Combined Effect of Bulkiness and NH···S Hydrogen Bonding Controls the Formation of Terminal and Bridging Hydrazine Ruthenium(II) Complexes with Thiolate Ligands

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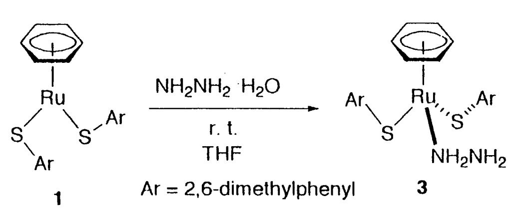
The coordinatively unsaturated 16 electron ruthenium—thiolate complexes $(\eta^6\text{-}C_6H_6)Ru(S\text{-}2,6\text{-}C_6H_3Me_2)_2$ (**1**) and $(\eta^6\text{-}C_6Me_6)Ru(S_2C_6H_4)$ (**2**: $S_2C_6H_4$ = 1,2-benzenedithiolate) react with an excess of hydrazine hydrate to afford a mononuclear η^1-hydrazine complex $(\eta^6\text{-}C_6H_6)Ru(\eta^1\text{-}NH_2NH_2)(S\text{-}2,6\text{-}C_6H_3Me_2)_2$ (**3**) and a dinuclear μ-hydrazine complex $[(\eta^6\text{-}C_6Me_6)Ru(S_2C_6H_4)]_2(\mu\text{-}NH_2NH_2)$ (**4**), respectively.

The interaction of thiolate complexes of group 8 metals with nitrogen containing molecules such as hydrazine,[1-4] diazene,[3,5,6] and ammonia[3] has been investigated recently. With the first synthesis of coordinatively unsaturated 16 electron ruthenium-thiolate complexes such as $(\eta^6\text{-}C_6H_6)Ru(S\text{-}2,6\text{-}C_6H_3Me_2)_2$ (**1**) and $(\eta^6\text{-}C_6Me_6)Ru(S_2C_6H_4)$ (**2**: $S_2C_6H_4$ = 1,2-benzenedithiolate),[7,8] we have a unique opportunity to study the reaction of these ruthenium complexes with hydrazine. Herein we report synthesis and characterization of a mononuclear η^1-hydrazine complex $(\eta^6\text{-}C_6H_6)Ru(\eta^1\text{-}NH_2NH_2)(S\text{-}2,6\text{-}C_6H_3Me_2)_2$ (**3**) and a dinuclear μ-hydrazine complex $[(\eta^6\text{-}C_6Me_6)Ru(S_2C_6H_4)]_2(\mu\text{-}NH_2NH_2)$ (**4**).

Addition of an excess of $NH_2NH_2 \cdot H_2O$ to a solution of **1**[8] in THF induced a rapid change of the solution color from deep blue to deep red. From the concentrated solution, a hydrazine adduct **3** was obtained in 70% yield as red crystalline solids (eq 1).[9]



(1)

Figure 1 shows the structure of **3**[10] that has the discrete monomeric three-legged piano stool geometry. The η^1-coordination mode of hydrazine derivative was already found for organoruthenium complexes such as $[Ru(\eta^1\text{-}NH_2NHR)_4(cod)]^{2+}$ [11] and $[Ru(H)(\eta^1\text{-}NH_2NMe_2)_3(cod)]^+$ [12]. The Ru—S bond distances (2.396(2) and 2.420(2) Å) are longer than those (2.269(7) and 2.292(9) Å) found for **1**,[8] indicating that the coordination of a nitrogen atom of the hydrazine resulted in the formation of an 18-electron complex and in the diminution of donative $S(p\pi) \rightarrow Ru(d\pi^*)$ interaction that had stabilized the unsaturation of **1**.

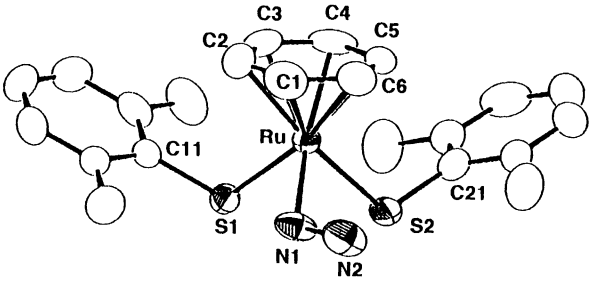
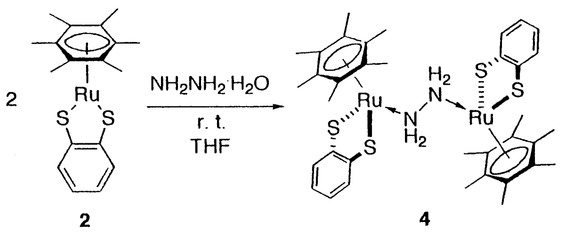


Figure 1. A drawing of **3** with a labeling scheme. Selected bond distances (Å) and angles (deg); Ru—S1 = 2.419(2), Ru—S2 = 2.398(3), Ru—CEN = 1.675, S1—C11 = 1.777(9), S2—C21 = 1.759(10), Ru—N1 = 2.143(7), N1—N2 = 1.378(10); Ru—S1—C11 = 110.0(3), Ru—S2—C21 = 109.7(3), S1—Ru—S2 = 82.24(9), S1—Ru—CEN = 131.8, S2—Ru—CEN = 133.0, N1—Ru—CEN = 127.6, Ru—N1—N2 = 117.9(6). CEN is the centroid of aromatic ring carbons, C1—C6.

The remaining nitrogen atom of **3** is free from the coordination and thus is expected to interact with **1**. However, this interaction did not proceed due to the combined steric bulkiness of two $SC_6H_3Me_2$ ligands. On the other hand, both nitrogen atoms of the hydrazine can coordinate to less sterically demanding complex **2**,[8] giving the hydrazine-bridged dinuclear complex **4**.[9] Treatment of **2** with an excess of hydrazine hydrate in THF and the following crystallization from a mixture of dichloromethane and hexane gave rise to **4** as red crystalline solids in 71% yield (eq. 2). The IR spectrum of the solid sample of **4** showed bands (ν(NH) 3160, 3080 cm^{-1}) due to the hydrazine coordinated to the ruthenium center. The ^1H NMR spectrum of **4** displayed only signals assignable to **2** along with hydrazine protons (δ 3.09) in the required ratio, indicating that the hydrazine is released in the solution. Actually the solution of **4** in THF exhibited the intense and characteristic LMCT band of **2** at 563 nm.[8] Thus, the whole structure involving the μ-hydrazine ligand was confirmed by X-ray analysis of **4**.



(2)

Figure 2 shows the dinuclear structure of **4**,[10] which crystallizes in the monoclinic space group *C2/c* with four dinuclear molecules that have a C_2 axis passing though the center of the N—N bond of the bridging hydrazine ligand. Each ruthenium center in the complex **4** also has three-legged piano stool geometry. The Ru—N bond distance (2.147(4) Å) is comparable to that of **3**. The N—N bond distance (1.454(8) Å) of **4** is comparable to those of ruthenium μ-hydrazine complexes

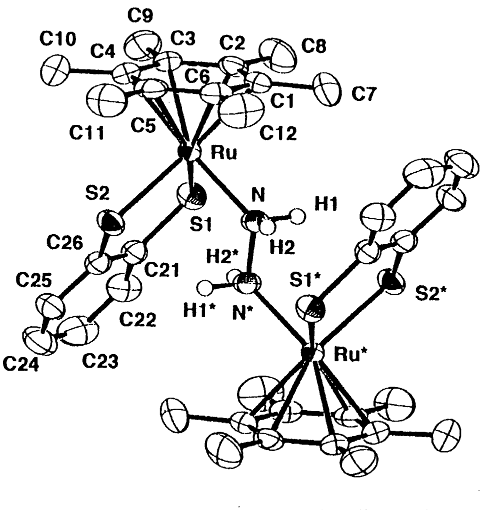


Figure 2. A drawing of **4** with a labeling scheme. Selected bond distances (Å) and angles (deg); Ru—S1 = 2.370(2), Ru—S2 = 2.364(1), Ru—CEN = 1.692, S1—C21 = 1.766(5), S2—C26 = 1.752(5), Ru—N1 = 2.147(4), N1—N1* = 1.454(8); Ru—S1—C21 = 106.0(2), Ru—S2—C26 = 105.9(2), S1—Ru—S2 = 85.87(5), S1—Ru—CEN = 129.0, S2—Ru—CEN = 125.2, N1—Ru—CEN = 121.5, Ru—N1—N1* = 120.8(4). CEN is the centroid of aromatic ring carbons, C1—C6.

such as $\{RuCl(P(OMe)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)(\mu\text{-}N_2H_4)$ (1.442(1) Å)[1] and $[\{Ru(acetonitrile)(P(OMe)_3)_2\}_2(\mu\text{-}S_2)(\mu\text{-}N_2H_4)_2]^{3+}$ (1.465(14) and 1.477(13) Å).[2] This bond distance in **4** is much longer than that (1.378(10) Å) of the mononuclear **3**, where the σ-donation of lone pair electrons on a nitrogen atom of the hydrazine was enforced by further σ-donative interaction of the lone pair electrons of the neighboring nitrogen atom. Thus the N-N bond distance in **3** was shortened by 0.07 Å relative to the value found in **4**. It is noteworthy that the hydrazine functions as a bridging ligand through the formation of NH···S hydrogen bonds; the NH···S bond distances (3.18 and 3.22 Å) of **4** being in the range of NH···S bond distances observed in $[Me_2NHCH_2CH_2NHMe_2][Pd(SC_6F_5)_4]$ (3.256(6) Å),[13] $[Me_3NCH_2CONH_2]_2[Co(SPh)_4]$ (3.316(3)—3.453(3) Å),[14] and $[Mo(O)(S\text{-}o\text{-}CH_3CONHC_6H_4)_4]^-$ (2.97—3.03 Å).[15] Such NH···S hydrogen bonds were also found in dinuclear μ-diazene complexes of iron[5] and ruthenium.[3]

Thus, the present study shows the unique capability of the 16-electron (η^6-arene)$Ru(SR)_2$ core to bind the hydrazine molecule in two modes: the η^1-terminal and μ^2-bridging coordinations, whose bonding features are compared on the basis of X-ray analysis of **3** and **4**. The latter mode was stabilized by the existence of hydrogen bonds between the hydrazine and the sulfur atoms.

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9 **3**: red crystals, 70% yield, mp 138—140 °C (decomp). ^{1}H NMR ($CDCl_3$, 30 °C): δ 2.51 (s, 12H, 2,6-SC_6H_3*Me*$_2$), 3.97 (br, 4H, N_2*H*$_4$), 4.73 (s, 6H, C_6*H*$_6$), 7.01—7.15 (m, 6H, 2,6-SC_6*H*$_3Me_2$); IR (Nujol): ν (NH)/cm^{-1} 3300 (s), 3200 (m). Anal. Calcd for $C_{22}H_{28}N_2RuS_2$: C, 54.40; H, 5.81; N, 5.77%. Found: C, 54.20; H, 6.07; N, 5.95%; **4**: red crystals, 71% yield, mp 128—130 °C (decomp). ^{1}H NMR ($CDCl_3$, 30 °C): δ 2.37 (s, 36H, C_6Me_6), 3.09 (br, 4H, N*H*$_2$N*H*$_2$), 7.05 and 7.91 (AA'BB' pattern, ^3J = 6.1 Hz, ^4J = 3.2 Hz, 8H, 1,2–S_2C_6*H*$_4$); IR (Nujol): ν (NH)/cm^{-1} 3160 (m), 3080 (m). Anal. Calcd for $C_{36}H_{48}N_2Ru_2S_4(CH_2Cl_2)_{0.25}$: C, 50.59; H, 5.68; N, 3.26%. Found: C, 50.54; H, 5.73; N, 4.10%.
10 Crystal data for **3**: formula = $C_{22}H_{28}N_2RuS_2$, FW = 485.67, trigonal (R-centered) space group $R\bar{3}$ (h) (# 148), a = 32.595(7), c = 10.862(8) Å, Z = 18, V = 9994(9) Å^3, d_{calcd} = 1.452 gcm^{-3}, $2\theta_{max}$ = 55.1°, R (R_w) = 0.056 (0.071) for 3955 reflection data with $I > 1.5\sigma(I)$ and 244 valuables; Crystal data for **4**: formula = $C_{37}H_{50}N_2Cl_2Ru_2S_4$ (one dichloromethane as a solvated molecule), FW = 924.10, monoclinic space group $C2/c$ (# 15), a = 19.892(4), b = 12.038(3), c = 17.107(4) Å, β = 105.52(2)°, Z = 4, V = 3947(1) Å^3, d_{calcd} = 1.555 gcm^{-3}, $2\theta_{max}$ = 55.0°, R (R_w) = 0.045 (0.048) for 3919 reflection data with $I > 3\sigma(I)$ and 213 valuables.
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