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Isolation of a Cubane-Type Metal Sulfido Cluster with a Molecular Nitrogen Ligand**

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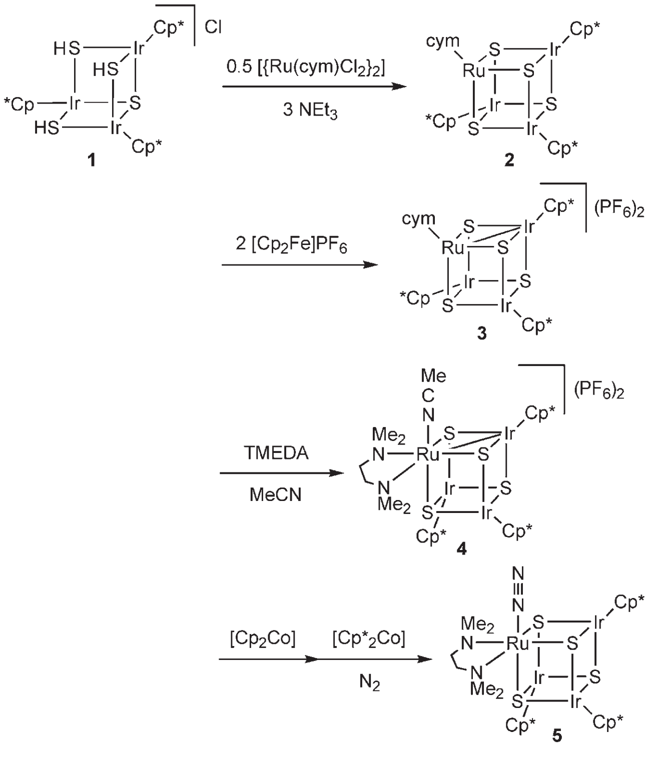
In memory of Yoshihiko Ito

Nitrogenase can catalyze the reduction of the rather inert N_2 molecule to ammonia under ambient conditions.[1] Details of this enzyme have long attracted much attention, since clarification of the mechanism of its function may provide useful information for development of new industrial N_2-fixing systems that operate under mild conditions. However, in spite of significant progress in the elucidation of the X-ray structure of the active site, that is, the FeMo cofactor (FeMo-co) with an $MoFe_7S_9X$ core in the case of Mo-containing nitrogenase,[2] it is still uncertain where and how the N_2 molecule is converted to ammonia in this mixed-metal sulfido cluster,[3] although several coordination modes of N_2 or nitrogenase substrates in this enzyme have been proposed, based mainly on theoretical studies.

In this context, isolation of well-defined metal sulfido clusters with dinitrogen ligands and elucidation of the reactivity of the coordinated N_2 are of particular interest. However, in spite of the existence of a number of stable N_2 complexes with coligands such as phosphines, thioethers, imides, cyclopentadienyls, and thiolates,[4] metal sulfido clusters with N_2 ligands are unprecedented.

Recent studies by us have focused on new and rational synthetic routes to metal sulfido clusters and resulted in the preparation of a series of hydrosulfido-bridged di- and trinuclear noble metal complexes that can serve as precursors for a variety of homo- and heterometallic cubane-type sulfido clusters.[5] These include the incomplete cubane-type Ir sulfido hydrosulfido cluster $[(Cp^*Ir)_3(\mu_3\text{-}S)(\mu_2\text{-}SH)_3]Cl$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$),[6] which reacts with not only compounds of main group metals such as Sb and Bi, but also with those of the transition metals present in FeMo-co, Fe and Mo, to give clusters with cubane-type Ir_3MS_4 cores (M = Sb, Bi,[7] Fe,[8] Mo[9]). However, even for the last two compounds, as synthetic models of FeMo-co, N_2 binding to the Fe or Mo site has not yet been observed.

Now we have found that **1** can also incorporate a Ru fragment into its void corner to afford a cubane-type $\{Ir_3RuS_4\}$ cluster and the Ru^{II} center in this core can bind molecular N_2 to yield the first metal sulfido cluster with an N_2 ligand (Scheme 1).



Scheme 1. Synthesis of N_2-containing cluster **5** starting from **1**.

When a solution of **1** in MeCN was treated with 0.5 equiv of $[\{Ru(cym)Cl_2\}_2]$ (cym = η^6-*p*-*i*PrC_6H_4Me) in the presence of 3 equiv of NEt_3, incorporation of the {Ru(cym)} fragment afforded cubane-type cluster $[(Cp^*Ir)_3\{Ru(cym)\}(\mu_3\text{-}S)_4]$ (**2**), which was isolated as orange crystals in 83% yield. Single-crystal X-ray analysis unambiguously confirmed formation of the cubane core (Figure 1).[10] The absence of metal–metal bonds in the $\{Ir^{III}_3Ru^{II}\}$ framework of **2** is consistent with its 72-electron count.

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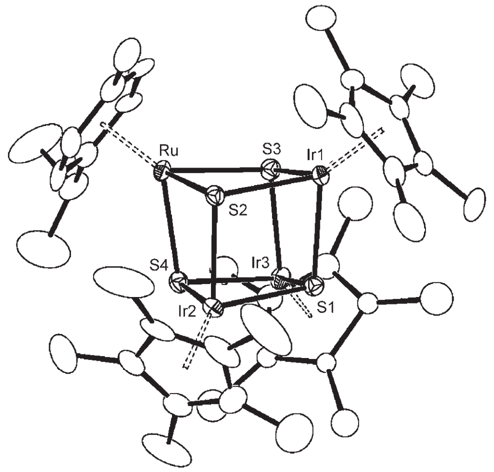

Figure 1. ORTEP view of one of the two independent molecules of **2**. Hydrogen atoms and one disordered Cp* ligand attached to Ir3 are omitted for clarity (thermal ellipsoids shown at 30% probability).

Although the Ru fragment was incorporated into the cubane core successfully, the cym ligand in **2** turned out to be bound so tightly to the Ru^{II} center that its replacement by other neutral ligands hardly took place. Therefore, the Ru center was oxidized. When **2** was treated with 2 equiv of $[Cp_2Fe]PF_6$ in THF, the cationic cluster $[(Cp^*Ir)_3\{Ru(cym)\}(\mu_3\text{-}S)_4](PF_6)_2$ (**3**) was obtained in 93% yield as dark green crystals. The structure of the cation with a formal $\{Ir^{III}{}_3Ru^{IV}\}$ (or $\{Ir^{III}{}_2Ir^{IV}Ru^{III}\}$) core was determined by X-ray diffraction (Figure 2). The cubane core is more distorted than that of **2** due to formation of an Ru–Ir single bond with a length at 2.7890(7) Å, which is associated with a decrease of the cluster electron count by two.

As expected, substitution of the cym ligand proceeded readily for oxidized cluster **3**, and the reaction with $Me_2NCH_2CH_2NMe_2$ (tmeda) in MeCN at 50°C afforded $[(Cp^*Ir)_3\{Ru(tmeda)(MeCN)\}(\mu_3\text{-}S)_4](PF_6)_2$ (**4**) in 78% yield as dark green crystals, in which the vacant sixth site of the octahedrally coordinated Ru center is occupied by MeCN, as confirmed by X-ray analysis (Figure 3). Metrical parameters associated with the $\{Ir_3RuS_4\}$ core are essentially identical to those of **3**.

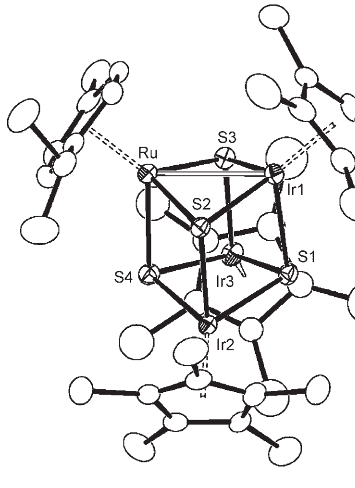

Figure 2. ORTEP view of the cation in **3**. Hydrogen atoms and one disordered Cp* ligand attached to Ir3 are omitted for clarity (thermal ellipsoids shown at 30% probability).

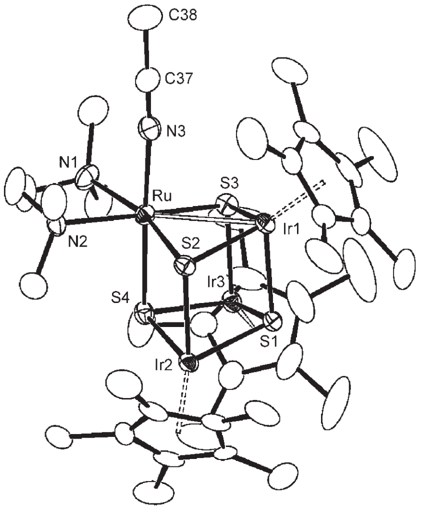

Figure 3. ORTEP view of the cation in **4**. Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 50% probability).

Finally, **4** was reduced to give the cluster containing an Ru^{II} center. Reduction of **4** with 2 equiv of $[Cp^*{}_2Co]$ in THF/MeCN indeed gave the desired N_2-containing cluster $[(Cp^*Ir)_3\{Ru(tmeda)(N_2)\}(\mu_3\text{-}S)_4]$ (**5**) after crystallization from hexane under N_2, albeit in low yield (ca. 5%). However, when **4** was reduced first with 1 equiv of $[Cp_2Co]$ in THF/MeCN, and then the one-electron-reduced species generated in the reaction mixture was reduced further with $[Cp^*{}_2Co]$ in THF alone under N_2, **5** could be isolated as a mixture of dark orange crystals and orange solid in 82% yield by concentrating a solution of the product in hexane. X-ray analysis clearly showed the presence of an N_2 ligand bonded to the Ru^{II} center in an end-on manner (Figure 4), for which the observed N–N and Ru–N bond lengths and Ru-N-N angle are 1.06(1) Å, 1.917(7) Å, and 172.6(9)°, respectively. The IR spectrum exhibits a characteristic $\nu(N{\equiv}N)$ band at 2019 cm^{-1}.

Since the isolation of $[Ru(N_2)(NH_3)_5]X_2$ as the first N_2 complex, which shows a $\nu(N{\equiv}N)$ band at 2118 cm^{-1} for X = Br,[11] a significant number of Ru^{II}–N_2 complexes have been reported. These include the dithiolato complex $[Ru(N_2)(P\mathit{i}Pr_3)(SC_6H_4NMeCH_2CH_2NMeC_6H_4S)]$ (N–N 1.110(4) Å, $\tilde{\nu}(N{\equiv}N) = 2113\ cm^{-1}$),[12] the triphosphine complex $[RuH_2(N_2)\{PhP(CH_2CH_2CH_2PCy_2)_2\}]$ (Cy = cyclohexyl; N–N 1.093(8) Å, $\tilde{\nu}(N{\equiv}N) = 2100\ cm^{-1}$),[13] and the pincer-ligated complex $[RuH(N_2)(PPh_3)\{C_6H_3\text{-}2,6\text{-}(PCy_2)_2\}]$ (N–N 1.111(6) Å, $\tilde{\nu}(N{\equiv}N) = 2134\ cm^{-1}$).[14] To the best of our knowledge, the lowest $\tilde{\nu}(N{\equiv}N)$ value of 2055 cm^{-1} was observed for the tetraamine complex $[Ru(OH)(N_2)(L)]^+$ (L = 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane),[15] and that of the related, structurally characterized tetraamine complex $[RuCl(N_2)(L')]^+$ (L′ = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) is 2066 cm^{-1} with an N–N bond

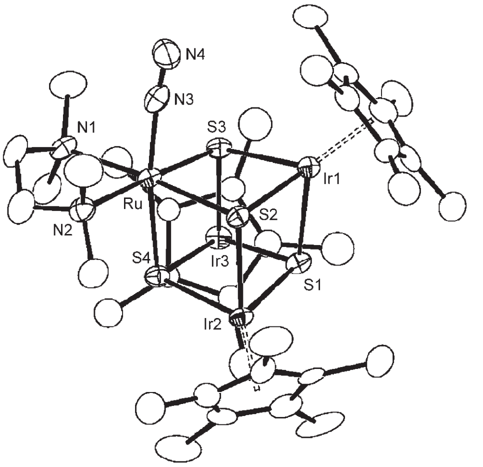

Figure 4. ORTEP view of **5**. Hydrogen atoms and one disordered Cp* ligand attached to Ir3 are omitted for clarity (thermal ellipsoids shown at 50% probability).

length of 1.01(1) Å.[16] The N–N distance in **5** is comparable to those of the above Ru^{II} complexes, but its $\tilde{\nu}$(N≡N) value of 2019 cm^{-1} is considerably lower, and even lower than that of Ru^0 complex $[Ru(N_2)\{P(CH_2CH_2PPh_2)_3\}]$ with a P coligand.[17] This can be ascribed to the strong electron-donating ability of the three sulfido ligands bound to Ru.

Analogous synthesis of cubane-type sulfido clusters from incomplete cubane-type cluster has extensively been studied for Mo precursors such as $[Mo_3S_4(H_2O)_9]^{4+}$[18] and $[(Cp'Mo)_3S_4]^+$ (Cp′ = η^5-C_5H_4Me[19] or Cp*[20]), and a number of $\{Mo_3MS_4\}$ clusters are known. However, coordination of N_2 to the M site in these cubanes has not yet been observed, even at the Ru site of the $\{(Cp^*Mo)_3RuS_4\}$ clusters,[21] although some of these clusters are effective in catalytic disproportionation of hydrazine.[20a] This difference in reactivity presumably arises from the stronger electron-donating ability of the $\{(Cp^*Ir)_3S_4\}$ moiety containing d^6 Ir^{III} centers in **5** compared to the $\{Mo_3S_4\}$ fragment with d^2 Mo^{IV} centers.[22] Studies on the reactivities of the N_2 ligand in **5** and the isolation of related N_2 clusters from **1** are now in progress.

Experimental Section

All manipulations were carried out under N_2 by standard Schlenk techniques. Solvents were dried by common methods and distilled under N_2 before use. Complex **1**[6] and $[\{Ru(cym)Cl_2\}_2]$[23] were prepared according to literature methods, while other chemicals were obtained commercially and used as received.

2: NEt_3 (210 μL, 1.51 mmol) was added to a mixture of **1** (575 mg, 0.500 mmol) and $[\{Ru(cym)Cl_2\}_2]$ (153 mg, 0.250 mmol) in MeCN (50 mL) at −40 °C. The mixture was warmed gradually to room temperature and stirred continuously. After 24 h, orange microcrystals of **2** were collected by filtration, washed with MeCN, and dried in vacuo (559 mg, 83% yield). ^1H NMR (C_6D_6): $\delta = 1.32$ (d, $J = 6.8$ Hz, 6H; CHMe_2), 1.74 (s, 45H; Cp*), 1.98 (s, 3H; C_6H_4Me), 2.86 (sept, $J = 6.8$ Hz, 1H; CHMe$_2$), 4.43, 4.72 ppm (d, $J = 5.6$ Hz, 2H each; C_6H_4). C,H analysis (%) calcd for $C_{40}H_{59}Ir_3RuS_4$: C 35.70, H 4.42; found: C 35.53, H 4.39. Single crystals for X-ray crystallography were obtained by recrystallization from THF/MeCN.

3: $[Cp_2Fe]PF_6$ (271 mg, 0.819 mmol) was added to a solution of **2** (550 mg, 0.409 mmol) in THF (40 mL) at −70 °C, and the mixture was thoroughly degassed. Then, the mixture was gradually warmed to room temperature and stirred continuously for 21 h under N_2. Dark green microcrystals of **3**·1.5 THF precipitated, which were filtered off, washed with THF, and dried in vacuo (661 mg, 93% yield). ^1H NMR (CD_2Cl_2): $\delta = 1.43$ (br d, 6H, CHMe_2), 1.82 (br s, 45H, Cp*), 2.40 (br s, 3H, C_6H_4Me), 2.89 (br sept, 1H, CHMe$_2$), 5.34–6.07 ppm (br m, 4H, C_6H_4). C,H analysis (%) calcd for $C_{46}H_{71}F_{12}Ir_3O_{1.5}P_2RuS_4$: C 31.68, H 4.10.; found: C 31.95, H 4.07. Single crystals for X-ray crystallography were obtained from CH_2Cl_2/hexane as CH_2Cl_2 monosolvate.

4: A solution of **3** (131 mg, 0.0750 mmol) and tmeda (12 μL, 0.080 mmol) in MeCN (10 mL) was stirred at 50 °C for 6 h. The resultant dark green solution was filtered and the filtrate was concentrated in vacuo. Addition of diethyl ether afforded **4** as dark green crystals (97 mg, 78% yield). IR (KBr disk): $\tilde{\nu} = 2307$ cm^{-1} (C≡N). ^1H NMR (CD_3CN): $\delta = 1.65$ (s, 30H; Cp*), 1.78 (s, 15H; Cp*), 1.96 (s, 3H; MeCN), 3.03–3.10, 3.18–3.24 (m, 2H each; CH_2CH_2), 3.06, 3.33 ppm (s, 6H each; NMe_2). C,H,N analysis (%) calcd for $C_{38}H_{64}F_{12}Ir_3N_3P_2RuS_4$: C 27.51, H 3.89, N 2.53; found: C 27.36, H 3.84, N 2.59.

5: A mixture containing **4** (81 mg, 0.049 mmol), $[Cp_2Co]$ (14 mg, 0.074 mmol), MeCN (3 mL), and THF (7 mL) was stirred at room temperature for 21 h. The solvents of the resultant dark green solution were removed in vacuo, and the residue extracted with THF (10 mL). $[Cp^*_2Co]$ (31 mg, 0.094 mmol) was added to the extract, and the mixture was stirred at room temperature for 16 h. A dark orange solution was obtained, the solvents of which were removed in vacuo, and the residue was extracted with hexane. Slow concentration of the extract deposited **5**·0.5 C_6H_{14} as a mixture of dark orange crystals and orange oily solid (56 mg, 82% yield). IR (KBr disk): $\tilde{\nu} = 2019$ cm^{-1} (N≡N). ^1H NMR (C_6D_6 solution): 1.76 (s, 30H; Cp*), 1.91 (s, 15H; Cp*), 2.35, 2.39 ppm (s, 6H each; NMe_2). C,H,N analysis (%) calcd for $C_{39}H_{68}Ir_3N_4RuS_4$: C 33.48, H 4.90, N 4.00; found: C 33.27, H 5.18, N 3.74.

Single crystals of **2** and **3**·CH_2Cl_2, sealed in glass capillaries under argon, and single crystals of **4** and **5**·0.5 C_6H_{14}, coated with grease and stuck to a glass fiber, were mounted on a Rigaku Mercury-CCD diffractometer equipped with a source of graphite-monochromatized $Mo_{K\alpha}$ radiation. Diffraction studies were done at 20 °C for **2** and **3**·CH_2Cl_2 and at −140 °C for **4** and **5**·0.5 C_6H_{14}. Structure solution and refinement were carried out by using the CrystalStructure program package.[24] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[25] and subsequent Fourier synthesis (DIRDIF99),[26] and were refined with anisotropic thermal parameters by full-matrix least-squares techniques. Hydrogen atoms were placed at calculated positions and included at the final stages of the refinements with fixed parameters.

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[10] X-ray data for **2**: $M_r = 1345.88$, $0.25 \times 0.20 \times 0.12\ \text{mm}^3$, triclinic, space group $P\bar{1}$, $a = 11.458(2)$, $b = 20.407(3)$, $c = 20.800(3)$ Å, $\alpha = 114.068(2)$, $\beta = 97.869(1)$, $\gamma = 94.524(1)°$, $V = 4350(1)\ \text{Å}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.055\ \text{g cm}^{-3}$, $R1 = 0.0404$ (12935 data with $I > 2\sigma(I)$) and $wR2 = 0.130$ (all 19101 unique data) for 933 variables, GOF = 1.035. **3**·CH_2Cl_2: $M_r = 1720.74$, $0.27 \times 0.11 \times 0.11\ \text{mm}^3$, monoclinic, space group $P2_1/c$, $a = 12.912(2)$, $b = 24.451(3)$, $c = 16.925(2)$ Å, $\beta = 91.3270(8)°$, $V = 5342(1)\ \text{Å}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.140\ \text{g cm}^{-3}$, $R1 = 0.0380$ (7235 data with $I > 2\sigma(I)$) and $wR2 = 0.124$ (all 121851 unique data) for 712 variables, GOF = 1.021. **4**: $M_r = 1658.84$, $0.30 \times 0.15 \times 0.05\ \text{mm}^3$, monoclinic, space group $P2/c$, $a = 20.636(3)$, $b = 11.389(2)$, $c = 21.060(3)$ Å, $\beta = 94.6928(7)$, $\gamma = 94.524(1)°$, $V = 4933(1)\ \text{Å}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.233\ \text{g cm}^{-3}$, $R1 = 0.0396$ (8115 data with $I > 2\sigma(I)$) and $wR2 = 0.122$ (all 11278 unique data) for 670 variables, GOF = 1.026. **5**·$0.5\,C_6H_{14}$: $M_r = 1398.96$, $0.14 \times 0.08 \times 0.06\ \text{mm}^3$, monoclinic, space group $C2/c$, $a = 42.677(7)$, $b = 10.806(2)$, $c = 22.326(4)$ Å, $\beta = 117.2910(5)°$, $V = 9143(3)\ \text{Å}^3$, $Z = 8$, $\rho_{\text{calcd}} = 2.031\ \text{g cm}^{-3}$, $R1 = 0.0443$ (6974 data with $I > 2\sigma(I)$) and $wR2 = 0.127$ (all 10462 unique data) for 505 variables, GOF = 1.033. CCDC-633248, -633249, -639460, and -633251 (**2**, **3**, **4**, and **5**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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