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Communications

Catalytic N–N Bond Cleavage of Hydrazines at the Coordinatively Unsaturated Diruthenium Center in $[Cp^*Ru(\mu\text{-}SR)_2RuCp^*]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; $R = Pr^i$, 2,6-$Me_2C_6H_3$) and Isolation of μ-Phenyldiazene Complexes $[Cp^*Ru(\mu\text{-}PhN{=}NH)(\mu\text{-}SR)_2RuCp^*]$

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Structural models of the FeMo cofactor recently deduced from X-ray analysis of the FeMo proteins of *Azotobacter vinelandii* and *Clostridium pasteurianum* contain Fe_4S_3 and $MoFe_3S_3$ cuboidal subunits bridged by three sulfide ligands.[1] The significant feature demonstrated by these models is the presence of six coordinatively unsaturated Fe atoms with trigonal planar geometry forming a trigonal prism, and although the actual N_2 binding mode is yet uncertain, more than two of these Fe atoms have been suggested to be associated with N_2 coordination.[1a,2] Reactions of N_2 as well as diazenes and hydrazines which proceed at a multimetallic site surrounded by sulfur ligands are therefore of increasing interest. However, in contrast to the significant progress in the chemistry of coordinated dinitrogen in mononuclear complexes, especially $[M(N_2)_2(\mathbf{P})_4]$ (M = Mo, W; **P** = tertiary phosphine),[3] reactivities of multinuclear complexes toward N_2 and relating nitrogenous substrates are relatively unexplored.[4]

Our recent studies on the reactivities of a series of thiolate-bridged diruthenium complexes[5] have shown that $[Cp^*Ru(\mu\text{-}SPr^i)_2RuCp^*]$ (**1a**; $Cp^* = \eta^5\text{-}C_5Me_5$), which has two coordinatively unsaturated Ru(II) centers bridged by two thiolate ligands, displays intriguing reactivities toward various substrates including H_2, CO, and alkynes.[5d,6] As an extension of these studies, we have now found that reactions of hydrazines with **1a** result in the catalytic N–N bond cleavage under mild conditions. Intermediate dinuclear μ-diazene complexes have been isolated or detected spectroscopically.

Treatment of **1** with 2 equiv of phenylhydrazine in toluene at room temperature afforded dinuclear phenyldiazene complexes $[Cp^*Ru(\mu\text{-}\eta^1\text{:}\eta^1\text{-}PhN{=}NH)(\mu\text{-}SR)_2RuCp^*]$ (**2**) as a blue oil (**2a**, $R = Pr^i$)[7] or a deep green crystalline solid (**2b**, R = Xy; Xy = 2,6-$Me_2C_6H_3$)[8] in moderate yields. Concurrent formation of nearly equimolar amounts of aniline and ammonia per **1** was observed (eq 1), and neither H_2 nor N_2 was evolved during the reaction. The ^1H NMR spectra of **2** exhibit a singlet with the

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(7) To a deep blue-green solution of **1a** (151.5 mg, 0.243 mmol) in toluene (4 mL) was added phenylhydrazine (56.8 mg, 0.525 mmol), and the mixture was stirred for 8 h. After the amounts of aniline (0.76 mol/mol of **1a**) and ammonia (0.75 mol/mol of **1a**) in the reaction mixture were determined,[9] the evaporated reaction mixture residue was chromatographed on silica gel with THF–hexane (6% v/v). Evaporation of the solvent from a deep blue band gave **2a** as a blue oil (92.3 mg, 52%). Satisfactory analytical data are not yet available for **2a** despite the repeated purification, although the ^1H NMR spectrum is completely consistent with the dinuclear structure. ^1H NMR (C_6D_6): δ 12.67 (s, 1H, NH, disappeared upon treatment with D_2O), 6.91–7.52 (m, 5H, C_6H_5), 2.22 (sep, 2H, SC*H*Me_2), 1.74, 1.66 (s, 15H each, Cp*), 1.12, 1.11 (d, 6H each, SCH*Me*$_2$).

(8) To a purple solution of **1b** (95.5 mg, 0.128 mmol) in toluene (4 mL) was added phenylhydrazine (28.9 mg, 0.267 mmol), and the reaction mixture was stirred for 8 h. Aniline (0.90 mol/mol of **1b**) and ammonia (0.88 mol/mol of **1b**) produced were quantitatively analyzed.[9] Addition of acetonitrile to the concentrated reaction mixture gave **2b** as a crystalline solid (59.9 mg, 73%). ^1H NMR (C_6D_6): δ 13.40 (s, 1H, NH, disappeared upon treatment with D_2O), 6.99–7.82 (m, 11H, aryl), 3.14, 1.89 (s, 6H each, SC_6H_3*Me*$_2$), 1.35, 1.32 (s, 15H each, Cp*). Anal. Calcd for $C_{42}H_{54}N_2S_2Ru_2$: C, 59.13; H, 6.38; N, 3.28. Found: C, 58.64; H, 6.47; N, 3.36.

(9) Yields of aniline, N_2, and H_2 were determined by GLC. Ammonia and hydrazine were quantified as previously reported.[10]

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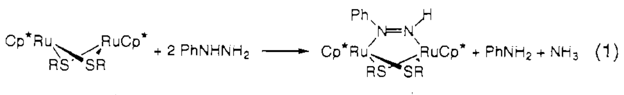


1a (R = Pr^i)
1b (R = Xy)

2a, R = Pr^i, 52%
2b, R = Xy, 73%

intensity of 1 H in an extremely low field (**2a**, 12.67; **2b**, 13.40 ppm), which is characteristic of the proton attached to the η^1-N atom in the diazene ligand.[11] Other ^{1}H NMR data are also consistent with the dinuclear structure of **2** shown in eq 1. The presence of a bridging phenyldiazene ligand in **2** has also been suggested by the IR spectra (KBr disk), showing strong absorptions at 1246 (**2a**) and 1233 cm^{-1} (**2b**) assignable to $\nu_{N=N}$. Relatively low frequencies may be ascribed to the 4c–6e π bonding in the Ru⋯N⋯N⋯Ru core as observed in other μ-diazene complexes.[12]

Although how 2 mol of phenylhydrazine disproportionate into aniline, ammonia, and a bridging phenyldiazene ligand is still obscure, the adjacent coordinatively unsaturated metals in **1** seem to play an important role in the N–N bond cleavage in this reaction. An osmium cluster with labile nitrile ligands, [Os$_3$(CO)$_{10}$(MeCN)$_2$], is known to react with phenylhydrazine to give μ-phenyldiazenido–μ-hydrido cluster [(μ-H)Os$_3$(CO)$_{10}$(μ-η^1:η^1-N=NPh)], but the reaction stoichiometry and mechanism are not clear.[13]

Interestingly, reaction of **1a** with 50 equiv of phenylhydrazine gave aniline and ammonia in higher yields than those expected by the stoichiometry shown in eq 1, accompanied by evolution of some N$_2$ gas.[14] This may indicate that the generated **2a** reacted further with phenylhydrazine to give these nitrogenous products. Actually, treatment of the isolated **2a** with excess phenylhydrazine produced aniline, ammonia, and N$_2$.

These findings prompted us to extend this reaction system to that containing unsubstituted hydrazine, and we have found that the catalytic disproportionation reaction of hydrazine into ammonia and N$_2$ takes place smoothly in the presence of **1** (eq 2). Results of the reactions using 50 equiv of N$_2$H$_4$ per **1** are

$$3\,N_2H_4 \xrightarrow{1} N_2 + 4\,NH_3 \qquad (2)$$

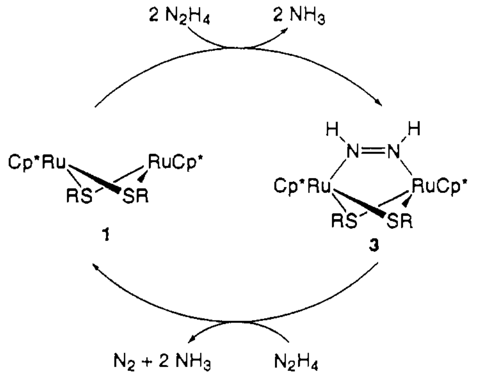
summarized in Table 1. On the other hand, treatment of 10 equiv of N$_2$H$_4$ with **1a** at room temperature resulted in the completion of this disproportionation reaction in 16 h and the ^{1}H NMR spectrum of the reaction mixture confirmed the almost quantitative regeneration of **1a**. Although isolation and full characterization of intermediate complexes were unsuccessful, ^{1}H NMR spectra of the mixtures at the early stages of the reaction have shown the resonances assignable to diazene complexes [Cp*Ru(μ-η^1:η^1-HN=NH)(μ-SR)$_2$RuCp*] (**3a**, R = Pr^i; **3b**, R = Xy).[15] It is to be noted that several dinuclear diazene complexes reported previously[4a] contain μ-η^1:η^1-*trans*[12] or μ-η^2:η^2 bound[16] diazene ligands and, to our knowledge, μ-η^1:η^1-*cis*-diazene complexes are unknown despite that such a coordination mode has been demonstrated in certain diphenyldiazene complexes.[17] In the absence of hydrazine, **3a** does not react further, yielding neither hydrazine, ammonia, nor N$_2$, which suggests that the conversion of **3** into **1** proceeds through the reaction of **3** with hydrazine. A plausible catalytic cycle based on these observations is depicted in Scheme 1.

Table 1. Catalytic Disproportionation of Hydrazine[a]

complex	temp (°C)	conversion of N$_2$H$_4$ (%)[b]	yield[c,d] NH$_3$	yield[c,d] N$_2$
1a	rt	44	32	5.5
1a	40	91	66	13
1b	rt	6	4	0.9

[a] Reaction conditions: **1**, 0.04 mmol; N$_2$H$_4$·H$_2$O (80%), 2 mmol; toluene, 4 mL; 16 h; under Ar. [b] (mol of N$_2$H$_4$ consumed/mol of N$_2$H$_4$ charged) × 100. [c] See ref 9. [d] mol per mol of **1**.

Scheme 1



The present study has demonstrated that the diruthenium(II) center bridged by thiolate ligands can facilitate the N–N bond cleavage of hydrazines under mild conditions and provides the catalytic site for disproportionation of hydrazine into ammonia and dinitrogen. Involvement of diazene in the catalytic cycle is noteworthy. Relating catalytic disproportionation of hydrazine using a certain dimolybdenum complex as a catalyst precursor was reported recently.[18] Although disproportionation[19] and catalytic reduction[20] of hydrazine are known to be promoted also at a single metal center, the results reported here are of considerable interest since they might have some relevance to the activation and transformation of dinitrogen in the FeMo cofactor. Further studies are now under way to clarify not only the mechanism operating in this hydrazine disproportionation reaction but also the new reactivities of the diazene complexes reported here.

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(14) To a solution of **1a** (65.5 mg, 0.105 mmol) in toluene (4 mL) was added phenylhydrazine (0.52 mL, 5.3 mmol) under Ar, and the reaction mixture was stirred for 42 h. Yields of N$_2$, aniline, and ammonia were 0.3, 4.2, and 1.2 mol/mol of **1a**, respectively.[9]

(15) ^{1}H NMR (C$_6$D$_6$) for **3a**: δ 12.30 (s, 2H, NH), 2.08 (sep, 2 H, SC*H*Me$_2$), 1.83 (s, 30 H, Cp*), 0.93 (d, 12 H, SCH*Me*$_2$). For **3b**: δ 12.74 (s, 2 H, NH), 6.82–7.30 (m, 6 H, SC$_6$*H*$_3$Me$_2$), 3.08, 1.53 (s, 6 H each, SC$_6$H$_3$*Me*$_2$), 1.46 (s, 30 H, Cp*).

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