Synthesis of Bimetallic Cubane-Type $Mo_2M_2S_4$ Clusters ($M = Ir, Rh, Ru$) and Reductive Cleavage of the N−N Bond of 1,1-Methylphenylhydrazine Affording *N*-Methylaniline Using $Mo_2Ir_2S_4$ and $Mo_2Rh_2S_4$ Clusters as Catalyst Precursors

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Reactions of $[\{Mo({=}O)(DMF)_3\}_2(\mu_2\text{-}S)_2]I_2$ (**1**) with an equimolar amount of $[(Cp^*MCl)_2(\mu_2\text{-}SH)_2]$ ($M = Ir, Rh$; $Cp^* = \eta^5\text{-}C_5Me_5$) and excess $[Me_4N]Cl$ in DMF at room temperature afforded cubane-type clusters with a terminal oxo ligand, $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*M)_2(\mu_3\text{-}S)_4]$ ($M = Ir$ (**5**), Rh (**6**)), while treatment of **1** with $[(Cp'RuCl)_2(\mu_2\text{-}SH)_2]$ ($Cp' = Cp^*, Cp°$; $Cp° = \eta^5\text{-}C_5EtMe_4$) under analogous conditions gave cubane-type clusters without oxo ligands, $[\{MoCl_2(DMF)\}_2(Cp'Ru)_2(\mu_3\text{-}S)_4]$ ($Cp' = Cp^*$, $Cp°$ (**7′**)). Cluster **5** reacted with $MePhNNH_2$ in DMF at room temperature, yielding the methylphenylhydrazido(2−) cluster $[\{Mo(NNMePh)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**9**), which upon treatment with lutidinium chloride (Lut·HCl) as the source of protons and cobaltocene as the source of electrons produced PhNHMe in considerable yield. Catalytic conversion of $MePhNNH_2$ into PhNHMe through the reductive cleavage of the N−N bond by a Lut·HCl/cobaltocene mixture was attained by the use of the cubane-type clusters as catalyst precursors, which include **5**, **6**, and their mixed-chalcogenido analogues $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*M)_2(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$ ($M = Ir, Rh$). X-ray analyses have been undertaken for **5**, **7′**, and **9** to determine their detailed structures.

Introduction

Our recent studies have focused on exploration of the potential synthetic pathways to prepare cuboidal metal−sulfido cores with desired metal/sulfur compositions in high yields.[1] In previous papers we have reported that dinuclear complexes containing both bridging and terminal sulfido ligands, $[\{M({=}S)(S_2CNEt_2)\}_2(\mu_2\text{-}S)_2]$ ($M = Mo, W$), are promising precursors to heterobimetallic clusters with $M_2M'(\mu_3\text{-}S)(\mu_2\text{-}S)_3$ and $M_2M'_2(\mu_3\text{-}S)_4$ cores ($M' = Pd$, Pt,[2] Rh, Ir,[3] Ru[4]). The hydrosulfido-bridged dinuclear complexes $[(Cp^*MCl)_2(\mu_2\text{-}SH)_2]$ ($M = Rh, Ir, Ru$; $Cp^* = \eta^5\text{-}C_5Me_5$) and $[\{(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)RuCl\}_2(\mu_2\text{-}SH)_2]$ have also been shown to serve as excellent starting compounds for the synthesis of the cubane-type $M_4(\mu_3\text{-}S)_4$ ($M = Ir, Rh, Ru$) clusters by in situ generation of the coordinatively unsaturated sulfido-bridged dinuclear species $\{M_2(\mu_2\text{-}S)_2\}$ through the loss of HCl, followed by dimerization.[5−7] It is noteworthy that this method can be extended, for example, to the condensation of the heterobimetallic hydrosulfido-bridged complex $[Cp_2Ti(\mu\text{-}SH)_2RuCp^*Cl]$, forming $[(CpTi)_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ with concomitant loss of HCl and CpH,[8] and crossed condensation between this dinuclear Ti−Ru complex and $[(Cp^*RuCl)_2(\mu_2\text{-}SH)_2]$ to give $[(CpTi)(Cp^*Ru)_3(\mu_3\text{-}S)_4]$.[9]

Stimulated by the presence of the Mo−Fe−S aggregate at the active site of nitrogenase, whose detailed structure containing the $MoFe_7S_9$ core has recently been demonstrated crystallographically,[10] efforts have been made to prepare the Mo−Fe mixed-metal sulfido clusters, and now a significant number of cuboidal Mo−Fe clusters relevant to the active site of this enzyme are known.[11] However, clusters containing nitrogenous ligands relating to nitrogen fixation are still rare, except for $MoFe_3S_4$ clusters with coordinating hydra-

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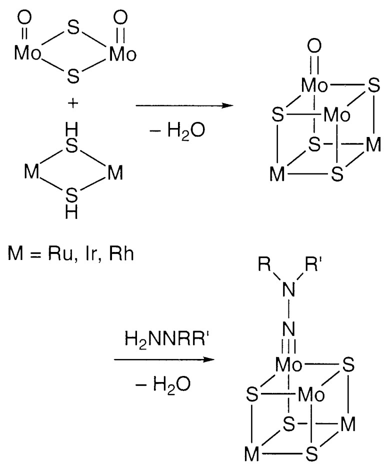
Scheme 1



zines such as $[\{MoFe_3S_4Cl_2(L)\}_2(\mu_2\text{-}S)(\mu_2\text{-}N_2H_4)]^{4-}$,[12] $[\{MoFe_3S_4Cl_3(L)\}_2(\mu_2\text{-}N_2H_4)]^{4-}$,[13] and $[MoFe_3S_4(SC_6H_4Cl)_3(L)(PhNHNH_2)]^{2-}$.[14]

Previously, it has been shown that the hydrazido(2−) species ($MNNH_2$) represent one of the most important intermediate stages for the reduction of the ligating N_2 in complexes of the type $[M(N_2)_2(\mathbf{P})_4]$ (M = Mo, W; **P** = tertiary phosphine) into NH_3 and/or N_2H_4.[15] Hence, synthesis of the cubane-type mixed-metal sulfido clusters with a hydrazido(2−) ligand and clarification of their reactivity are of particular interest.

In this context, we have attempted to prepare cubane-type sulfido clusters having a terminal oxo ligand, which might be convertible to the hydrazido(2−) ligand through condensation with hydrazines (Scheme 1), since the formation of hydrazido(2−) ligands by treating the terminal oxo moiety in certain polyoxomolybdates with organohydrazines has already been substantiated.[16] It should be noted that the reactions of trinuclear gold clusters containing a μ_3-O ligand with hydrazines H_2NNR_2 (R = Me, Ph) and N_2H_4 have been reported to yield the organohydrazido(2−) ($Au_3N{-}NHR$) and hydrazido(4−) ($Au_3N{-}NAu_3$) clusters, respectively.[17]

Our strategy to obtain cubane-type clusters with terminal oxo ligands was to employ condensation reactions between an oxo−sulfido dimolybdenum complex containing the $Mo({=}O)(\mu_2\text{-}S)_2Mo({=}O)$ core and the hydrosulfido-bridged Ir_2, Rh_2, and Ru_2 complexes shown above (Scheme 1). The complex comprising Ru in the Fe triad was the first choice among the latter, owing to its closer relevance to the nitrogenase active site. However, although the reaction of the dimolybdenum complex $[\{Mo({=}O)(DMF)_3\}_2(\mu_2\text{-}S)_2]I_2$ (**1**) with $[(Cp^*RuCl)_2(\mu_2\text{-}SH)_2]$ (**2**) was found to yield a $Mo_2Ru_2(\mu_3\text{-}S)_4$ cluster, this product did not contain the desired oxo ligand. Instead, extension of this reaction to that with the Ir and Rh complexes $[(Cp^*MCl)_2(\mu_2\text{-}SH)_2]$ (**3**, M = Ir; **4**, M = Rh) has resulted in the isolation of the expected $Mo_2M_2S_4$ clusters with the terminal oxo ligand on a Mo center. Furthermore, it has been found that the cluster with M = Ir was treated with $MePhNNH_2$ to afford a hydrazido(2−) cluster through dehydration and, interestingly, this cluster can be treated with a mixture of a proton source and a reducing agent under ambient conditions to yield *N*-methylaniline, resulting from the reductive N−N bond cleavage. In this paper, these findings as well as the catalytic N−N bond scission of the organohydrazine $MePhNNH_2$ by using these new cubane-type clusters as catalyst precursors are summarized. Part of this work has been reported as a communication.[18]

Results and Discussion

Reactions of 1 with Hydrosulfido-Bridged Dinuclear Complexes of Ir, Rh, and Ru. Black crystals were obtained by treatment of the oxo−μ-sulfido dimolybdenum complex **1** with an equimolar amount of the hydrosulfido-bridged diiridium complex **3** in CH_2Cl_2 at room temperature and the subsequent workup of the reaction mixture. Although the yield was quite low, single-crystal X-ray analysis has shown that this crystalline product is the desired $Mo_2Ir_2(\mu_3\text{-}S)_4$ cluster, formulated as $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**5**). Despite the presence of both the Cl and I anions in a 1:1 ratio in the reaction mixture, **5** contains only the Cl anion. Since this might explain, at least in part, the poor yield of crystalline product **5**, the reaction of **1** with an equimolar amount of **3** was attempted in the presence of 3−5 equiv of $[Me_4N]Cl$. As expected, it has turned out that when the reaction is carried out under these conditions by using DMF as a solvent, **5** forms almost quantitatively, as elucidated by the ^1H NMR spectrum of the evaporated reaction mixture residue. Crystallization from CH_2Cl_2−hexane of this residue gave $\mathbf{5}\cdot CH_2Cl_2$ as black crystals in 79% yield. The stoichiometry of this reaction forming **5** may be described as eq 1, although the amount of the generated H_2O was not determined.

The reaction of **1** with the Rh hydrosulfido complex **4** proceeded similarly under analogous conditions (eq 1), and the dark brown product $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Rh)_2(\mu_3\text{-}S)_4]$ (**6**) was isolated as a mono-DMF solvate in 84% yield by crystallizing the reaction mixture from DMF−ether. Detailed structures for **5** and **6** have been determined by single-crystal X-ray diffraction studies (vide infra).

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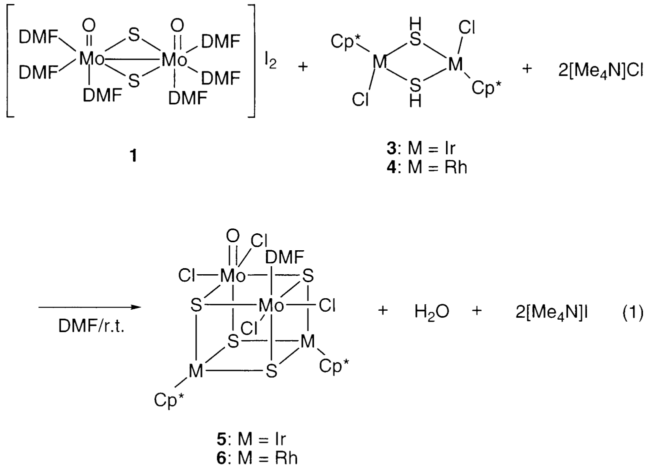
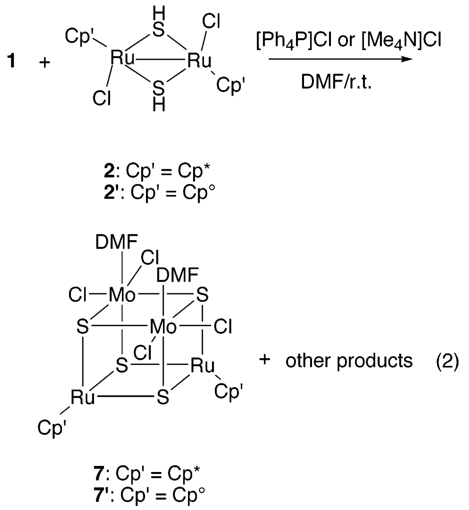
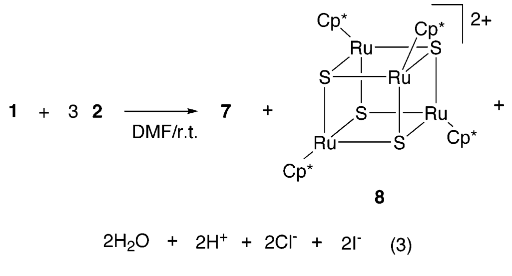


In contrast, treatment of **1** with the Ru complex **2** in the presence of excess $[Me_4N]Cl$ or $[Ph_4P]Cl$ resulted in the formation of a dark red $Mo_2Ru_2S_4$ cubane cluster without oxo ligands, $[\{MoCl_2(DMF)\}_2(Cp^*Ru)_2(\mu_3\text{-}S)_4]$ (**7**), which was isolated in ca. 40% yield (eq 2). Since the Mo_2Ru_2 core in **7** has a total oxidation state of +14 despite the use of the $\{Mo^V\}_2$ and $\{Ru^{III}\}_2$ complexes as reactants, two-electron reduction per Mo_2Ru_2 unit must take place during this reaction. Though the yield was low, we could isolate the cationic Ru_4S_4 cubane cluster $[(Cp^*Ru)_4(\mu_3\text{-}S)_4]^{2+}$ (**8**), having a formal $Ru^{III}{}_2Ru^{IV}{}_2$ core,[19] which might correspond, at least in part, to the oxidation product coupled to the reduction product **7**. The stoichiometry affording **7** can be described as eq 3.





As expected, by reacting **1** with 3 equiv of **2**, we could obtain a mixture containing only **7** and **8** as the products detectable by ^1H NMR spectroscopy, whose ratio was ca. 1:1. As for the X-ray analysis of **7**, the molecular structure could be refined to a satisfactory level but somehow even the non-H atoms for the solvating DMF could not be located. Meanwhile, it has been found that the Cp° analogue $[\{MoCl_2(DMF)\}_2(Cp°Ru)_2(\mu_3\text{-}S)_4]$ (**7′**; Cp° = C_5EtMe_4), prepared in essentially the same manner as **7** (eq 2), also gives single crystals, and the X-ray diffraction study of **7′** could be completed; details of the structure of the $Mo_2Ru_2S_4$ cluster will be described below for **7′**.

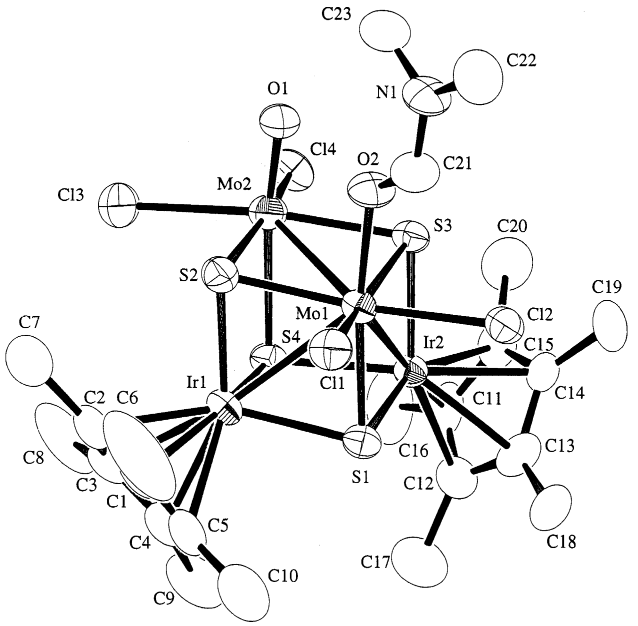


Figure 1. ORTEP drawing of $[\{Mo(=O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**5**). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles in 5

(a) Bond Distances (Å)			
Ir(1)···Ir(2)	3.5521(8)	Ir(1)−Mo(1)	2.894(1)
Ir(1)···Mo(2)	3.496(2)	Ir(2)−Mo(1)	2.893(1)
Ir(2)···Mo(2)	3.542(1)	Mo(1)−Mo(2)	2.960(2)
Ir(1)−S(1)	2.318(3)	Ir(1)−S(2)	2.329(3)
Ir(1)−S(4)	2.381(4)	Ir(2)−S(1)	2.332(4)
Ir(2)−S(3)	2.318(3)	Ir(2)−S(4)	2.382(3)
Mo(1)−S(1)	2.304(3)	Mo(1)−S(2)	2.335(3)
Mo(1)−S(3)	2.348(4)	Mo(2)−S(2)	2.380(4)
Mo(2)−S(3)	2.391(3)	Mo(2)−S(4)	2.611(3)
Mo(1)−O(2)	2.168(8)	Mo(2)−O(1)	1.679(8)
(b) Bond Angles (deg)			
S(1)−Ir(1)−S(2)	102.7(1)	S(1)−Ir(1)−S(4)	81.1(1)
S(2)−Ir(1)−S(4)	90.9(1)	S(1)−Ir(2)−S(3)	103.1(1)
S(1)−Ir(2)−S(4)	80.8(1)	S(3)−Ir(2)−S(4)	89.33(10)
S(1)−Mo(1)−S(2)	102.9(1)	S(1)−Mo(1)−S(3)	103.0(1)
S(1)−Mo(1)−O(2)	169.3(3)	S(2)−Mo(1)−S(3)	103.6(1)
S(2)−Mo(1)−O(2)	84.4(2)	S(3)−Mo(1)−O(2)	82.5(3)
S(2)−Mo(2)−S(3)	101.0(1)	S(2)−Mo(2)−S(4)	84.4(1)
S(2)−Mo(2)−O(1)	94.7(4)	S(3)−Mo(2)−S(4)	82.59(10)
S(3)−Mo(2)−O(1)	90.2(3)	S(4)−Mo(2)−O(1)	172.4(3)

Description of the Structures for 5, 6, and 7′. For **5**, an ORTEP drawing is shown in Figure 1, while important bond distances and angles are listed in Table 1. Metric parameters observed for **6** are quite analogous to those for **5**, which are submitted as Supporting Information.

Cluster **5** has a cubane-type $Mo_2Ir_2S_4$ core consisting of a distorted Ir_2Mo_2 tetrahedron with metal−metal

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[19] (a) Hashizume, K.; Mizobe, Y.; Hidai, M. *Organometallics* **1996**, *15*, 3303. (b) See also: Feng, Q.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 4702.

bonding interactions only for the Ir(1)−Mo(1), Ir(2)−Mo(1), and Mo(1)−Mo(2) edges, all involving Mo(1). Distances of these three bonds at 2.894(1), 2.893(1), and 2.960(2) Å, respectively, are consistent with the presence of a metal−metal single bond. The remaining three metal−metal separations are 3.5521(8) Å from Ir(1) to Ir(2), 3.496(2) Å from Ir(1) to Mo(2), and 3.542(1) Å from Ir(2) to Mo(2), which are all apparently nonbonding distances. Four sulfido ligands cap the four faces of this M_4 core as a μ_3 ligand. Two Ir centers have a three-legged piano-stool structure with one η^5-Cp* and three μ_3-sulfido ligands, while the geometry around the two Mo centers is octahedral with two Cl ligands and one DMF ligand for Mo(1) or two Cl ligands and one terminal oxo ligand for Mo(2) together with three μ_3-sulfido ligands.

Among the M−S bonds, the Mo(2)−S(4) bond is unusually long at 2.611(3) Å. For the remaining five Mo−S bonds, the distances around Mo(2) (2.380(4) and 2.391(3) Å) are longer than those around Mo(1) (2.304(3)−2.348(4) Å). Among the Ir−S bonds, those related to S(4), which caps the Mo(2)−Ir(1)−Ir(2) triangle without any metal−metal bonds, are relatively long at 2.381(4) and 2.382(3) Å. This distortion of the cubane-type core, viz. long Mo(2)−S(4) and short Mo(1)−S(1) bonds, arises from the difference in trans influence between the oxo ligand and the DMF ligand, that for the former being much stronger than for the latter. The Mo(2)−O(1) bond length at 1.679(8) Å is comparable to those of the terminal oxo groups in a series of dimolybdenum complexes related to **1** with a $[Mo_2O_2(\mu\text{-}S)_2]^{2+}$ core (ca. 1.64−1.69 Å)[20] along with the Mo(V) complexes $[\{Cp^*Mo(O)Cl\}_2(\mu\text{-}O)]$ (1.676(5) Å)[21] and $[Cp^*Mo(O)Cl_2]$ (1.683(2) Å)[22] and the Mo(IV) complex $[Mo(O)(H_2O)(CN)_4]^{2-}$ (1.668(5) Å).[23] For all of these Mo−O bonds, a significant triple-bond contribution (M≡O) is assumed, since these Mo−O bond lengths are much shorter than the sum of the covalent radii (1.84 Å)[24] and the typical Mo=O double-bond distance as in, for example, *trans*-$[Mo(O)_2(Ph_2PCH{=}CHPPh_2)_2]$ (1.804(2) Å) with 18-electron Mo center by assuming 4-electron-donating O^{2-} ligands.[25] Indeed, when the O^{2-} ligand is considered as a 6-electron donor, the electron count of the Mo_2Ir_2 core in **5** becomes the ideal value of 72 by taking the three metal−metal bonds into account.

The DMF ligand, in which five non-hydrogen atoms are almost coplanar, is coordinated to Mo(1) by the use of one lone electron pair on the sp^2-hybridized O atom with the Mo−O distance and the Mo−O−C angle at 2.168(8) Å and 127.7(9)°, respectively, where the direction of the DMF plane essentially coincides with that of the Mo−Mo vector. Hence, the total structure of **5** has a pseudo mirror plane defined by Mo(1), Mo(2), S(1), and S(4) atoms.

As described already, the structure of the Mo_2Rh_2 cluster **6** is in good agreement with that of the Mo_2Ir_2 cluster **5**; e.g., the metal−metal distances are 3.5332(9) Å for Rh(1)−Rh(2), 3.467(1) Å for Rh(1)−Mo(2), 3.514(1) Å for Rh(2)−Mo(2), 2.903(1) Å for Rh(1)−Mo(1), 2.9007(9) Å for Rh(2)−Mo(1), and 2.949(1) Å for Mo(1)−Mo(2), while the M−S bond lengths show features analogous to those in **5** (e.g. Mo(2)−S(4) = 2.616(2) Å) with the Mo(2)−O(1) bond length at 1.686(5) Å.

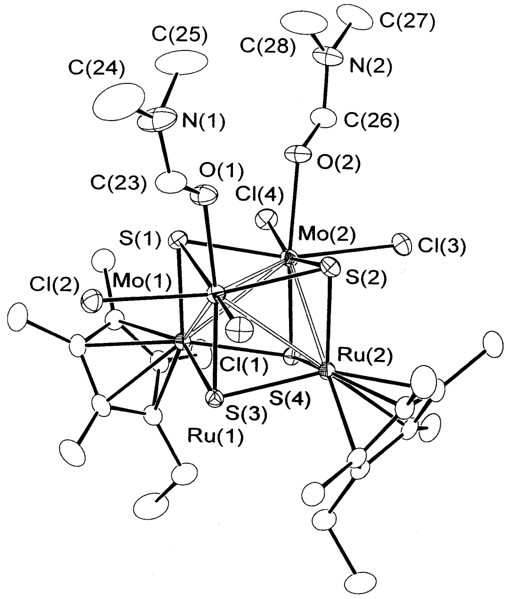

Figure 2. ORTEP drawing of $[\{MoCl_2(DMF)\}_2(Cp^{\circ}Ru)_2(\mu_3\text{-}S)_4]$ (**7′**). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles in 7′

(a) Bond Distances (Å)			
Ru(1)···Ru(2)	3.480(1)	Ru(1)−Mo(1)	2.880(1)
Ru(1)−Mo(2)	2.873(1)	Ru(2)−Mo(1)	2.861(1)
Ru(2)−Mo(2)	2.871(1)	Mo(1)−Mo(2)	2.817(1)
Ru(1)−S(1)	2.293(2)	Ru(1)−S(3)	2.349(1)
Ru(1)−S(4)	2.338(1)	Ru(2)−S(2)	2.290(2)
Ru(2)−S(3)	2.344(1)	Ru(2)−S(4)	2.344(1)
Mo(1)−S(1)	2.330(1)	Mo(1)−S(2)	2.340(1)
Mo(1)−S(3)	2.276(2)	Mo(2)−S(1)	2.340(1)
Mo(2)−S(2)	2.332(1)	Mo(2)−S(4)	2.277(2)
Mo(1)−O(1)	2.212(3)	Mo(2)−O(2)	2.230(3)
(b) Bond Angles (deg)			
S(1)−Ru(1)−S(3)	102.32(5)	S(1)−Ru(1)−S(4)	102.94(4)
S(3)−Ru(1)−S(4)	79.37(4)	S(2)−Ru(2)−S(3)	103.26(4)
S(2)−Ru(2)−S(4)	102.74(4)	S(3)−Ru(2)−S(4)	79.35(4)
S(1)−Mo(1)−S(2)	100.63(4)	S(1)−Mo(1)−S(3)	103.44(5)
S(1)−Mo(1)−O(1)	83.1(1)	S(2)−Mo(1)−S(3)	103.83(5)
S(2)−Mo(1)−O(1)	83.8(1)	S(3)−Mo(1)−O(1)	168.58(9)
S(1)−Mo(2)−S(2)	100.55(4)	S(1)−Mo(2)−S(4)	103.36(5)
S(1)−Mo(2)−O(2)	84.1(1)	S(2)−Mo(2)−S(4)	103.54(5)
S(2)−Mo(2)−O(2)	83.3(1)	S(4)−Mo(2)−O(2)	168.61(9)

The results of the X-ray analysis for the Mo_2Ru_2 cluster **7′** are shown in Figure 2 and Table 2. In **7′**, the tetrametallic core has five metal−metal bonds, whose distances are in the range 2.817(1)−2.880(1) Å. For the remaining Ru(1)−Ru(2) edge, its distance at 3.480(1) Å is indicative of the absence of any bonding interactions between these two metal centers. By the presence of five metal−metal single bonds, the 72-electron count expected for the $Mo^{V}{}_2Ru^{II}{}_2$ core is satisfied. The M−S bonds in **7′** varying from 2.276(2) to 2.349(1) Å are all unexceptional. The two Mo atoms each have a DMF ligand with an Mo−O distance at 2.212(3) Å for Mo(1) or 2.230(3) Å for Mo(2), which are comparable to those of the DMF ligand in **5** and **6**. In **7′**, there exist two pseudo mirror planes; one is defined by Mo(1), Mo(2),

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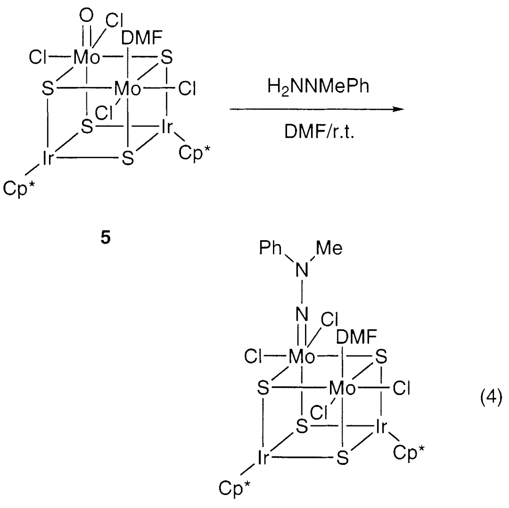
S(3), and S(4) atoms as in **5** and the other includes Ru(1), Ru(2), S(1), and S(2) atoms.

Formation of the Mo_2Ir_2 Cluster with a Hydrazido(2−) Ligand. When **5** was treated with an equimolar amount of $MePhNNH_2$ in DMF at room temperature, condensation between the oxo ligand in **5** and the hydrazine took place to afford the dehydration product $[\{Mo(NNMePh)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**9**) as black crystals in 69% yield (eq 4). Appearance of new signals due to the Me and Ph protons in the ^1H NMR spectrum along with the lack of a ν(Mo═O) band in the IR spectrum for **9** suggest the formation of the methylphenylhydrazido(2−) ligand in an expected manner, which has been confirmed by the X-ray analysis.



5

9

(4)

A number of mononuclear and dinuclear hydrazido(2−) and organohydrazido(2−) complexes have been synthesized[26] and crystallographically characterized[27] as potential models of the intermediates for the transformations of dinitrogen into ammonia or other nitrogenous compounds, which include a series of Mo organohydrazido(2−) complexes obtained from condensation of the oxo complexes with organohydrazines: e.g., $[Mo({=}O)(NNPhR)Br_2(o\text{-phen})]$ (*o*-phen = 1,10-phenanthroline, R = Me, Ph) from $[Mo({=}O)_2Br_2(o\text{-phen})]$ and $PhRNNH_2$.[28] However, previous examples of condensation reactions of chalcogenido clusters containing a terminal oxo ligand with hydrazines are, to the best of our knowledge, quite rare except for the formation of, e.g., $[Mo_4O_{10}(OMe)_2(NNPhR)]^{2-}$ (R = Ph, Me) from the polyoxomolybdate anion $[Mo_8O_{26}]^{4-}$ with $PhRNNH_2$ in $MeOH{-}CH_2Cl_2$.[16]

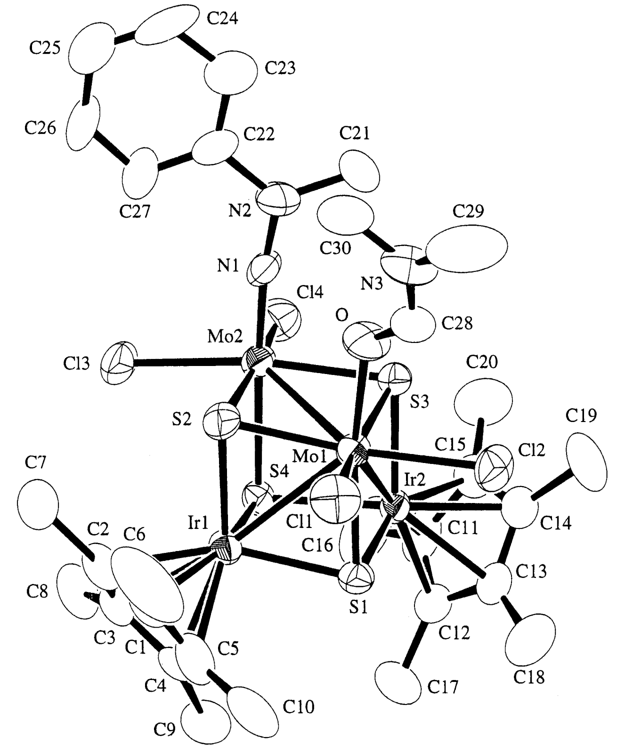


Figure 3. ORTEP drawing of $[\{Mo(NNMePh)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_4]$ (**9**). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances and Angles in 9

(a) Bond Distances (Å)			
Ir(1)···Ir(2)	3.563(1)	Ir(1)−Mo(1)	2.884(2)
Ir(1)···Mo(2)	3.474(2)	Ir(2)−Mo(1)	2.896(2)
Ir(2)···Mo(2)	3.496(2)	Mo(1)−Mo(2)	2.974(2)
Ir(1)−S(1)	2.320(4)	Ir(1)−S(2)	2.334(4)
Ir(1)−S(4)	2.385(4)	Ir(2)−S(1)	2.328(4)
Ir(2)−S(3)	2.329(4)	Ir(2)−S(4)	2.382(4)
Mo(1)−S(1)	2.308(4)	Mo(1)−S(2)	2.339(4)
Mo(1)−S(3)	2.345(5)	Mo(2)−S(2)	2.380(5)
Mo(2)−S(3)	2.379(4)	Mo(2)−S(4)	2.541(4)
Mo(1)−O	2.18(1)	Mo(2)−N(1)	1.74(1)
N(1)−N(2)	1.32(2)		
(b) Bond Angles (deg)			
S(1)−Ir(1)−S(2)	103.2(1)	S(1)−Ir(1)−S(4)	80.5(1)
S(2)−Ir(1)−S(4)	90.0(1)	S(1)−Ir(2)−S(3)	103.0(1)
S(1)−Ir(2)−S(4)	80.4(1)	S(3)−Ir(2)−S(4)	89.2(1)
S(1)−Mo(1)−S(2)	103.4(1)	S(1)−Mo(1)−S(3)	103.1(1)
S(1)−Mo(1)−O	167.2(3)	S(2)−Mo(1)−S(3)	102.6(2)
S(2)−Mo(1)−O	84.3(3)	S(3)−Mo(1)−O	84.9(4)
S(2)−Mo(2)−S(3)	100.4(2)	S(2)−Mo(2)−S(4)	85.3(1)
S(2)−Mo(2)−N(1)	96.0(5)	S(3)−Mo(2)−S(4)	84.4(1)
S(3)−Mo(2)−N(1)	92.4(4)	S(4)−Mo(2)−N(1)	176.7(4)
Mo(2)−N(1)−N(2)	172(1)	N(1)−N(2)−C(21)	117(1)
N(1)−N(2)−C(22)	120(1)	C(21)−N(2)−C(22)	121(1)

For **9**, the molecular structure determined by X-ray analysis is depicted in Figure 3, while important bond distances and angles are listed in Table 3. These results clearly show that the replacement of the terminal oxo ligand in **5** by the methylphenylhydrazido(2−) ligand has proceeded in an expected manner. With respect to the $Mo_2Ir_2S_4$ core, the bonding parameters in **9** are quite analogous to those in **5**, except that the elongation of the Mo(2)−S(4) bond from the standard Mo−S single bond is smaller in the former than in the latter (Mo(2)−S(4) bond length: **9**, 2.541(4) Å; **5**, 2.611(3) Å). This indicates unambiguously that the trans influence of the methylphenylhydrazido(2−) ligand is weaker than that of the oxo ligand.

The methylphenylhydrazido(2−) ligand bound to Mo(2) has an essentially linear Mo−N−N linkage (172(1)°) with quite a short Mo−N bond length at 1.74(1) Å, which indicates the sp character of the inner N atom. Hence, this organohydrazido(2−) ligand can be assigned as a six-electron donor (Mo≡NNMePh), and this is

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diagnostic of the finding that the core structure of **9** is quite comparable to that of **5**, containing a six-electron-donating oxo ligand. The N−N bond length at 1.32(2) Å falls in the range between typical single and double bonds (1.47 and 1.25 Å), while the sum of the two N−N−C angles and one C−N−C angle of 358° around the outer N atom N(2) is close to 360°, suggesting some sp^2 nature of this N atom. These structural features are common for many hydrazido(2−) and organohydrazido(2−) ligands assumed to be a six-electron donor,[27] which include those in the Mo(IV) complex $[MoF(NNH_2)(dppe)_2][BF_4]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with Mo−N and N−N bond lengths at 1.76(1) and 1.33(2) Å and an Mo−N−N angle of 176(1)°,[29] the Mo(V) complex $[MoBr_3(NNH_2)(dppe)]$ (Mo−N, 1.79(2) Å; N−N, 1.28(3) Å; Mo−N−N, 173(2)°),[30] the Mo(VI) complexes $[Mo({=}O)(NNMe_2)(S_2CNMe_2)_2]$ (Mo−N, 1.708(6) Å; N−N, 1.288(10) Å, Mo−N−N, 168.0(7)°)[31] and $[MoBr_2({=}O)(NNPh_2)(o\text{-phen})]$ (Mo−N, 1.770(3) Å; N−N, 1.330(4) Å; Mo−N−N, 171.7(2)°),[28] along with the oxomolybdate(VI) clusters $[Mo_4O_{10}(OMe)_2(NNPh_2)_2]^{2-}$ (Mo−N, 1.780(7) Å; N−N, 1.32(1) Å; Mo−N−N, 173.7(6)°)[16] and $[Mo_6O_{18}(NNMePh)]^{2-}$ (Mo−N, 1.769(6) Å; N−N, 1.318(10) Å; Mo−N−N, 173.9(6)°).[32]

Cleavage of the N−N Bond of the Hydrazido(2−) Ligand in 9. Reductive cleavage of the N−N bond in the hydrazido(2−) as well as organohydrazido(2−) ligands has already been studied extensively for certain Mo complexes and their W analogues to get an insight into the mechanism of biological nitrogen fixation.

Thus, the hydrazido(2−) complexes *cis*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo, W; X = Cl, Br, I), derived from protonation of the N_2 complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ with aqueous HX, react further with a series of protic acids to afford ammonia and, less commonly, hydrazine in high yields.[15,33] In these reactions, Mo and W atoms serve as the source of electrons. With respect to the organohydrazido(2−) congener, the W complex $[WCl_2(NNPh_2)(PMe_2Ph)_3]$ is known to react with excess HCl or H_2O to give Ph_2NH.[34] The higher-valent Mo and W hydrazido(2−) complexes $[Cp^*MMe_3(NNR_2)]$ (M = Mo, R = Me; M = W, R = H, Me) are also known to undergo an analogous N−N bond cleavage reaction by treatment with 2,6-lutidinium chloride (Lut·HCl) as a proton source, when zinc amalgam or cobaltocene is added as an external electron source.[35]

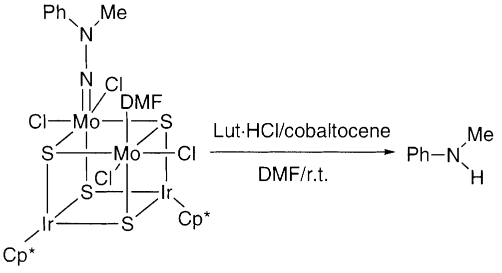
Interestingly, these results have led to the finding that the $[Cp^*MMe_3]^+$ fragment, which binds hydrazine in an η^2 manner, can serve as a site for the catalytic conversion of hydrazine into ammonia in the presence of excess amounts of both Lut·HCl and cobaltocene: e.g., reactions of 6 equiv of hydrazine using $[Cp^*MMe_3(\eta^2\text{-}NH_2NH_2)][OSO_2CF_3]$ afford 11.62 and 11.32 mol of NH_3 per Mo and W atom, respectively.[35] It should be noted that quite efficient reduction of hydrazine into ammonia by Lut·HCl/cobaltocene using cubane-type clusters as catalyst has been elucidated for $[NEt_4]_2[MoFe_3(\mu_3\text{-}S)_4Cl_3(Cl_4\text{-cat})(MeCN)]$ (Cl_4-cat = tetrachlorocatecholate) and related clusters.[36]

Table 4. Catalytic Conversion of $MePhNNH_2$ into PhNHMe Using Cubane-Type Oxo Clusters[a]

cluster	proton source	conversn of $MePhNNH_2$[b]	yield of PhNHMe[c]
5	none	17	8
	Lut·HCl	75	64
	Lut·HBF_4	49	30
	NEt_3·HCl	25	24
6	Lut·HCl	47	31
10	Lut·HCl	90	70
11	Lut·HCl	77	56
none	Lut·HCl	0	0

[a] Conditions: cluster, 0.010 mmol; $MePhNNH_2$, 0.10 mmol; proton source, 0.20 mmol; cobaltocene, 0.20 mmol; DMF, 5 mL; room temperature; 12 h. [b] In percent, ($MePhNNH_2$ consumed)/($MePhNNH_2$ charged). [c] In percent, (PhNHMe formed)/($MePhNNH_2$ charged).

For **9**, upon reaction with excess HCl gas in DMF at room temperature, *N*-methylaniline by the cleavage of the NNMePh ligand was obtained, but in only 9% yield. Meanwhile, when **9** was treated with 2 equiv of Lut·HCl/cobaltocene in DMF at room temperature, the yield of *N*-methylaniline increased to 21% yield (eq 5). Attempts to isolate the metal-containing products from these reaction mixtures were unsuccessful. The fate of the inner N atom of the hydrazido(2−) ligand is also unknown.



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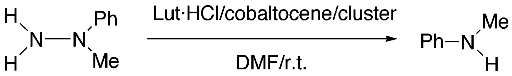
(5)

Although the details are still not clear for this N−N bond cleavage of the methylphenylhydrazido(2−) ligand in **9**, catalytic conversion of $MePhNNH_2$ into the reduction product PhNHMe using cubane-type oxo clusters as the catalyst precursor was investigated. The results are summarized in Table 4, where the yields of PhNHMe are based on the stoichiometry shown in eq 6. Thus, the reaction of $MePhNNH_2$ with 2 equiv of cobaltocene in the presence of **5** (10 mol %) at room temperature led to the consumption of 17% of the



(6)

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hydrazine and the formation of PhNHMe in 8% yield. The proton source is probably the trace amount of water present in DMF used as a solvent. In contrast, when 2 equiv of Lut·HCl as the proton source was added further to this reaction mixture, the yield of PhNHMe was improved up to 64%. Without any catalysts, reaction did not occur and the hydrazine charged was recovered quantitatively. Other proton sources such as Lut·HBF_4 and NEt_3·HCl were less effective than Lut·HCl. We believe that the reaction at first proceeds through the hydrazido(2−) stage as the initial intermediate. However, none of the intermediate species or the final metal-containing products were yet characterizable. A possible other product from this N−N bond scission reaction is ammonia. However, quantitative analysis of ammonia was not undertaken, since reliable data are hardly available, due to the use of a huge amount of nitrogenous compound, DMF, as a solvent.

For comparison, reactions were carried out by adding other cubane-type oxo clusters as the catalyst precursor. Under the same reaction conditions, **6**, the Mo_2Rh_2 analogue of **5**, showed much lower activity in the reaction with Lut·HCl/cobaltocene (31% yield as compared to 64% for **5**), whereas the mixed chalcogenido clusters isolated quite recently in this group[37] exhibited higher or comparable activities: 70% yield by $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Ir)_2(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$ (**10**) and 56% yield by $[\{Mo({=}O)Cl_2\}\{MoCl_2(DMF)\}(Cp^*Rh)_2(\mu_3\text{-}S)_2(\mu_3\text{-}Se)_2]$ (**11**). Further studies are in progress to explore the reaction systems in which the reduction of hydrazines proceeds catalytically with retention of the cubane-type metal chalcogenido cluster cores employed as the catalysts.

Experimental Section

General Considerations. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by common procedures and distilled under nitrogen just before use. Complexes **1**,[38] **2**,[19a] **3**, **4**,[39] **10**, and **11**[37] were prepared according to the literature methods, and $[(Cp^\circ RuCl)_2(\mu_2\text{-}SH)_2]$ (**2′**) was obtained by a procedure analogous to that for preparing **2**. Other chemicals were commercially available and used as received.

^1H NMR spectra were recorded on a JEOL alpha-400 spectrometer, where the chemical shifts were referred to the impurity signals of the solvents (δ 5.30 for CD_2Cl_2 and δ 2.74 for DMF-d_7), while IR spectra were obtained on a JASCO FT/IR-420 spectrometer. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer. Organic compounds present in the product mixtures were characterized by GC-MS methods using a Shimadzu GC-MS QP-5050 spectrometer, and their quantities were determined by GLC methods on a Shimadzu GC-14B gas chromatograph equipped with a 25 m × 0.25 mm CBP 10 fused silica capillary column.

Preparation of 5. (1) A DMF solution (50 mL) containing **1** (1.27 g, 1.29 mmol), **3** (1.02 g, 1.29 mmol), and $[Me_4N]Cl$ (0.423 g, 3.86 mmol) was stirred at room temperature for 2 days. The resultant dark red-brown mixture was filtered, and the filtrate was dried in vacuo. The residue was extracted twice with CH_2Cl_2 (20 mL × 2), and ether (10 mL) was added to the filtrate with stirring. After being stored overnight at −20 °C, the mixture was filtered, and then ether (200 mL) was added slowly to the filtrate. The cluster **5**·CH_2Cl_2 precipitated as black crystals, which were collected and dried (1.32 g, 79% yield). ^1H NMR (CD_2Cl_2 solution): δ 1.97 (s, 30H, Cp*), 2.71, 2.93 (s, 3H each, NMe), 5.31 (s, 2H, CH_2Cl_2), 7.71 (s, 1H, CHO). IR (KBr, cm^{-1}): ν(C=O), 1637; ν(Mo=O), 930 (s). Anal. Calcd for $C_{24}H_{39}NO_2Cl_6S_4Ir_2Mo_2$: C, 22.33; H, 3.05; N, 1.09. Found: C, 22.52; H, 3.17; N, 1.10.

(2) A CH_2Cl_2 solution (5 mL) of **1** (53 mg, 0.054 mmol) and **3** (43 mg, 0.054 mmol) was stirred overnight at room temperature, and the resultant mixture was filtered. Addition of hexane to the filtrate deposited a mixture of black crystals of **5** and red crystals of unreacted **3**. Recrystallization of this mixture from DMF−hexanes−ether gave only black crystals in low yield, which were characterized to be **5**·DMF from the X-ray analysis and microanalysis. Anal. Calcd for $C_{26}H_{44}N_2O_3Cl_4S_4Ir_2Mo_2$: C, 24.42; H, 3.47; N, 2.19. Found: C, 24.76; H, 3.66; N, 2.78.

Preparation of 6. A mixture of **1** (206 mg, 0.211 mmol), **4** (131 mg, 0.213 mmol), and $[Me_4N]Cl$ (76 mg, 0.70 mmol) in DMF (20 mL) was stirred at room temperature for 36 h. The resultant dark red-brown mixture was concentrated to ca. 10 mL under reduced pressure. After addition of ether (10 mL) with stirring, the mixture was allowed to stand for 15 min and filtered to remove a pale brown solid. Ether (30 mL) was added again to the filtrate slowly to give dark brown crystals of **6**·DMF (196 mg, 84% yield). ^1H NMR (CD_2Cl_2 solution): δ 1.91 (s, 30H, Cp*), 2.63, 2.89 (s, 3H each, NMe in coordinated DMF), 2.80, 2.89 (s, 3H each, NMe in free DMF), 7.57 (br s, 1H, CHO in coordinated DMF), 7.94 (br s, 1H, CHO in free DMF). IR (KBr, cm^{-1}): ν(C=O), 1667 (sh), 1638; ν(Mo=O), 928. Anal. Calcd for $C_{26}H_{44}N_2O_3Cl_4S_4Rh_2Mo_2$: C, 28.38; H, 4.03; N, 2.55. Found: C, 28.28; H, 4.36; N, 2.48.

Preparation of 7 and 7′. A mixture of **1** (98 mg, 0.10 mmol), **2** (61 mg, 0.10 mmol), and $[Me_4N]Cl$ (40 mg, 0.36 mmol) in DMF (10 mL) was stirred at room temperature for 24 h. The resultant dark brown mixture was concentrated to ca. 3 mL under reduced pressure, and ether (5 mL) was added with stirring. After standing for 15 min, the mixture was filtered. Addition of ether (15 mL) to the concentrated filtrate (ca. 2.5 mL) afforded **7**·DMF (5 mg, 4% yield) as dark reddish brown prisms, while the residue was extracted by CH_2Cl_2 (7 mL). The extract was dried and crystallized from DMF−ether, giving **7**·DMF (42 mg, 36% yield) together with a small amount of **8**$[(MoOCl_2)(\mu_2\text{-}S)_2]\cdot{}^3/_2$DMF (2 mg, 2% yield based on Ru). Data for **7**·DMF are as follows. ^1H NMR (DMF-d_7 solution): δ 1.96 (s, 30H, Cp*), 2.79, 2.95 (s, 9H each, NMe in DMF). IR (KBr, cm^{-1}): ν(C=O), 1673 (sh), 1644. Anal. Calcd for $C_{29}H_{51}N_3O_3Cl_4S_4Ru_2Mo_2$: C, 30.19; H, 4.46; N, 3.64. Found: C, 30.21; H, 4.51; N, 3.69. Data for **8**$[(MoOCl_2)(\mu_2\text{-}S)_2]\cdot{}^3/_2$DMF are as follows. ^1H NMR (DMF-d_7 solution): δ 1.91 (s, Cp*). IR (KBr, cm^{-1}): ν(C=O), 1655; ν(Mo=O), 970. Anal. Calcd for $C_{44.5}H_{70.5}N_{1.5}O_{3.5}Cl_4S_6Ru_4Mo_2$: C, 33.14; H, 4.41; N, 1.30. Found: C, 32.85; H, 4.07; N, 0.99.

Cluster **7′** was obtained similarly from **1** and **2′** as dark brown prisms in 21% yield. Data for **7′**·DMF are as follows. ^1H NMR (DMF-d_7 solution): δ 1.12 (t, J = 7.8 Hz, 6H, CH_2CH_3), 1.95, 1.97 (s, 12H each, C_5Me_4), 2.48 (br q, J = 7.8 Hz, 4H, CH_2CH_3), 2.79, 2.95 (s, 9H each, NMe in DMF). IR (KBr, cm^{-1}): ν(C=O), 1644 cm^{-1}. Anal. Calcd for $C_{31}H_{55}N_3O_3Cl_4S_4Ru_2Mo_2$: C, 31.50; H, 4.69; N, 3.56. Found: C, 31.45; H, 4.58; N, 3.26.

Reaction of 1 with 3 Equiv of 2. Stirring a mixture of **1** (44 mg, 0.045 mmol) and **2** (83 mg, 0.14 mmol) in DMF (10 mL) at room temperature for 24 h gave a dark brown solution. Measurement of the NMR spectrum of the crude mixture showed the formation of **7** and **8** in a ratio of 1:2 as the only Cp*-containing products. Addition of ether (15 mL) to the concentrated product solution (3 mL) afforded a mixture of crystals (94 mg) of **7** and **8**X_2 with anions X_2 of unknown composition.

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Table 5. Crystallographic Data for 5, 7′, and 9

	5·DMF	**7′**·DMF	**9**·2CH$_2$Cl$_2$
formula	$C_{26}H_{44}N_2O_3S_4Cl_4Mo_2Ir_2$	$C_{31}H_{55}N_3O_3S_4Cl_4Mo_2Ru_2$	$C_{32}H_{49}N_3OS_4Cl_8Mo_2Ir_2$
fw	1279.02	1181.87	1479.94
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	10.782(3)	11.340(1)	14.334(4)
b (Å)	22.056(3)	26.09(1)	15.625(2)
c (Å)	17.219(3)	16.148(4)	21.365(3)
α (deg)	90.00	90.00	90.00
β (deg)	107.77(2)	108.64(1)	91.51(2)
γ (deg)	90.00	90.00	90.00
V (Å^3)	3899(1)	4526.3(2)	4783(1)
Z	4	4	4
ρ_{calc} (g cm^{-3})	2.178	1.734	2.055
F_c (cm^{-1})	79.68	16.49	67.24
cryst size (mm^3)	$0.40 \times 0.40 \times 0.05$	$0.40 \times 0.40 \times 0.20$	$0.20 \times 0.20 \times 0.10$
no. of data	5902 ($I > 3.00\sigma(I)$)	7442 ($I > 3.00\sigma(I)$)	4957 ($I > 3.00\sigma(I)$)
no. of variables	388	498	469
transmissn factor	0.22−1.00	0.82−1.00	0.75−1.00
R^a	0.049	0.032	0.049
$R_w{}^b$ or wR2^c	0.054^b	0.082^c	0.050^b
GOF	1.99^d	1.00^e	1.41^d
residual peaks (e Å^{-3})	2.28, −1.70	0.80, −0.53	2.22, −1.17

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$ ($w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o{}^2]^{-1}$). [c] $\mathrm{wR2} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$. [d] $\mathrm{GOF} = [\Sigma w(|F_o| - |F_c|)^2/\{(\text{no. observns}) - (\text{no. variables})\}]^{1/2}$. [e] $\mathrm{GOF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\{(\text{no. observns}) - (\text{no. variables})\}]^{1/2}$.

Preparation of 9. To a solution of **5** (298 mg, 0.231 mmol) in DMF (15 mL) was added MePhNNH$_2$ (27.0 μL, 0.230 mmol). After the mixture was stirred at room temperature for 24 h, solvent was removed under reduced pressure from the reaction mixture and the residue was extracted with CH$_2$Cl$_2$ (15 mL). Addition of hexane to the extract deposited black needles of **9**·2CH$_2$Cl$_2$ (236 mg, 69% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.97 (s, 30H, Cp*), 2.13, 2.60 (s, 3H each, NMe in coordinated DMF), 4.22 (s, 3H, NN*Me*Ph), 5.31 (s, 4H, CH$_2$Cl$_2$), 6.95 (t, J = 7.4 Hz, 1H, *p*-H in NPh), 7.21 (d, J = 8.2 Hz, 2H, *o*-H in NPh), 7.39 (dd, J = 8.2, 7.4 Hz, *m*-H in NPh), 7.63 (br s, 1H, CHO). IR (KBr, cm^{-1}): ν(C═O), 1637. Anal. Calcd for $C_{32}H_{49}N_3OCl_8S_4Ir_2Mo_2$: C, 25.97; H, 3.34; N, 2.84. Found: C, 26.33; H, 3.48; N, 2.94.

Reaction of 9 with HCl Gas. Hydrogen chloride gas was bubbled through a DMF solution (5 mL) of **9** (50 mg, 0.034 mmol) at room temperature for a few minutes, and the resultant mixture was stirred overnight. The obtained mixture was dried, treated with aqueous NaOH, and then extracted with ether. The qualitative GC-MS analysis as well as the quantitative GC analysis of the extract revealed the formation of PhNHMe in 9% yield.

Reaction of 9 with Lut·HCl and Cobaltocene. A solution containing **9** (52 mg, 0.036 mmol), Lut·HCl (11 mg, 0.075 mmol), and cobaltocene (14 mg, 0.071 mmol) in DMF (5 mL) was stirred at room temperature overnight. The yield of PhNHMe was determined by the same procedure as described above.

Catalytic Conversion of MePhNNH$_2$ into PhNHMe Using Cubane-Type Oxo Clusters. To a DMF solution (5 mL) of a cluster (0.010 mmol) and Lut·HCl (0.20 mmol) was added MePhNNH$_2$ (0.10 mmol). After the solution was stirred for 10 min at room temperature, cobaltocene (0.20 mmol) was added and the mixture was stirred continuously at room temperature for 12 h. GLC analyses were undertaken for the resultant dark brown reaction mixtures.

X-ray Crystallography. Single crystals of **5**·DMF, **7′**·DMF, and **9**·2CH$_2$Cl$_2$ were sealed in glass capillaries under argon and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromated Mo Kα source. All diffraction studies were done at room temperature. Details are summarized in Table 5.

Structure solution and refinements were carried out by using the teXsan[40] (**5**·DMF and **9**·2CH$_2$Cl$_2$) and CrystalStructure[41] (**7′**·DMF) program packages. The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY[42] for **5**·DMF and **9**·2CH$_2$Cl$_2$ and SHELXS-97[43] for **7′**·DMF) and subsequent Fourier synthesis (DIRDIF[44]) and refined anisotropically. The hydrogen atoms were placed at calculated positions and included in the final stages of the refinements with fixed parameters.

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Supporting Information Available: Table of the details of X-ray crystallography for **6**·DMF and tables listing extensive atomic and bonding parameters in **5**·DMF, **6**·DMF, **7′**·DMF, and **9**·2CH$_2$Cl$_2$; crystallographic data are also available as electronic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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