Synthesis and Reactivities of Sulfido-bridged Ir–W and Ir–Re Heterodinuclear Complexes with Imido Ligands

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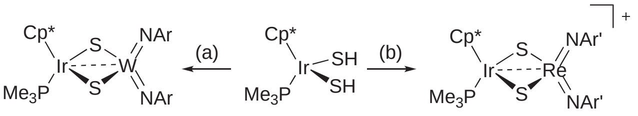
The iridium hydrosulfido complexes [Cp*IrH(SH)(PPh_3)] (Cp* = η^5-C_5Me_5) and [Cp*Ir$(SH)_2$(PMe_3)] were found to serve as effective building blocks for the synthesis of mono- and bis(sulfido)-bridged heterodinuclear complexes with a high-valent tungsten or rhenium–imido center.

Early–late heterobimetallic (ELHB) complexes are the class of compounds which are currently attracting considerable attention, because the cooperative action of an electron-deficient early-transition-metal and an electron-rich late-transition-metal is expected to give novel functionalities to these compounds in activation and transformation of various substrate molecules.[1] During ongoing research in our laboratory to synthesize the mixed-metal di- and polynuclear complexes bridged by sulfido ligands, a synthetic strategy for ELHB complexes has been established by the use of mononuclear hydrosulfido complexes as building blocks for multimetallic cores.[2] We have more recently applied this methodology to the synthesis of group 9–group 6 heterodinuclear complexes with a nitrosyl ligand [Cp*M(PMe_3)(μ-S)$_2$M′(NO)Cp*] (M = Rh, Ir; M′ = Mo, W; Cp* = η^5-C_5Me_5), which exemplify the effective bimetallic activation of the nitrosyl ligand at their ELHB cores.[3] In order to expand the scope of this synthetic method, we have turned our attention to sulfido-bridged ELHB complexes with high oxidation state early-transition metals, because synthesis of this class of ELHB compounds has so far relied mainly on the use of thiometalates and related compounds as metalloligands.[4] Here, we describe the synthesis, structures, and reactivities of novel sulfido-bridged Ir–W or Ir–Re heterodinuclear complexes containing high-valent tungsten– and rhenium–imido moieties.

When the iridium bis(hydrosulfido) complex [Cp*Ir$(SH)_2$(PMe_3)] (**1**) was treated with [$WCl_2(NAr)_2$(dme)] (**2**, Ar = 2,6-$Pr^i_2C_6H_3$, dme = $MeOCH_2CH_2OMe$) in the presence of NEt_3, the bis(sulfido)-bridged Ir–W heterodinuclear complex [Cp*Ir(PMe_3)(μ-S)$_2$W$(NAr)_2$] (**3**) was obtained as orange crystals in 64% yield (Scheme 1). The ^{1}H NMR spectrum of **3** exhibits a set of signals assignable to one Cp*, one PMe_3, and two distinct NAr ligands, being in full agreement with the formulation.[5] A preliminary X-ray crystallographic study also confirmed the formation of the IrS_2W core with two imido ligands at the tungsten center. An analogous reaction with [$ReCl_3(NAr')_2$(py)] (**4**, Ar′ = 2,6-$Me_2C_6H_3$, py = NC_5H_5) afforded the corresponding cationic complex [Cp*Ir(PMe_3)(μ-S)$_2$Re$(NAr')_2$]$^+$ (**5**$^+$), which was isolated in 84% yield as red solids of **5**$^+$$BAr^F_4{}^-$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$) after anion metathesis with $NaBAr^F_4$ (Scheme 1). An X-ray analysis of **5**$^+$$BAr^F_4{}^-$•$2C_6H_6$ has been performed to clarify the detailed molecular structure (Figure 1).[6] The Ir–Re distance (2.8519(2) Å) as well as the acute Ir–S–Re angles (75.9°, mean) indicates the existence of the Ir→Re dative bond. The Re–N bond distances (Re(1)–N(1) 1.745(3) Å, Re(1)–N(2) 1.750(3) Å) are not exceptional for 4e-donating arylimido ligands bound to rhenium.[7] The Re(1)–N(1)–C(14) moiety (158.9(3)°) is slightly more bent than the Re(1)–N(1)–C(22) bond (168.9(3)°) probably due to the steric interaction between the Cp* and NAr′ ligand.

With the novel heterodinuclear imido complexes in hand, reactivities of the imido ligands at the dinuclear core have been investigated. Treatment of **3** in THF–H_2O at room temperature afforded the dioxo complex [Cp*Ir(PMe_3)(μ-S)$_2$W$(O)_2$] (**6**)[8] in 76% yield, which was formed through the hydrolysis of the two imido ligands (Graphical Information). An X-ray crystallographic study (structure not shown)[6] established the structure of **6** with the dioxotungsten moiety, whose IrS_2W core structure is closely related to the IrS_2Re core of **5**$^+$$BAr^F_4{}^-$. On the other hand, treatment of **3** with H_2S (1 atm) in toluene at room temperature resulted in the formation of three dinuclear species **7a**–**7c** in the ratio of 3:1:2. The ^{1}H NMR of the major product **7a** exhibits signals at δ 1.89 (d, J = 1.5 Hz, Cp*, 15H), 1.59 (d, J = 10.5 Hz, PMe_3, 9H), 1.28 (d, J = 7.0 Hz, CHMe_2, 12H), and 3.94 (septet, J = 7.0 Hz, C$H$$Me_2$, 2H), indicating that one



Scheme 1. Reaction conditions: (a) [$WCl_2(NAr)_2$(dme)] (**2**), NEt_3; (b) [$ReCl_3(NAr')_2$(py)] (**4**), NEt_3.

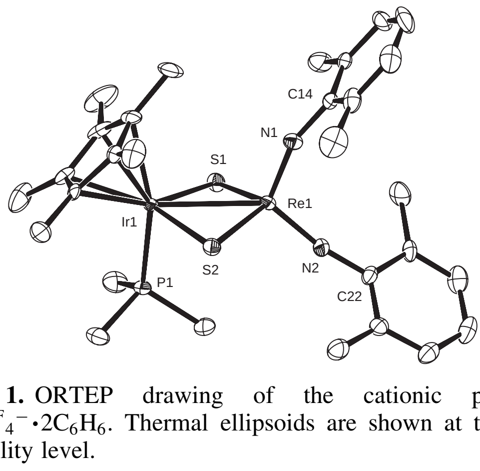


Figure 1. ORTEP drawing of the cationic part of **5**$^+$$BAr^F_4{}^-$•$2C_6H_6$. Thermal ellipsoids are shown at the 50% probability level.

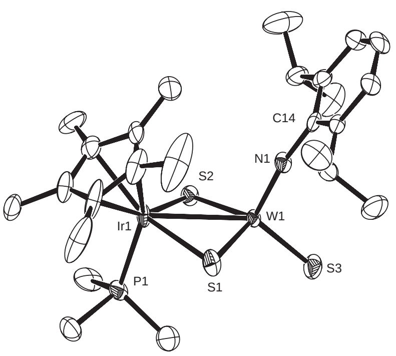
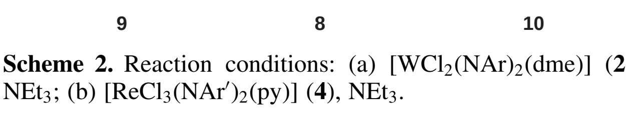


Figure 2. ORTEP drawing of **7a**. Thermal ellipsoids are shown at the 50% probability level.

of the two imido ligands has been displaced. An X-ray diffraction study (Figure 2) has been performed to reveal that this product is the (imido)(terminal sulfido) complex [Cp*Ir(PMe$_3$)(μ-S)$_2$W(S)(NAr)], where the imido ligand in **3** cis to the PMe$_3$ ligand is replaced with a sulfido ligand.[6] The metric features for the IrS$_2$W core in complex **7a** are comparable to those for **6**. It should be noted that the stereoisomer of **7a** in which the sulfido and PMe$_3$ ligands are located trans to each other is not formed by this reaction. The ^{1}H NMR analyses of the other two products indicate that they have no NAr group coordinated to the dinuclear cores. The minor product **7b** is identified as the bis(terminal sulfido) complex [Cp*Ir(PMe$_3$)(μ-S)$_2$W(S)$_2$],[8] while the second major product **7c** is tentatively assigned as the (oxo)(terminal sulfido) complex [Cp*Ir(PMe$_3$)(μ-S)$_2$W(O)(S)] formed by the hydrolysis of **7a** with adventitious water. In contrast to complex **3**, complex **5**$^+$BAr$^F{}_4{}^-$ is inert to H$_2$O and H$_2$S even at elevated temperatures.

On the other hand, the reaction of the iridium (hydrido)(hydrosulfido) complex [Cp*IrH(SH)(PPh$_3$)] (**8**) with the bis(imido) tungsten complex **2** in the presence of NEt$_3$ led to the mono(sulfido)-bridged heterodinuclear complex [Cp*IrH(PPh$_3$)(μ-S)WCl(NAr)$_2$] (**9**) as yellow crystals in 76% yield (Scheme 2). The molecular structure of **9** has also been determined by X-ray crystallography[6] (structure not shown) to disclose that the sulfido ligand bridges the tungsten and iridium atoms to form the triangular IrWS core, where the separation between the metal centers at 2.9945(3) Å and the Ir(1)–S(1)–W(1) bond angle of 79.22(7)° suggest the existence of some metal–metal bonding interaction. Although the hydrido ligand in **9** could not be found by Fourier syntheses, its IR and ^{1}H NMR spectra exhibit a ν(Ir–H) band at 2021 cm^{-1} and a hydrido signal at δ −11.96 as a doublet ($J_{PH} = 26.5$ Hz), respectively, which clearly indicates that the hydrido ligand is coordinated to the iridium center in an end-on fashion. A similar reaction of **8** with **4** also generated the mono(sulfido)-bridged Ir–Re complex [Cp*Ir(PPh$_3$)(μ-S)ReCl(NAr′)$_2$]•0.5C$_6$H$_6$ (**10**•0.5C$_6$H$_6$) as dark brown crystalline solids in 73% yield (Scheme 2). Complex **10** shows neither Ir–H nor SH resonance in the ^{1}H NMR, and its preliminary diffraction study has confirmed the 34e triangular IrReS structure with a terminal chloro ligand.



Scheme 2. Reaction conditions: (a) [WCl$_2$(NAr)$_2$(dme)] (**2**), NEt$_3$; (b) [ReCl$_3$(NAr′)$_2$(py)] (**4**), NEt$_3$.

In conclusion, we have demonstrated that mono- and bis(sulfido)-bridged heterodinuclear complexes with a high-valent tungsten– or rhenium–imido center can be synthesized effectively by adopting iridium hydrosulfido complexes **1** and **8** as the building blocks. Further studies on reactivities of the newly synthesized Ir–W and Ir–Re imido complexes are now in progress.

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References and Notes

1 a) N. Wheatley, P. Kalck, *Chem. Rev.* **1999**, *99*, 3379. b) T. A. Hanna, A. M. Baranger, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 11363. c) S. Kuwata, S. Kabashima, Y. Ishii, M. Hidai, *J. Am. Chem. Soc.* **2001**, *123*, 3826. d) J. Kuwabara, D. Takeuchi, K. Osakada, *Chem. Commun.* **2006**, 3815. e) H. Nagashima, T. Sue, T. Oda, A. Kanemitsu, T. Matsumoto, Y. Motoyama, Y. Sunada, *Organometallics* **2006**, *25*, 1987.

2 a) T. Nagano, S. Kuwata, Y. Ishii, M. Hidai, *Organometallics* **2000**, *19*, 4176. b) S. Kuwata, T. Nagano, A. Matsubayashi, Y. Ishii, M. Hidai, *Inorg. Chem.* **2002**, *41*, 4324.

3 K. Arashiba, S. Matsukawa, S. Kuwata, Y. Tanabe, M. Iwasaki, Y. Ishii, *Organometallics* **2006**, *25*, 560.

4 a) B. Kure, S. Ogo, D. Inoki, H. Nakai, K. Isobe, S. Fukuzumi, *J. Am. Chem. Soc.* **2005**, *127*, 14366. b) Y. Ohki, N. Matsuura, T. Marumoto, H. Kawaguchi, K. Tatsumi, *J. Am. Chem. Soc.* **2003**, *125*, 7978. c) H. Seino, N. Iwata, N. Kawarai, M. Hidai, Y. Mizobe, *Inorg. Chem.* **2003**, *42*, 7387. d) K. E. Howard, J. R. Lockemeyer, M. A. Massa, T. B. Rauchfuss, S. R. Wilson, X. Yang, *Inorg. Chem.* **1990**, *29*, 4385.

5 Supporting information is available electronically on the CSJ-Journal Web Site, http://www.csj.jp/journals/chem-lett/index.html.

6 Crystal data for **5**$^+$BAr$^F{}_4{}^-$•2C$_6$H$_6$: FW 1911.63, triclinic, space group $P\bar{1}$, $a = 13.817(8)$, $b = 15.322(15)$, $c = 17.809(15)$ Å, $\alpha = 89.15(5)°$, $\beta = 86.44(4)°$, $\gamma = 77.36(4)°$, $V = 3672(5)$ Å^3, $Z = 2$, $\rho = 1.729$ g cm^{-3}, R (R_w) = 0.0328 (0.0383) for 1013 variables, 12413 unique reflections ($I > 3\sigma(I)$), and GOF = 1.000. For **6**: FW 683.50, orthorhombic, space group $P2_12_12_1$, $a = 8.4702(12)$, $b = 12.985(2)$, $c = 16.275(3)$ Å, $V = 1790.0(5)$ Å^3, $Z = 4$, $\rho = 2.536$ g cm^{-3}, R (R_w) = 0.0220 (0.0254) for 197 variables, 3664 unique reflections ($I > 3\sigma(I)$), and GOF = 1.005. For **7a**: FW 858.83, monoclinic, space group $P2_1/n$, $a = 9.5917(16)$, $b = 14.842(2)$, $c = 21.050(4)$ Å, $\beta = 102.0544(19)°$, $V = 2930.5(9)$ Å^3, $Z = 4$, $\rho = 1.946$ g cm^{-3}, R (R_w) = 0.0563 (0.0562) for 331 variables, 5526 unique reflections ($I > 3\sigma(I)$), and GOF = 1.000. For **9**: FW 1192.66, orthorhombic, space group $Pca2_1$, $a = 21.684(3)$, $b = 12.9161(19)$, $c = 17.115(3)$ Å, $V = 4793.3(12)$ Å^3, $Z = 4$, $\rho = 1.653$ g cm^{-3}, R (R_w) = 0.0333 (0.0359) for 592 variables, 8191 unique reflections ($I > 3\sigma(I)$), and GOF = 1.004. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC 636073 (**5**$^+$BAr$^F{}_4{}^-$•2C$_6$H$_6$), 636074 (**6**), 636075 (**7a**), and 636076 (**9**).

7 a) A. K. Burrell, A. J. Steedman, *J. Chem. Soc., Dalton Trans.* **2000**, 2501. b) W. A. Herrmann, H. Ding, F. E. Kühn, W. Scherer, *Organometallics* **1998**, *17*, 2751.

8 Preparation of **6** and **7b** by using thiotungstates has recently been reported, although **6** has not been isolated in a pure form: M. Herberhold, G.-X. Jin, A. L. Rheingold, *Z. Anorg. Allg. Chem.* **2005**, *631*, 135.