium complexes [Cp*MCl(μ_2-SH)$_2$MCp*Cl] (**3**, M = Ir; **4**, M = Rh; Cp* = η^5-C$_5$Me$_5$) were obtained by the reaction of [Cp*MCl(μ_2-Cl)$_2$MCp*Cl] (M = Ir, Rh) with excess H$_2$S gas. Treatment of **3** and **4** with NEt$_3$ gave the cuboidal sulfido clusters [(Cp*M)$_4$(μ_3-S)$_4$] (M = Ir, Rh), while their reaction with [RhCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) or [Pd(PPh$_3$)$_4$] afforded the cationic triangular sulfido clusters [(Cp*M)$_2$Rh(μ_3-S)$_2$(cod)]$^+$ (M = Ir, Rh) or [(Cp*Ir)$_2$Pd(μ_3-S)$_2$Cl(PPh$_3$)]$^+$, respectively.*

Multinuclear transition-metal complexes with sulfur ligands have recently been receiving much attention,[1] not only because they have some relevance to metal sulfide hydrodesulfurization catalysts[2] but also because they provide model compounds for the active sites of the metalloenzymes such as nitrogenase.[3] In the course of our study on the syntheses and reactivities of multinuclear noble-metal complexes with bridging chalcogen ligands, we have developed a series of diruthenium complexes with two or three bridging thiolato ligands such as [Cp*Ru(μ_2-SPr^i)$_2$RuCp*], [Cp*Ru(μ_2-SPr^i)$_3$-RuCp*], and [Cp*RuCl(μ_2-SPr^i)$_2$RuClCp*] (Cp* = η^5-C$_5$-Me$_5$) and have revealed that the bimetallic sites in these complexes exhibit intriguing reactivities toward various substrates, including alkynes, hydrazines, alkyl halides, and other transition-metal compounds.[4] More recently we have demonstrated that treatment of [Cp*RuCl(μ_2-Cl)$_2$RuCp*Cl] or [(Cp*Ru)$_4$(μ_3-Cl)$_4$] with H$_2$S gas leads to the formation of the hydrosulfido-bridged diruthenium complex [Cp*RuCl(μ_2-SH)$_2$RuCp*Cl], which is

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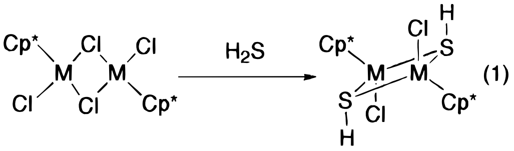
further transformed into the triangular heterobimetallic sulfido cluster [(Cp*Ru)$_2$(μ_2-H)(μ_3-S)$_2$RhCl$_2$(PPh$_3$)] in high yield on reaction with [RhCl(PPh$_3$)$_3$].[5] Aiming at the development of versatile and rational methods for the synthesis of heterobimetallic sulfido clusters, we have extended our study to the preparation of the corresponding hydrosulfido-bridged dirhodium and diiridium complexes containing Cp*M (M = Ir, Rh) units and their use in cluster synthesis. Although several hydrosulfido-bridged dirhodium and diiridium complexes have been reported in the literature,[6] their application to cluster synthesis has not been investigated.[7] Here we wish to describe the synthesis and structures of the hydrosulfido-bridged complexes [Cp*MCl(μ_2-SH)$_2$MCp*Cl] (**3**, M = Ir; **4**, M = Rh) together with their conversions to cuboidal and triangular sulfido clusters.



(1)

1: M = Ir
2: M = Rh

3: M = Ir
4: M = Rh

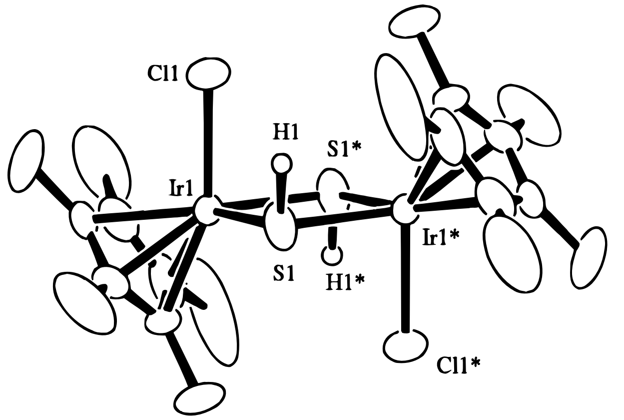


Figure 1. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Ir(1)−Cl(1) = 2.401(3), Ir(1)−S(1) = 2.385(2), Ir(1)−S(1*) = 2.385(2), Cl(1)−Ir(1)−S(1) = 88.25(10), Cl(1)−Ir(1)−S(1*) = 86.79(9), S(1)−Ir(1)−S(1*) = 80.0(7), Ir(1)−S(1)−Ir(1*) = 100.00(7). Selected bond distances (Å) and angles (deg) for the Rh analogue **4**:[10] Rh(1)−Cl(1) = 2.406(2), Rh(1)−S(1) = 2.403(2), Rh(1)−S(1*) = 2.400(2), Rh(2)−Cl(2) = 2.409(2), Rh(2)−S(2) = 2.393(2), Rh(2)−S(2*) = 2.397(2), Cl(1)−Rh(1)−S(1) = 89.22(8), Cl(1)−Rh(1)−S(1*) = 88.43(8), S(1)−Rh(1)−S(1*) = 81.85(8), Rh(1)−S(1)−Rh(1*) = 98.15(8), Cl(2)−Rh(2)−S(2) = 88.62(9), Cl(2)−Rh(2)−S(2*) = 89.46(9), S(2)−Rh(2)−S(2*) = 82.16(8), Rh(2)−S(2)−Rh(2*) = 97.84(8).

When it was stirred for 5 min under an H$_2$S atmosphere at room temperature, a red suspension of [Cp*IrCl(μ_2-Cl)$_2$IrCp*Cl] (**1**) in CH$_2$Cl$_2$ quickly changed to a yellow solution, from which the analytically pure complex **3** was obtained in 84% yield as orange crystals. A similar reaction of [Cp*RhCl(μ_2-Cl)$_2$RhCp*Cl] (**2**) afforded complex **4** in 87% yield as red crystals (eq 1).[8] Both **3**[9] and **4**[10] were structurally characterized by single-crystal X-ray diffraction analysis. An ORTEP view of **3** is shown in Figure 1. The overall structure consists of two Cp*Ir fragments bridged by two hydrosulfido ligands, in which the long Ir···Ir distance of 3.6540(6) Å indicates the absence of a bonding interaction between the two Ir atoms. The molecule has a crystallographic inversion center at the midpoint of the Ir-Ir vector. Thus, the two Cp* and two chloro ligands are *trans* to each other, respectively, and the two bridging SH ligands take the *anti* configuration with respect to the Ir$_2$S$_2$ plane. Complex **4** has a structure analogous to that of **3**, and the Rh$_2$(SH)$_2$ framework in **4** is similar to those found in the related complexes [(PPh$_3$)$_2$ClHRh(μ_2-SH)$_2$RhHCl(PPh$_3$)$_2$][6a] and [(triphos)HRh(μ_2-SH)$_2$RhH(triphos)]$^{2+}$ (triphos = MeC(CH$_2$PPh$_2$)$_3$).[6b]

The IR spectra of **3** and **4** showed weak bands at 2492 and 2511 cm^{-1}, respectively, which are characteristic of the SH ligands. The ^{1}H NMR spectrum in C$_6$D$_6$ indicates that **3** in the solution is present as a mixture of two isomers in the ratio of ca. 3:2. The major isomer showed the two Cp* signals at δ 1.30 and 1.53 together with one SH resonance at 0.91, while the minor species exhibited one Cp* and one SH resonance at δ 1.41 and 1.01, respectively. This feature may be interpreted in terms of the presence of the *anti* and *syn* isomers in a solution state with respect to the two SH groups for **3**, with the *syn* configuration being predominant. Complex **4** also exhibited spectral features closely related to those observed for **3**. Similar *syn*−*anti* isomerization of two bridging SH groups has been reported for the ruthenium analogue [Cp*RuCl(μ_2-SH)$_2$RuCp*Cl].[5]

The hydrosulfido complexes **3** and **4** have proved to be excellent starting materials for cluster syntheses. Treatment of complexes **3** and **4** with excess NEt$_3$ at room temperature readily provided the cubane clusters [(Cp*M)$_4$(μ_3-S)]$_4$ (**7**, M = Ir;[11] **8**, M = Rh[12]) in 63% and

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(7) Only the dimerization reactions of the dirhodium complexes [Cp*Rh(μ_2-CH$_2$)$_2$(μ_2-SH)RhCp*]$^+$ were reported to give tetranuclear complexes with two Rh$_2$ cores: (a) Nishioka, T.; Kukushkin, V.; Isobe, K.; Miguel, A. V. *Inorg. Chem.* **1994**, *33*, 2501. (b) Isobe, K.; Ozawa, Y.; Miguel, A. V.; Zhu, T. W.; Zhao, K. M.; Nishioka, T.; Ogura, T.; Kitagawa, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1882.

(8) Reactions of **1** and **2** with H$_2$S for a longer reaction time (**1**, 15 h; **2**, 14 days) led to formation of the cationic dinuclear complexes [Cp*M(μ_2-SH)$_3$MCp*]Cl (M = Ir, Rh) in good yields, which will be reported in a future publication.

(9) Crystallographic data for **3**: C$_{20}$H$_{32}$S$_2$Cl$_2$Ir$_2$, fw = 791.94, monoclinic, space group $P2_1/n$, $a = 8.5190(6)$ Å, $b = 9.2733(7)$ Å, $c = 15.6790(7)$ Å, $\beta = 104.060(5)°$, $V = 1201.5(1)$ Å^3, $Z = 2$, $D_c = 2.189$ g cm^{-3}, $F_{000} = 744$, $\mu = 114.94$ cm^{-1}, $R = 0.033$, and $R_w = 0.024$ for 2043 unique reflections ($I > 3.00\sigma(I)$).

(10) Crystallographic data for **4**: C$_{20}$H$_{32}$S$_2$Cl$_2$Rh$_2$, fw = 613.31, triclinic, space group $P\bar{1}$, $a = 8.8238(9)$ Å, $b = 15.946(2)$ Å, $c = 8.693(1)$ Å, $\alpha = 103.753(9)°$, $\beta = 94.079(9)°$, $\gamma = 92.000(9)°$, $V = 1183.3(2)$ Å^3, $Z = 2$, $D_c = 1.721$ g cm^{-3}, $F_{000} = 616$, $\mu = 17.97$ cm^{-1}, $R = 0.047$, and $R_w = 0.038$ for 3570 unique reflections ($I > 3.00\sigma(I)$). The unit cell contains two independent molecules, each of which has an inversion center at the midpoint of the two rhodium atoms.

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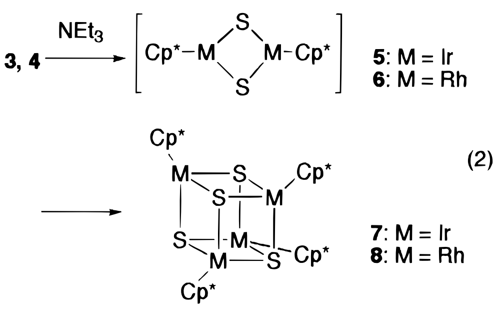
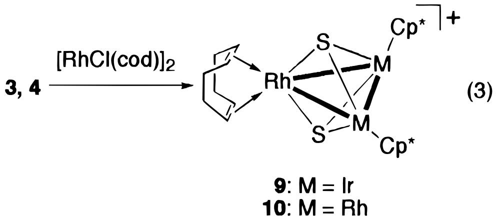
64% isolated yields, respectively (eq 2). Bergman[11b] and Rauchfuss[12b] have reported the synthesis of those clusters from [Cp*Ir(PMe$_3$)(μ_2-S)$_2$IrCp*] and [Cp*M(η^1:η^3-SC$_3$Me$_3$COMe)] (M = Ir, Rh), respectively, and have proposed that the formation of the cubane clusters involves dimerization of the doubly unsaturated intermediates [Cp*M(μ_2-S)]$_2$ (**5**, M = Ir; **6**, M = Rh). However, such species have not been observed experimentally. The reaction of complex **3** with NEt$_3$ in C$_6$D$_6$ was monitored by ^{1}H NMR spectroscopy, which showed that complex **3** was completely converted within 5 min to an intermediate with one Cp* resonance at δ 1.82. Judging from the lack of SH signals and the high symmetry indicated by the single Cp* signal, we have concluded that this intermediary species is complex **5**. At room temperature, the signal at δ 1.82 gradually disappeared within 3 h, and a signal at δ 1.72 due to cluster **7** emerged. In contrast, the conversion of complex **4** to cluster **8** was much faster. The ^{1}H NMR measurements indicated that the reaction is completed within 5 min at room temperature, and no signal assignable to complex **6** was detected even at a lower temperature.



Use of the hydrosulfido complexes **3** and **4** as a metallo ligand is expected to provide a versatile route to various metal clusters, especially those with heterobimetallic cores. In fact, complex **3** readily reacted with an equimolar amount of [RhCl(cod)]$_2$ in CH$_2$Cl$_2$ at room temperature to afford the cationic heterometallic triangular cluster [(Cp*Ir)$_2$Rh(μ_3-S)$_2$(cod)][RhCl$_2$(cod)] (**9**[RhCl$_2$(cod)]) in 91% yield as dark brown crystals (eq 3).



Similar reaction of **3** with 0.5 equiv of [RhCl(cod)]$_2$ followed by anion metathesis with NaBPh$_4$ in THF gave **9**[BPh$_4$] in 68% yield. Further, treatment of complex **4** with [RhCl(cod)]$_2$ (1 equiv) followed by anion metathesis with NaBPh$_4$ gave the cationic trirhodium cluster [(Cp*Rh)$_2$Rh(μ_3-S)$_2$(cod)][BPh$_4$] (**10**[BPh$_4$]) in 46% yield.

The ^{1}H NMR spectra of **9**[BPh$_4$] and **10**[BPh$_4$] indicated that each cluster has two equivalent Cp* ligands (**9**[BPh$_4$], δ 2.04; **10**[BPh$_4$], δ 1.84) and one cod ligand, in accordance with the formulation. The molecular structure of **9**[RhCl$_2$(cod)][13] was unambiguously determined by an X-ray diffraction study, and an ORTEP drawing of the cationic part is given in Figure 2. Cluster **9** has a triangular Ir$_2$Rh core, for which the two Ir–Rh contacts of 2.906(1) and 2.913(9) Å as well as the Ir–Ir contact of 2.8643(8) Å are all consistent with a metal–metal bond order of unity. The Ir$_2$Rh plane is capped by the μ_3-sulfido ligands from both sides almost symmetrically. Both Cp* planes are almost perpendicular to the Ir$_2$Rh plane. If we neglect the two Ir–Rh bonds, the geometry around the rhodium atom is square planar.

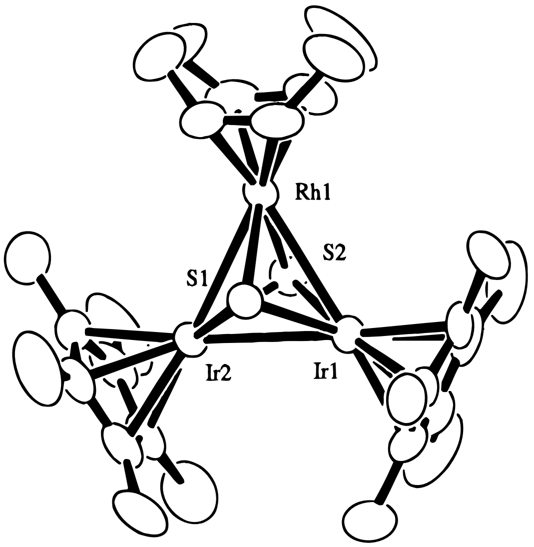
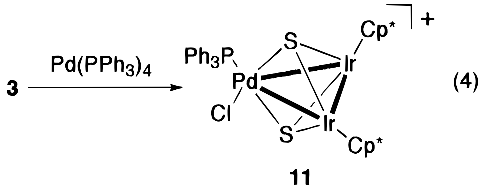


Figure 2. Molecular structure of the cationic part in **9**[RhCl$_2$(cod)]. Selected bond distances (Å) and angles (deg): Ir(1)–Ir(2) = 2.8643(8), Ir(1)–Rh(2) = 2.906(1), Ir(2)–Rh(1) = 2.9130(9), Ir(1)–Ir(2)–Rh(1) = 60.39(3), Ir(2)–Ir(1)–Rh(1) = 60.64(2), Ir(1)–Rh(1)–Ir(2) = 58.98(2).

Reaction of **3** with an equimolar amount of [Pd(PPh$_3$)$_4$] also produced the cationic sulfido cluster [(Cp*Ir)$_2$Pd(μ_3-S)$_2$Cl(PPh$_3$)]Cl (**11**[Cl]) in 34% yield (eq 4). The sulfido-capped triangular structure of **11**[Cl]·CH$_2$Cl$_2$[14] was confirmed by an X-ray diffraction analysis. The molecule has a crystallographic mirror plane on which the Pd, S, Cl, and P atoms are located. The Ir–Pd and Ir–Ir contacts of 2.9991(9) and 2.9068(8) Å, respectively, indicate the metal–metal single bonds. The ^{1}H NMR spectrum of **11** showing one Cp* singlet (δ 2.09) is also consistent with the solid-state structure. Although several triiridium and trirhodium clusters



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[13] Crystallographic data for **9**[RhCl$_2$(cod)]: C$_{36}$H$_{54}$S$_3$Cl$_2$Rh$_2$Ir$_2$, fw = 1212.10, monoclinic, space group $P2_1/c$, a = 10.737(3) Å, b = 11.115(3) Å, c = 32.890(4) Å, β = 90.19(2)°, V = 3924(2) Å^3, Z = 4, D_c = 2.051 g cm^{-3}, F_{000} = 2320, μ = 78.69 cm^{-1}, R = 0.036, and R_w = 0.030 for 4985 unique reflections ($I > 3.00\sigma(I)$).

[14] Crystallographic data for **11**[Cl]: C$_{39}$H$_{47}$PS$_2$Cl$_4$PdIr$_2$, fw = 1243.55, monoclinic, space group $P2_1/m$, a = 12.054(1) Å, b = 12.512(2) Å, c = 14.701(14) Å, β = 93.219(7)°, V = 2215.8(3) Å^3, Z = 2, D_c = 1.864 g cm^{-3}, F_{000} = 1192, μ = 68.07 cm^{-1}, R = 0.038, and R_w = 0.028 for 3398 unique reflections ($I > 3.00\sigma(I)$).

with two μ_3-sulfido ligands have been reported so far,[15] to our knowledge, both the $Ir_2Rh(\mu_3\text{-}S)_2$ core and $Ir_2Pd(\mu_3\text{-}S)_2$ core observed for **9** and **11** are unprecedented.

We have here revealed that, in addition to [Cp*RuCl(μ_2-SH)$_2$RuCp*Cl], the corresponding hydrosulfido-bridged diiridium and dirhodium complexes **3** and **4** are also potential precursors for tri- and tetranuclear sulfido cluster synthesis. Further study toward the synthesis of heterobimetallic clusters starting from complexes **3** and **4** is now in progress.

Acknowledgment. Financial support by the Ministry of Education, Science, and Culture of Japan is appreciated.

Supporting Information Available: Text giving experimental details and tables containing atomic coordinates, anisotropic temperature factors, and bond distances and angles for **3**, **4**, **9**[$RhCl_2$(cod)], and **11**(Cl)·CH_2Cl_2 (26 pages). Ordering information is given on any current masthead page.

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