Sulfido-Bridged $IrRh_2$ Clusters Derived from (Hydrogensulfido)iridium Complexes and Dirhodium Fragment. Comparison between Hydrido–Hydrogensulfido and Bis(hydrogensulfido) Systems

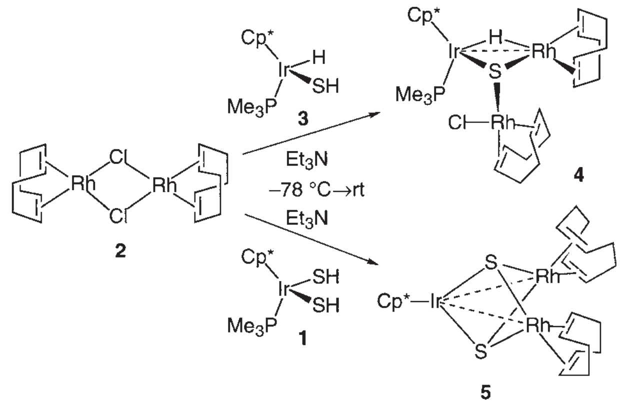
Akihiro Matsubayashi, Shigeki Kuwata, Youichi Ishii,* and Masanobu Hidai*†
Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656
†*Department of Materials Science and Technology, Faculty of Industrial Science and Technology,*
Science University of Tokyo, Noda, Chiba 278-8510

(Received January 29, 2002; CL-020110)

Treatment of $[Rh(\mu_2\text{-}Cl)(cod)]_2$ (cod = 1,5-cyclooctadiene) with the hydrido–hydrogensulfido complex $[Cp^*IrH(SH)(PMe_3)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) in the presence of triethylamine afforded the hydrido–mono(sulfido) complex $[Cp^*Ir(PMe_3)(\mu_2\text{-}H)(\mu_3\text{-}S)\{Rh(cod)\}\{RhCl(cod)\}]$, whereas the corresponding reaction with the bis(hydrogensulfido) complex $[Cp^*Ir(SH)_2(PMe_3)]$ gave the bis(sulfido) complex $[Cp^*Ir(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ with liberation of trimethylphosphine.

Hydrogensulfido complexes are now recognized as fundamental modules for construction of sulfur-bridged polynuclear complexes.[1–3] In one manifestation of this chemistry, the bis(hydrogensulfido) complex $[Cp^*Ir(SH)_2(PMe_3)]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) reacts with $[TiCl_4(thf)_2]$ and $[Cp^*Ir(\equiv NBu^t)]$ as a bidentate metalloligand to afford the sulfido-bridged complexes $[Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2TiCl_2]$[4] and $[Cp^*Ir(PMe_3)(\mu_2\text{-}S)_2IrCp^*]$,[5] respectively. The two bridging sulfido ligands that formed in these reactions benefit the stabilization of the dinuclear frameworks. Conversely, these strongly bound sulfido ligands block some of the coordination sites between the two metal centers, which would play a crucial role to realize cooperative reactivities of both metals. To overcome this drawback, we planned to reduce the number of the bridging sulfido ligands by using hydrido–mono(hydrogensulfido) complexes as a precursor. We report here the reactions of the chloro-bridged dirhodium complex $[Rh(\mu_2\text{-}Cl)(cod)]_2$ (**2**; cod = 1,5-cyclooctadiene) with the hydrido–hydrogensulfido complex $[Cp^*IrH(SH)(PMe_3)]$ (**3**),[6] which resulted in the formation of a hydrido- and sulfido-bridged $IrRh_2$ triangular complex. The reaction of **2** with the corresponding bis(hydrogensulfido) complex **1** is also described to compare the mono(hydrogensulfido) system with the bis(hydrogensulfido) one.

When the dirhodium complex **2** was allowed to react with an equimolar amount of the hydrido–hydrogensulfido complex **3** in the presence of triethylamine, the hydrido- and sulfido-bridged mixed-metal complex $[Cp^*Ir(PMe_3)(\mu_2\text{-}H)(\mu_3\text{-}S)\{Rh(cod)\}\{RhCl(cod)\}]$ (**4**) was obtained in 49% yield (Scheme 1).[7,8] The X-ray analysis of **4** has disclosed the $IrRh_2$ triangular core capped by a μ_3-sulfido ligand, derived from the hydrogensulfido functionality in **3** (Figure 1).[9] One of the two Ir–Rh edges is further bridged by a hydrido ligand, whereas a terminal chloride binds to the other Rh atom (Rh(2)). The hydrido and chloro ligands are almost coplanar with the three metal atoms. The μ_3-bridging sulfido ligand lies above the $IrRh_2$ trimetallic plane only by 0.617 Å. The iridium(III) center has a three-legged piano-stool geometry, and the two rhodium(I) centers are distorted square-planar. The Ir–Rh(1) distance of 2.8278(8) Å is consistent with a three-center–two-electron bond involving the bridging hydrido ligand, whereas the Rh(2) atom is situated far from the other two metal atoms (Ir–Rh(2), 4.207(1); Rh(1)–Rh(2), 4.264(1) Å).



Scheme 1.

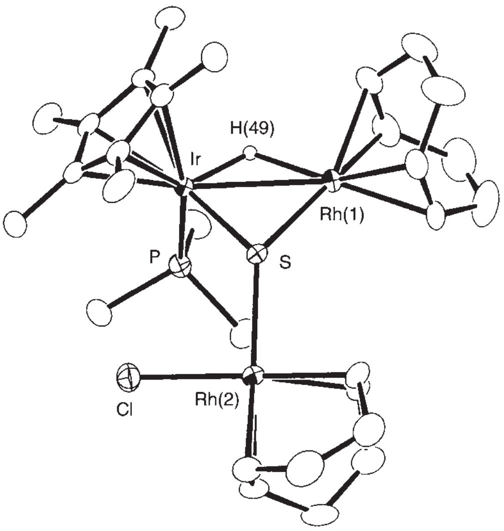


Figure 1. Molecular structure of **4**. Selected interatomic distances (Å): Ir–Rh(1) 2.8278(8), Ir–Rh(2) 4.207(1), Rh(1)–Rh(2) 4.264(1), Ir–S 2.339(2), Ir–P 2.269(2), Rh(1)–S 2.287(1), Rh(2)–S 2.354(1), Rh(2)–Cl 2.386(2), Ir–H(49) 1.52(6), Rh(1)–H(49) 1.84(6).

Despite the unsymmetric solid state structure of **4**, the hydrido resonance in the room-temperature ^1H NMR spectrum was observed as a doublet of triplets split by the phosphorous and two apparently equivalent rhodium nuclei. At −60 °C, the signal changed to much more complex, unresolved multiplets. These observations suggest the presence of a dynamic process at room temperature, which renders the two rhodium centers equivalent in solution. However, the details of the mechanism for the fluxionality are unclear at present.

Use of mono(hydrogensulfido) complexes as templates for sulfido-bridged polynuclear architectures is much less developed compared with that of bis(hydrogensulfido) complexes,[3,10,11] and in most of the mono(hydrogensulfido) systems, it is only the sulfur atom that bridges the metal centers in the polynuclear products. For example, the reactions of the hydrido–hydrogensulfido complex $[(t\text{-BuCp})_2\mathrm{TaH_2(SH)}]$ ($t\text{-BuCp} = \eta^5\text{-C}_5\text{H}_4\text{Bu}^t$) with $[\mathrm{M(CO)_5(thf)}]$ (M = Cr, W) give the heterobimetallic complexes $[(t\text{-BuCp})_2\mathrm{TaH_2}(\mu_2\text{-SH})\mathrm{M(CO)_5}]$, in which the two metal centers are bridged only by a hydrogensulfido ligand, and the hydrido ligands remain terminal.[10]

On the other hand, treatment of the dirhodium complex **2** with the bis(hydrogensulfido) complex **1** in place of the hydrido-hydrogensulfido complex **3** resulted in the formation of the bis(sulfido)-capped $\mathrm{IrRh_2}$ cluster $[\mathrm{Cp^*Ir}(\mu_3\text{-S})_2\{\mathrm{Rh(cod)}\}_2]$ (**5**) in 69% yield (Scheme 1).[12] In contrast to the formation of the mono(sulfido) complex **4**, the phosphine ligand in **1** has been lost during the reaction. Figure 2 depicts the X-ray structure of **5**,[13] which has an almost isosceles $\mathrm{IrRh_2}$ triangle capped by two μ_3-sulfido ligands from both sides; the mean distance between the sulfur atoms and the trimetallic plane is 1.549 Å. Although the 48e$^-$ cluster **5** should have three metal–metal bonds according to the effective atomic number rule, there are only two weak Ir–Rh interactions, judging from the metal–metal distances. This is probably because the high lying p_z orbitals in the square-planar Rh(I) metals in **5** are unavailable for bonding.[14] The series of the group 9 metal clusters having $(\mathrm{Cp^*M})_n\{(\mathrm{cod})\mathrm{M'}\}_{3-n}(\mu_3\text{-S})_2$ cores (n = 0–3)[15–17] have been completed by the isolation of **5** (n = 1).

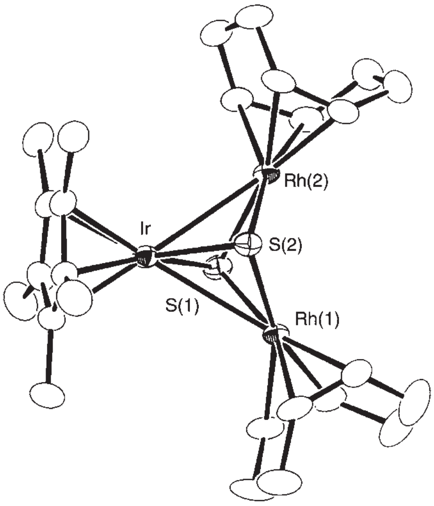


Figure 2. Molecular structure of **5**. Selected interatomic distances (Å): Ir–Rh(1) 2.9269(6), Ir–Rh(2) 2.8772(5), Rh(1)–Rh(2) 3.095(1), Ir–S(1) 2.309(2), Ir–S(2) 2.296(2), Rh(1)–S(1) 2.316(2), Rh(1)–S(2) 2.312(2), Rh(2)–S(1) 2.315(2), Rh(2)–S(2) 2.316(2).

In summary, we have demonstrated that the hydrido–hydrogensulfido complex **3** can be used as a novel type of chelating metalloligand, which binds to heterometals through the sulfur atom and, formally, σ-bond electrons of the Ir–H bond. The resultant cluster **4** has an open framework with the three metal centers linked only by one sulfido and hydrido ligands. This sharply contrasts with the closed structure of **5**, which was obtained from the bis(hydrogensulfido) complex **1**. We consider that the bridging hydrido ligand thus formed offers a reaction site for dinuclear activation of a substrate as well as introduction of bridging heteroelements other than sulfur into the polynuclear framework. Syntheses of hydrido- and sulfido-bridged complexes with more diversified metal compositions through this strategy are also in progress.

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan and the JSPS FY2000 "Research for the Future Program."

References and Notes

1 a) S. Kuwata and M. Hidai, *Coord. Chem. Rev.*, **213**, 211 (2001). b) M. Peruzzini, I. de los Rios, and A. Romerosa, *Prog. Inorg. Chem.*, **49**, 169 (2001).

2 a) S. Kuwata, S. Kabashima, Y. Ishii, and M. Hidai, *J. Am. Chem. Soc.*, **123**, 3826 (2001). b) S. Kuwata, S. Kabashima, N. Sugiyama, Y. Ishii, and M. Hidai, *Inorg. Chem.*, **40**, 2034 (2001). c) D. Masui, T. Kochi, Z. Tang, Y. Ishii, Y. Mizobe, and M. Hidai, *J. Organomet. Chem.*, **620**, 69 (2001). d) H. Seino, Y. Mizobe, and M. Hidai, *New J. Chem.*, **24**, 907 (2000).

3 J. Ruiz, V. Rodríguez, C. Vicente, J. M. Martí, G. López, and J. Pérez, *Inorg. Chem.*, **40**, 5354 (2001).

4 T. Nagano, S. Kuwata, Y. Ishii, and M. Hidai, *Organometallics*, **19**, 4176 (2000).

5 D. A. Dobbs and R. G. Bergman, *Inorg. Chem.*, **33**, 5329 (1994).

6 D. P. Klein, G. M. Kloster, and R. G. Bergman, *J. Am. Chem. Soc.*, **112**, 2022 (1990).

7 **4**: ^{1}H NMR ($\mathrm{C_6D_6}$, rt): δ 5.03–4.67 (br, 8H, cod), 2.28–2.14 (br, 8H, cod), 1.89 (s, 15H, $\mathrm{C_5Me_5}$), 1.82 (br s, 8H, cod), 1.61 (d, $^2J_{\mathrm{PH}} = 10.9$ Hz, 9H, $\mathrm{PMe_3}$), −17.28 (dt, $^2J_{\mathrm{PH}} = 23.2$ Hz, $J_{\mathrm{RhH}} = 7.9$ Hz, 1H, IrRhH). Anal. Found: C, 39.12; H, 5.59; Cl, 4.77; S, 3.58%. Calcd for $\mathrm{C_{29}H_{49}ClIrPRh_2S}$: C, 38.95; H, 5.52; Cl, 3.96; S, 3.59%.

8 Similar treatment of **2** with **3** in a Rh : Ir ratio of 1 : 1 resulted in the formation of a mixture containing **4**.

9 Crystallographic data for **4**: $\mathrm{C_{29}H_{49}ClIrPRh_2S}$, $M = 894.22$, monoclinic, $P2_1/n$, $a = 12.163(4)$, $b = 12.899(5)$, $c = 20.291(3)$ Å, $\beta = 92.41(2)^\circ$, $V = 3180(1)$ Å^3, $Z = 4$, $d_c = 1.867$ g cm^{-3}, 7299 unique reflections. Refinements of 320 parameters obtained by using 6008 reflections ($I > 3\sigma(I)$) gave residuals of $R = 0.033$ and $R_w = 0.036$. Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-180405 (**4**) and 180406 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

10 S. Challet, O. Blacque, G. Gehart, M. M. Kubicki, J.-C. Leblanc, C. Moïse, H. Brunner, and J. Wachter, *New J. Chem.*, **21**, 903 (1997).

11 a) V. Küllmer and H. Vahrenkamp, *Chem. Ber.*, **110**, 3810 (1977). b) D. J. Darensbourg, D. J. Zalewski, K. M. Sanchez, and T. Delord, *Inorg. Chem.*, **27**, 821 (1988). c) F. Canales, S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones, and A. Laguna, *Organometallics*, **17**, 1617 (1998).

12 **5**: ^{1}H NMR ($\mathrm{CDCl_3}$): d 4.26–4.22 (br, 8H, cod), 2.37–1.93 (br, 16H, cod), 2.10 (s, 15H, $\mathrm{C_5Me_5}$). Anal. Found: C, 38.07; H, 4.93%. Calcd for $\mathrm{C_{26}H_{39}IrRh_2S_2}$: C, 38.38; H, 4.83%.

13 Crystallographic data for **5**: $\mathrm{C_{23}H_{39}IrRh_2S_2}$, $M = 813.75$, monoclinic, $P2_1/a$, $a = 14.147(2)$, $b = 9.7706(9)$, $c = 19.627(1)$ Å, $\beta = 97.874(7)^\circ$, $V = 2687.4(4)$ Å^3, $Z = 4$, $d_c = 2.011$ g cm^{-3}, 6167 unique reflections. Refinements of 281 parameters obtained by using 5036 reflections ($I > 3\sigma(I)$) collected on a Rigaku AFC7R diffractometer gave residuals of $R = 0.036$ and $R_w = 0.043$.

14 D. M. P. Mingos and A. S. May, in "The Chemistry of Metal Cluster Complexes," ed. by D. F. Shriver, H. D. Kaesz, and R. D. Adams, VCH, New York (1990), Chap. 2.

15 a) A. M. Arif, J. G. Hefner, R. A. Jones, and S. U. Koschmieder, *Polyhedron*, **7**, 561 (1988). b) T. A. Bright, R. A. Jones, S. U. Koschmieder, and C. M. Nunn, *Inorg. Chem.*, **27**, 3819 (1988).

16 Z. Tang, Y. Nomura, Y. Ishii, Y. Mizobe, and M. Hidai, *Organometallics*, **16**, 151 (1997).

17 a) A. Venturelli and T. B. Rauchfuss, *J. Am. Chem. Soc.*, **116**, 4824 (1994). b) T. Nishioka and K. Isobe, *Chem. Lett.*, **1994**, 1661.