Structural Studies of the Hydrazine and Ammine Complexes of the Dinuclear Ruthenium Polysulfide Complexes

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The dinuclear ruthenium polysulfide complex, $[Ru^{II}_2(\mu\text{-}S_n)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**1**)·$0.5CH_2Cl_2$ ($n = 5$ or 6), was reacted with N-donor ligands, hydrazine, ammonia, and pyridine. The reaction of hydrazine with 1.2 equiv of **1**·$0.5CH_2Cl_2$ affords the crystallographically characterized dinuclear Ru^{II} complex, $\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)]_2(\mu\text{-}S_4)(\mu\text{-}N_2H_4)\}$ (**2**)·$0.5CH_2Cl_2$. The octahedrally coordinated Ru^{II} centers are doubly bridged by N_2H_4 and the S_4 chain. The S_4 chain is formed through a desulfurization reaction of the S_n ($n = 5$ or 6) ligand in **1**. The reaction yield was improved in the presence of one equiv of PPh_3. The space group and the cell data for **2**·$0.5CH_2Cl_2$ are as follows: triclinic, space group $P\bar{1}$ (No. 2) with $a = 20.003(3)$ Å, $b = 14.155(2)$ Å, $c = 10.061(2)$ Å, $\alpha = 110.70(1)°$, $\beta = 90.73(1)°$, $\gamma = 104.23(1)°$, $V = 2567.4(8)$ Å^3, and $Z = 2$. The dinuclear ruthenium pentasulfide $[Ru^{II}_2(\mu\text{-}S_5)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**1p**) and the hexasulfide $[Ru^{II}_2(\mu\text{-}S_6)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**1h**) complexes in the crystals of **1**·$0.5CH_2Cl_2$ were separated by partial recrystallization in benzene. The reaction between **1h** and NH_3 forms the dinuclear Ru^{II} ammine complex, $\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)(NH_3)]_2(\mu\text{-}S_6)\}$ (**3**)·$0.5CH_2Cl_2$, in which ammonia is terminally coordinated to the metal centers. Complex **3** crystallizes as the acetonitrile solvate in monoclinic space group $C2/c$(No. 15) with $a = 30.481(7)$ Å, $b = 12.455(2)$ Å, $c = 15.463(3)$ Å, $\beta = 113.90(2)°$, $V = 5367(1)$ Å^3, and $Z = 4$. The reaction between **1p** and excess amount of pyridine (py) yields $\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)(py)]_2(\mu\text{-}S_5)\}$ (**4**), of which structural information was obtained by ^{31}P NMR and elemental analysis due to the poor crystal quality. Upon dissolution in CH_2Cl_2, both **3**·$0.5CH_2Cl_2$ and **4** reinstate **1h** and **1p**, respectively, indicating that both complexes undergo intrinsically the same reaction. The N_2H_4 ligand in **2**·$0.5CH_2Cl_2$ is chemically reduced and quantitatively measured 8.4 mol % of ammonia liberation.

Introduction

Although a number of transition metal complexes having catenated polysufide ligands (S_n^{2-}, $n > 3$) are known, most of the studies are focused on the synthesis and structure determination, and little attention is paid on their reactivity.[1,2] This is probably due to the complicated chemical reactions of the ligand, which generally allows so many variable coordination modes to metals. Some examples of the coordination modes include bidentate chelation by the two terminal sulfur atoms known for S_3^{2-},[1−3] S_4^{2-},[2,4−6] S_5^{2-},[5,7] S_6^{2-},[2,8,9] and S_9^{2-}.[2,10] Novel tridentate chelation is known only for S_7^{2-}.[11] Some polysulfides participate in both chelating and bridging two or more metals.[2,12] In contrast to these flourishing structural data, reported reactions of polysulfides are limited. One typical reaction of higher polysulfides (so far known up to S_9^{2-}) is desulfurization of one or more sulfur atoms from a polysulfide chelate ring to a lower polysulfide ring, by addition of sulfur-abstracting reagents such as PR_3.[1] For example, $[Pt(S_5)_3]^{2-}$ is converted to $[Pt(PPh_3)_2(S_4)]$ and S^{2-} by addition of PPh_3.[13] In some reactions, addition of sulfur-abstracting reagent leads to dinucleation of a monomeric complex.[14] Thus, the addition of PR_3 to Cp_2TiS_5 gives $(Cp_2Ti)_2S_x$ ($x = 4$, 6). To obtain a more general view on the reactivity, several nucleophilic and electrophilic attack to coordinated polysulfides were attempted. For example, perthiocarbonate ligand is formed by the electrophilic attack of CS_2 on the coordinated S_4^{2-} ligand in $[SMo(S_4)_2]^{2-}$, yielding $[SMo(CS_4)_2]^{2-}$.[15] Similarly, in the reaction of ZnS_4(PMDETA) (PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) with

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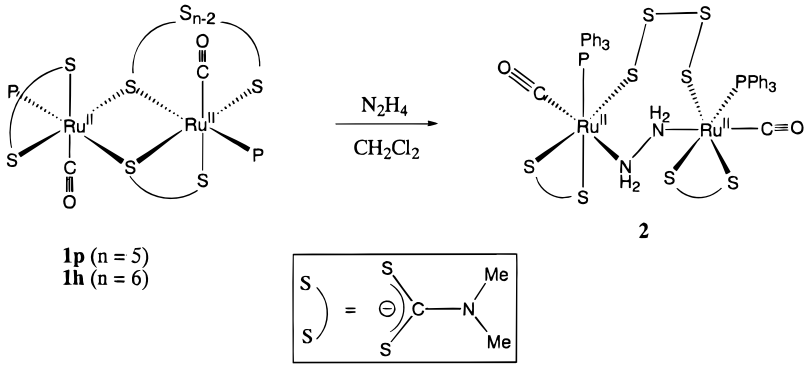
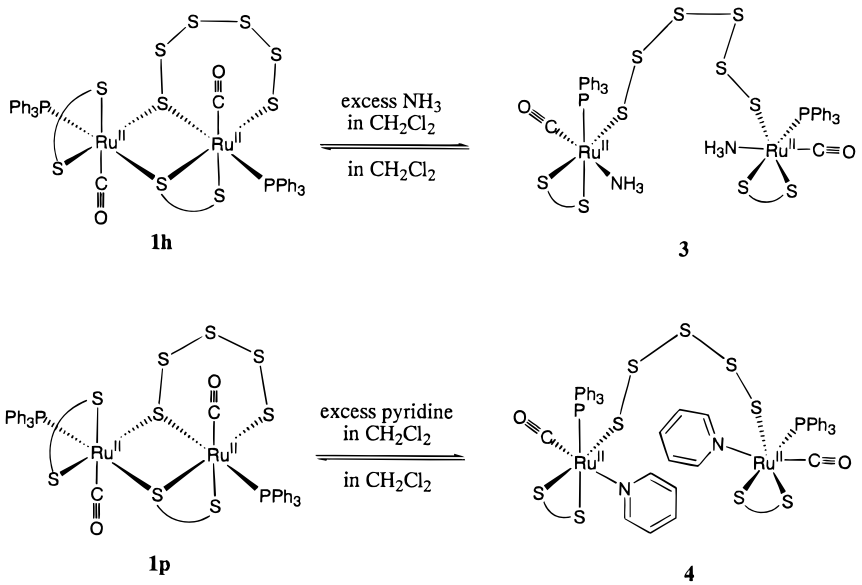
Scheme 1



Scheme 2



CS_2, insertion of the carbon atom takes place and ZnS_3CS-(PMDETA) is obtained together with elemental sulfur.[6a] Most widely reported reaction is the addition of acetylene and its derivatives to the chelated polysulfide ligands to give dithiolene ligands, $RCSCSR'^{2-}$.[1,16] For instance, the S_5^{2-} ligand in Cp_2TiS_5 reacts with (MeCOO)CC(COOMe) to give the dithiolene complex Cp_2Ti(MeCOO)CSCS(COOMe).[17] Similar reaction is also reported for $Ru(bpy)_2S_5$ (bpy = 2,2′-bipyridine),[7] and many other polysulfide complexes.[2,16] Comparison of the reactivities of ZnS_6(TMEDA) (TMEDA = tetramethylethylenediamine) and ZnS_4(PMDETA) toward electrophilic alkyne $C_2(CO_2Me)_2$ shows that the shorter S_4^{2-} ligand has more elevated nucleophilicity.[6a,8] All these reactions suggest that S_n^{2-} reacts with RCCR′ to give dithiolene ligand, regardless of the sulfur number of the polysulfide ring.

Another notable reaction of polysulfide ligand is the insertion of R_2C moiety into a polysulfide chelate ring. The insertion takes place not to the metal-to-sulfur ligand bond, but to the S−S bond in the middle of the polysulfide ligand. For instance, a reaction of Cp_2TiS_5 with R_2CBr_2 or R_2CO (R = H or alkyl) in the presence of $(NH_4)_2S$ produces 1,4-$Cp_2TiS_4CR_2$ and 1,3-$Cp_2TiS_4CH_2$.[5] The reaction is initiated by a sulfur atom abstraction from the pentasulfide ring by $(NH_4)_2S$ to give a bis(disulfide) complex or a mono- and trisulfide complex as the intermediate.

In contrast to the above reactions, simple polysulfide displacement reaction is known only for ZnS_6(TMEDA) by *N*-methylimidazole.[8] This is not surprising, considering the general stability of M−S(polysulfide) bonds. Previously, we reported the synthesis of S_5^{2-} and S_6^{2-} coordinated diruthenium(II) complexes, $[Ru^{II}_2(\mu\text{-}S_n)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ (**1**) (n = 5 (78.5%); n = 6 (21.5%)), and found that these polysulfide ligands are less electron donating than S^{2-} and S_2^{2-}, and are unstable to oxidation. In the present study, substitution reactions of **1** with N_2H_4, NH_3, and pyridine were studied. The crystal structures of the resulting ammine complex, **2**, and the hydrazine bridged complex, **3**, were determined by X-ray crystallography, and the pyridine complex by NMR and elemental analysis. These amine complexes revert to the original polysulfide-bridged complexes **1h** and **1p**, releasing the amine ligands in the absence of excess amine ligands. These results suggest the stability of polysulfide ligands relative to amine ligands. For the hydrazine complex, reducibility of the coordinated hydrazine to NH_3 was also examined.

Results and Discussion

Synthesis. Previously, we reported that complex **1**·0.5CH_2Cl_2 contains 78.5% of **1p** and 21.5% of **1h** in the lattice. The coordinates of the atoms are identical for the both complexes except the polysulfide chain length.[18,19] Despite this intermingling, a reaction of **1**·0.5CH_2Cl_2 with 1.2 equiv of hydrazine provided the tetrasulfide bridged $Ru^{II}Ru^{II}$ hydrazine complex,

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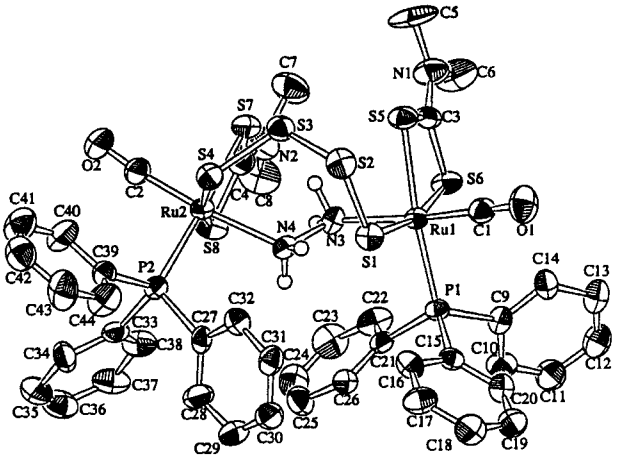

Figure 1. ORTEP diagram of $\{[Ru(S_2CNMe_2)(CO)(PPh_3)]_2(\mu\text{-}S_4)(\mu\text{-}N_2H_4\}$ (**2**)·$0.5CH_2Cl_2$ showing 50% probability thermal ellipsoids for all nonhydrogen atoms.

$\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)]_2(\mu\text{-}S_4)(\mu\text{-}N_2H_4)\}$ (**2**)·$0.5CH_2Cl_2$ (Scheme 1), as a unique product.

We have successfully separated **1p** from **1h** by partial recrystallization in benzene (see Experimental Section). Complex **1h** was then reacted with large excess of NH_3. The reaction produced the dinuclear ruthenium ammine complex, $\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)(NH_3)]_2(\mu\text{-}S_6)\}$ (**3**)·$0.5CH_2Cl_2$ (Scheme 2), with an excellent yield, and the orange X-ray quality crystals were grown by layer diffusion of ether into a CH_2Cl_2 solution. The reaction of **1p** with pyridine yielded yellow crystals of $\{[Ru^{II}(S_2CNMe_2)(CO)(PPh_3)(py)]_2(\mu\text{-}S_5)\}$ (**4**) (py = pyridine). The crystals of **4** were too fragile and were not suitable for X-ray diffraction, whereas the ^{31}P NMR and elemental analysis elucidated that the structure is akin to that of **3**·$0.5CH_2Cl_2$. This structure was further supported by the fact that dissolution of the crystals of **3**·$0.5CH_2Cl_2$ and **4** in CH_2Cl_2 readily reverted to **1h** and **1p**, respectively (Scheme 2).

X-ray Crystal Structures. Complex **2**·$0.5CH_2Cl_2$ crystallizes with one molecule of CH_2Cl_2 in the lattice. However, refinement of the CH_2Cl_2 molecule was impossible due to disorder in the position of C. Consequently, the Max Shift/Error value was limited to 4.03. The ORTEP diagram is shown in Figure 1 and the selected bond distances and angles are listed in Table 1.

The distorted octahedral coordination geometry around each ruthenium atom is completed by a bidentate dithiocarbamate, a terminal carbonyl, a triphenylphosphine, a bridging tetrasulfide, and a bridging N_2H_4. Each dithiocarbamate plane is perpendicular to the Ru−N bond. The μ-N_2H_4 group positions trans to the terminal CO groups, and separates the two Ru^{II} centers by 5.22 Å through the zigzag $Ru^{II}NNRu^{II}$ core with dihedral angle of 143.4(4)°. The observed geometry of the *trans*-$Ru^{II}NNRu^{II}$ core is similar to that in $[W(NPh)Me_3]_2(\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHNH)$,[20a] and several other complexes,[20b] while we previously prepared the μ-N_2H_4 bridged $Ru^{II}Ru^{III}$ mixed valence complexes, which possess the *cis*-$Ru^{III}NNRu^{II}$ core.[21,22] The N−N distance in the bridging hydrazine (1.48(1) Å) is slightly longer than the value in analogous μ-N_2H_4, μ-S_2 bridged $Ru^{II}Ru^{III}$ dinuclear complex, $\{[RuCl(TMP)_2]_2(\mu\text{-}Cl)(\mu\text{-}N_2H_4)(\mu\text{-}S_2)\}$ (**5**) (TMP = trimethyl phosphite),[24] and is comparable to the value in free N_2H_4 (1.47 Å).[23] The Ru−N distances (2.222(8) and 2.228(8) Å) are slightly longer than those in **5** (2.170(7) Å and 2.172(7) Å). The Ru^{II}−S (tetrasulfide) distances (2.389(3) Å and 2.407(3) Å) are longer than the $Ru^{II/III}$−S distance in **5** (2.281 Å (av)), and the Ru^{III}−S (disulfide) distance, which usually is in the range 2.19−2.22 Å.[24] The observed oxidation state dependence of the Ru−S distance is a consequence of the difference in the ionic radii of Ru^{II} and Ru^{III}, and also in the π-acceptor ability of ruthenium that decreases in order of $Ru^{III} > Ru^{III/II} > Ru^{II}$. As anticipated, the tetrasulfide chain is severely puckered (the Ru(1)−S(1)−S(2)−S(3), Ru(2)−S(4)−S(3)−S(2), and the S(1)−S(2)−S(3)−S(4) torsion angles are 65.5(2), −114.8(1), and 68.4(2)°, respectively) in order to pack in the void created by the two Ru^{II} centers and the μ-N_2H_4 ligand. The average S−S single bond distance (2.064 Å) is a typical value found in polysulfide chains.[25]

Complex **3**·$0.5CH_2Cl_2$ also crystallizes with one molecule of CH_2Cl_2 per two complex molecules in the lattice. The structure

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2**·$0.5CH_2Cl_2$[a,b]

Bond Distances			
Ru(1)−S(1)	2.389(3)	Ru(1)−S(5)	2.437(3)
Ru(1)−S(6)	2.414(3)	Ru(1)−P(1)	2.322(2)
Ru(1)−N(3)	2.222(8)	Ru(1)−C(1)	1.79(1)
Ru(2)−S(4)	2.407(3)	Ru(2)−S(7)	2.453(3)
Ru(2)−S(8)	2.428(3)	Ru(2)−P(2)	2.341(3)
Ru(2)−N(4)	2.228(8)	Ru(2)−C(2)	1.82(1)
S(1)−S(2)	2.058(4)	S(2)−S(3)	2.066(4)
S(3)−S(4)	2.069(4)	S(5)−C(3)	1.70(1)
S(6)−C(3)	1.726(10)	S(7)−C(4)	1.74(1)
S(8)−C(4)	1.71(1)	P(1)−C(9)	1.852(9)
P(1)−C(15)	1.833(10)	P(1)−C(21)	1.836(10)
P(2)−C(27)	1.855(10)	P(2)−C(33)	1.85(1)
P(2)−C(39)	1.851(10)	O(1)−C(1)	1.19(1)
O(2)−C(2)	1.16(1)	N(3)−N(4)	1.48(1)

Bond Angles			
S(1)−Ru(1)−S(5)	96.43(9)	S(1)−Ru(1)−S(6)	166.11(9)
S(1)−Ru(1)−P(1)	97.42(9)	S(1)−Ru(1)−N(3)	87.0(2)
S(1)−Ru(1)−C(1)	90.4(3)	S(5)−Ru(1)−S(6)	72.36(9)
S(5)−Ru(1)−P(1)	166.02(9)	S(5)−Ru(1)−N(3)	84.3(2)
S(5)−Ru(1)−C(1)	90.4(3)	S(6)−Ru(1)−P(1)	93.66(8)
S(6)−Ru(1)−N(3)	83.8(2)	S(6)−Ru(1)−C(1)	97.7(3)
P(1)−Ru(1)−N(3)	94.5(2)	P(1)−Ru(1)−C(1)	91.4(3)
N(3)−Ru(1)−C(1)	173.8(4)	S(4)−Ru(2)−S(7)	96.19(9)
S(4)−Ru(2)−S(8)	167.40(9)	S(4)−Ru(2)−P(2)	88.11(9)
S(4)−Ru(2)−N(4)	88.0(2)	S(4)−Ru(2)−C(2)	92.5(3)
S(7)−Ru(2)−S(8)	72.13(9)	S(7)−Ru(2)−P(2)	175.16(10)
S(7)−Ru(2)−N(4)	89.8(2)	S(7)−Ru(2)−C(2)	84.7(3)
S(8)−Ru(2)−P(2)	103.76(9)	S(8)−Ru(2)−N(4)	87.2(2)
S(8)−Ru(2)−C(2)	91.1(3)	P(2)−Ru(2)−N(4)	92.6(2)
P(2)−Ru(2)−C(2)	93.0(3)	N(4)−Ru(2)−C(2)	174.5(4)

Torsion Angles			
Ru(1)−S(1)−S(2)−S(3)	65.5(2)	Ru(2)−S(4)−S(3)−S(2)	−114.8(1)
Ru(1)−N(3)−N(4)−Ru(2)	143.4(4)	S(1)−S(2)−S(3)−S(4)	68.4(2)

[a] See Figure 1 for the atom-labeling scheme. [b] Numbers in parentheses are estimated standard deviations for the last significant digit.

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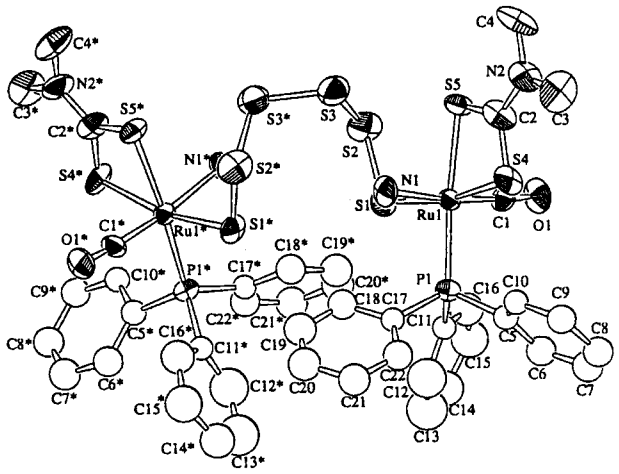

Figure 2. ORTEP diagram of $\{[Ru(S_2CNMe_2)(CO)(PPh_3)(NH_3)]_2(\mu\text{-}S_6)\}$ (**3**)·$0.5CH_2Cl_2$ showing 50% probability thermal ellipsoids for all nonhydrogen atoms.

is depicted in Figure 2, and the selected bond distances and angles are listed in Table 2.

Unlike **2**·$0.5CH_2Cl_2$, however, a true crystallographic C_2 axis relates the two halves of **3**·$0.5CH_2Cl_2$. The two Ru^{II} centers are bridged by the μ-S_6 ligand, which separates the metal centers by 7.68 Å. A distorted octahedron of each Ru^{II} center is completed by a bidentate dithiocarbamate, a terminal carbonyl, a terminal ammine, and a triphenylphosphine. The NH_3 group and the CO group are trans to each other that corresponds to the relation of μ-N_2H_4 to the CO group in **2**·$0.5CH_2Cl_2$. The plane of a dithiocarbamate is perpendicular to the Ru−N bond. Unlike **2**·$0.5CH_2Cl_2$, the polysulfide ligand remains intact throughout the reaction because, without any other bridging ligand, the S_6^{2-} chain can rearrange freely between the two Ru^{II} centers, and thus amasses no internal strain that induces desulfurization reaction. The Ru^{II}−S (hexasulfide) distances of 2.382(5) Å is comparable to those in **2**·$0.5CH_2Cl_2$, and thus the value is considered insensitive to presence or absence of the μ-N_2H_4 ligand.

Reaction Mechanism. Extended Hückel calculations of **1** show that the LUMO consists of virtually degenerate ruthenium orbitals, which will receive nucleophilic attack of the N_2H_4 ligand. Upon completion of the N_2H_4 coordination, PPh_3 dissociation is likely to occur as a minor path, although such a product was not isolated (route A in Scheme 3).

As a major path, the other end of the N_2H_4 coordinates on the other Ru^{II} atom concomitantly with cleavage of the Ru(1)−S(3) and Ru(2)−S(9) bonds (route B in Scheme 3). Significant strain is imposed on the polysulfide chain as a consequence of the four-center six-electron Ru−N−N−Ru bond formation. The free PPh_3 will serve in a desulfurization reaction[26] that will alleviate the strain, yielding **2**·$0.5CH_2Cl_2$. Desulfurization by PPh_3 was confirmed experimentally as follows. In the course of the reaction, the reaction solution changed its color from orange to yellow, and immediate addition of excess ether resulted in precipitation of the intermediate species whose ^{31}P NMR spectrum agrees with neither **1**·$0.5CH_2Cl_2$ nor **2**·$0.5CH_2Cl_2$. A crystallization attempt of the intermediate gave a mixture of **1**·$0.5CH_2Cl_2$ and metallic ruthenium in addition to $SPPh_3$ in the supernatant. The desulfurization reaction of PPh_3 was bolstered by the fact that the presence of 1 equiv of PPh_3 improved yield from 39% to ca. 70%. It is not clear, however, if both **1p** and **1h** have been converted to **2**·$0.5CH_2Cl_2$ or **1p** has reacted exclusively with N_2H_4.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**·$0.5CH_2Cl_2$[a]

Bond Distances			
Ru(1)−S(1)	2.382(5)	Ru(1)−S(4)	2.435(6)
Ru(1)−S(5)	2.439(6)	Ru(1)−P(1)	2.314(6)
Ru(1)−N(1)	2.21(2)	Ru(1)−C(1)	1.81(2)
S(4)−C(2)	1.72(3)	S(5)−C(2)	1.74(3)
S(1)−S(2)	2.043(9)	S(2)−S(3)	2.05(1)
P(1)−C(5)	1.84(2)	P(1)−C(11)	1.82(2)
P(1)−C(17)	1.83(2)		
Bond Angles			
S(1)−Ru(1)−S(4)	168.0(2)	S(1)−Ru(1)−S(5)	97.8(2)
S(1)−Ru(1)−P(1)	90.5(2)	S(1)−Ru(1)−N(1)	87.0(5)
S(1)−Ru(1)−C(1)	94.3(7)	S(4)−Ru(1)−S(5)	72.2(2)
S(4)−Ru(1)−P(1)	99.4(2)	S(4)−Ru(1)−N(1)	85.8(5)
S(4)−Ru(1)−C(1)	92.0(7)	S(5)−Ru(1)−P(1)	171.5(2)
S(5)−Ru(1)−N(1)	85.9(5)	S(5)−Ru(1)−C(1)	88.1(7)
P(1)−Ru(1)−N(1)	92.8(5)	P(1)−Ru(1)−C(1)	93.1(7)
N(1)−Ru(1)−C(1)	174.0(8)		

[a] See Figure 2 for the atom-labeling scheme.

Resemblance of the coordination geometry of **3**·$0.5CH_2Cl_2$ with that of **2**·$0.5CH_2Cl_2$ implies that the reaction between **1h** and NH_3 proceeds analogously.

An Attempted Reduction of the Bridging N_2H_4 to Ammonia. We attempted to reduce the N_2H_4 ligand in **2**·$0.5CH_2Cl_2$ to NH_3 in CH_2Cl_2 according to a literature method using 8 equiv of sodium amalgam as a reductant and 4 equiv of 2,6-lutidine hydrochloride as a proton source.[27] Liberated ammonia was trapped as NH_4Cl, which was subjected to quantitative measurement by the indophenol method.[28] The detected amount was only 8.4 mol % of NH_4^+, implying intrinsic difficulty in reduction of the coordinated N_2H_4. Reliability of the test was confirmed by applying the procedure to a CH_2Cl_2 solution of **3**·$0.5CH_2Cl_2$, which possesses NH_3 as a ligand, to detect nearly stoichiometric amount of NH_4^+ (97 mol %).

Conclusion

We discussed reactions of the dinuclear ruthenium polysulfides with the N-donor ligands. Hydrazine links the two Ru^{II} centers and forms the RuNNRu core that restricts relative positions of the two Ru^{II} centers in **2**·$0.5CH_2Cl_2$. In the course of **2**·$0.5CH_2Cl_2$ formation, the polysulfide chain in **1** is converted from penta- to tetrasulfide, which then fits between the two Ru^{II} centers. On the contrary, no desulfurization reaction occurs in preparations of **3**·$0.5CH_2Cl_2$ and **4**, where the polysulfide is the only bridging ligand. The reactions in Scheme 2 are significant in that these are the second example that polysulfide undergoes substitution by amine ligand. Since the polysulfides participate both in chelating and bridging in **1h** and **1p**, the coordination of these polysulfides to the Ru atoms would be weaker than they would be if they are only chelating to the Ru atom. Nevertheless, these substitution reactions are noteworthy and give information about the relative coordination stability between polysulfide and amine ligands. Since **3** and **4** revert to **1h** and **1p**, respectively, in the absence of excess amine, these two ligands seem to have comparable coordination stability. It

(26) (a) Bolinger C. M.; Hoots, J. E.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 223. (b) Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.

(27) (a) Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 2767. (b) Vale, M. G.; Schrock, R. R. *Organometallics* **1993**, *12*, 1140.

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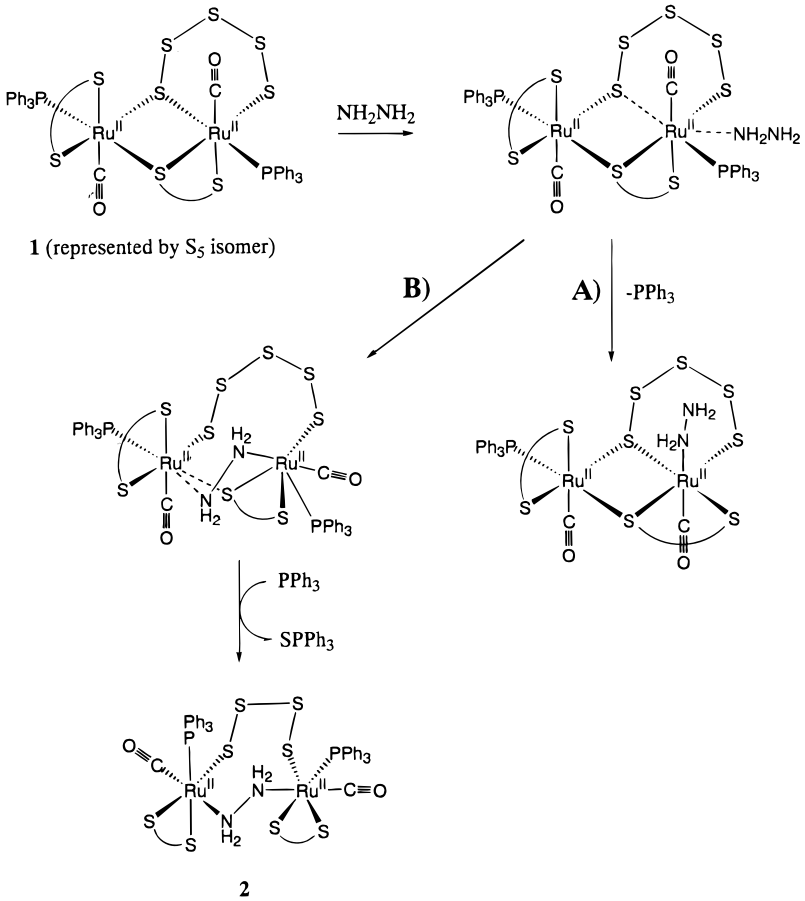
Scheme 3



is rather surprising that amine ligands, which are usually stable, can be removed so easily in these reactions, and this suggests strong chelating tendency of the polysulfides as well as strong bridging tendency of the dithiocarbamate ligand.

Although chemical reduction of the μ-N_2H_4 to NH_4^+ was not efficient enough for any practical use, electrochemical reduction of the dinuclear ruthenium complexes are planned as an alternative method and will be reported in future.

Experimental Section

General Methods. All synthetic procedures were performed under purified nitrogen using standard Schlenk techniques or in a nitrogen atmosphere glovebox unless otherwise mentioned. Solvents were distilled and degassed prior to use. Solution NMR spectra were obtained on a JEOL EX-270WB spectrometer using CD_2Cl_2. ^{31}P NMR chemical shifts were recorded in reference to $P(OMe)_3/(CD_3)_2CO$ external standard (140 ppm). UV−vis spectra were recorded on a Shimadzu UV-3101PC using a quartz cuvette with 1.0 cm optical path. [Ru^{II}_2-(μ-S_n)(μ-S_2CNMe_2)(S_2CNMe_2)$(CO)_2(PPh_3)_2$] (**1**)·0.5CH_2Cl_2 (Figure 3) was prepared as previously reported.[2] Molecular orbital calculations were performed within the extended Hückel formalism with use of the weighted H_{ij} formula using CaChe system.

Crystallographic Studies. Crystals were covered with epoxy-resin and adhered to a glass tip and mounted on a goniometer of a Rigaku AFC-7R four-circle automated diffractometer using graphite-monochromated Mo Kα radiation (0.710 69 Å). Data collection and cell determinations were performed in a manner previously described by using the $\theta-2\theta$ scan technique.[18] Absorption correction was made based on azimuthal scans of several reflections. The data were corrected for Lorentz and polarization effects. Pertinent details are given in Table 1. The structures were solved by a direct method and the model was refined using full-matrix least-squares techniques. One molecule of CH_2Cl_2 was found per complex molecule in the crystal lattice of **2**·0.5CH_2Cl_2 and **3**·0.5CH_2Cl_2. All non-hydrogen atoms were refined anisotropically, except the low-occupancy chlorine atoms and the phenyl carbons in **3**·0.5CH_2Cl_2, which were refined isotropically. Relevant crystallographic information is summarized in Table 3.

Chemical Reduction of 2·0.5CH_2Cl_2. A reductant was prepared by adding 8 equiv of 2,6-lutidine hydrochloride and 4 equiv of sodium amalgam in an appropriate flask under argon atmosphere. To this flask, a CH_2Cl_2 solution (10 mL) of the ruthenium complex (30 mg) was added via syringe and stirred at 0 °C. After 24 h, the solvent and volatiles were removed under vacuum. The residue was dissolved in water (50 mL) and stirred for 2 h before filtration. The filtrate was brought up to 100 mL with distilled water, and a portion (10 mL) was used for quantitative detection by the indophenol method.[28] First, a sodium phenoxide aqueous solution was prepared by dissolving phenol (25 g, 0.27 mol) in 55 mL of a NaOH/H_2O (20 wt %), and brought up to 200 mL with distilled water. A 0.2% EDTA/H_2O (5 mL) and a sodium phenoxide/H_2O (10 mL) were added to the filtrate under vigorous agitation. Following addition of a NaClO aqueous solution (5 mL, 1% effective Cl concentration), the solution mixture was brought up to 50 mL with distilled water, and allowed to stand at 25 °C for 40

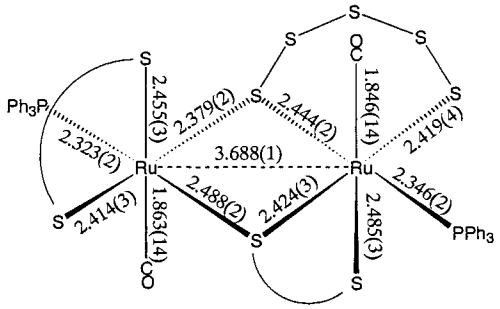


Figure 3. Bond distances (Å) in the diruthenium core of **1**·0.5CH_2Cl_2 (represented by the S_5 isomer).

Table 3. Crystal Data for **2**·0.5CH_2Cl_2 and **3**·0.5CH_2Cl_2

	2·0.5CH_2Cl_2	**3**·0.5CH_2Cl_2
formula	$C_{44.5}H_{47}O_2N_4Ru_2S_8P_2Cl$	$C_{44.5}H_{49}O_2N_4Ru_2S_{10}P_2Cl$
fw	1225.91	1292.04
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	20.003(3)	30.481(7)
b, Å	14.155(2)	12.455(2)
c, Å	10.061(2)	15.463(3)
α, deg	110.70(1)	90
β, deg	90.73(1)	113.90(2)
γ, deg	104.23(1)	90
V, Å^3	2567.4(8)	5367(1)
Z	2	4
d_{calcd}, g cm^{-3}	1.586	1.599
abs coeff (μ), cm^{-1}	10.69	11.02
radiation (λ), Å	Mo Kα 0.710 69	Mo Kα 0.710 69
R^a	0.055	0.072
$R_w{}^b$	0.075	0.097
GOF^c	1.14	1.13
T (deg)	20.0	20.0

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w = 1/\sigma(F_o)^2$. ^{c} GOF $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma(N_{reflcns} - N_{params})]^{1/2}$.

min. The resulting blue solution was subjected to measure its absorbance at 630 nm. The amount of NH_4^+ was determined by using a working curve obtained by plotting the measured absorbance of standard NH_4Cl solutions as a function of the NH_4^+ concentration.

Synthesis of {[Ru(S_2CNMe$_2$)(CO)(PPh_3)]$_2$(μ-S_4)(μ-N_2H_4)} (2)·0.5CH_2Cl_2. To a CH_2Cl_2 solution (10 mL) of [Ru_2(μ-S_n)(μ-S_2CNMe$_2$)(S_2CNMe$_2$)(CO)$_2$(PPh_3)$_2$] (**1**)·0.5CH_2Cl_2 (50 mg, ca. 0.04 mol) was added 1.2 equiv of anhydrous hydrazine (1.6 mL) and 1.2 equiv of PPh_3 (13 mg) in this order at ambient temperature. The resulting orange solution was stirred for 2 h until the solution turned yellow. The solution was then allowed to stand at −40 °C for 2 days. The volume of the resulting solution was reduced to a third by evaporation prior to ether layer addition. After two weeks at 5 °C, yellow crystals of **2**·0.5CH_2Cl_2 were obtained. Yield: 20 mg, 39%. Anal. Calcd for $C_{44.5}ClH_{47}N_4O_2P_2Ru_2S_8$: C, 43.60; H, 3.86; N, 4.57. Found: C, 43.71; H, 4.01; N, 4.27. ^{31}P NMR (ppm): 49.4.

Separation of 1p from 1h. The pentasulfide and the hexasulfide complexes were separated by partial recrystallization as follows. The complex **1**·0.5CH_2Cl_2 was redissolved in the minimum amount of benzene at ambient temperature and then recrystallized at −40 °C to obtain orange crystals of **1p**. The supernatant was collected and the volume was reduced to a half by evaporation. The resulting solution was stored at −40 °C to yield crystals of **1h**.

Synthesis of {[Ru(S_2CNMe$_2$)(CO)(PPh_3)(NH_3)]$_2$(μ-S_6)} (3)·0.5CH_2Cl_2. A CH_2Cl_2 solution (10 mL) of [Ru_2(μ-S_6)(μ-S_2CNMe$_2$)(S_2CNMe$_2$)(CO)$_2$(PPh_3)$_2$] (50 mg, 0.04 mmol) was stirred vigorously in the presence of NH_3/H_2O (28%, 2 mL) for 12 h at ambient temperature. The yellow solution was layered with ether and allowed to equilibrate at 5 °C. The resulting orange crystals of **3**·0.5CH_2Cl_2 were rinsed with ether. Yield: 49 mg, 90%. Anal. Calcd for $C_{44.5}ClH_{49}N_4O_2P_2Ru_2S_{10}$: C, 41.37; H, 3.82; N, 4.34. Found: C, 41.50; H, 3.83; N, 4.36. ^{31}P NMR (ppm): 51.8.

Synthesis of {[Ru(μ-S_2CNMe$_2$)(CO)(PPh_3)(py)]$_2$(μ-S_5)} (4). To a CH_2Cl_2 solution (10 mL) of [Ru_2(μ-S_5)(μ-S_2CNMe$_2$)(S_2CNMe$_2$)(CO)$_2$(PPh_3)$_2$] (**1p**) (50 mg, 0.04 mmol) was added pyridine (0.2 mL, 2.5 mmol) at ambient temperature. The solution was then stored at 5 °C to yield yellow plate-shaped crystals of **4**. Yield: 57 mg, 93%. Anal. Calcd (with a molecule of pyridine per complex molecule) for $C_{59}H_{57}N_5O_2P_2Ru_2S_9$: C, 49.88; H, 4.04; N, 4.98. Found: C, 49.58; H, 4.03; N, 5.27. ^{31}P NMR (ppm): 43.35.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **2**·0.5CH_2Cl_2 and **3**·0.5CH_2Cl_2 are available on the Internet only. Access information is given on any current masthead page.

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