bioactive natural products.[1] Moreover, this work suggests that E_p can accept greater C2/C3 steric bulk in the substrate (relative to **3**), which opens the door to even more imaginative substitutions at these positions. Efforts are in progress to further expand the scope of this methodology.

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$[Ru(N_2)(PiPr_3)('N_2Me_2S_2')]$: Coordination of Molecular N_2 to Metal Thiolate Cores under Mild Conditions[**]

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Dedicated to Professor Ernst-Gottfried Jäger on the occasion of his 65th birthday

X-ray crystallography has revealed the structure of FeMo nitrogenase and its FeMo cofactors, however, the molecular mechanism of biological N_2 fixation has remained as unknown as low-molecular weight compounds catalyzing the reduction of N_2 under mild and biologically compatible conditions.[1] These conditions rule out the use of alkali metals or comparably strong reductants at any stage in the design of a nonenzymatic chemical system for modeling the biological N_2 reduction. This includes the first stage, the synthesis of N_2 complexes.

All mechanisms postulated for biological N_2 fixation consider the coordination of N_2 to the metal sulfur core of the Fe_7MoS_9 cofactors as the first key step.[1] However, *metal sulfur complexes* that bind N_2 under mild conditions are unknown, in spite of numerous intensive efforts.[2] There are only 12 N_2 complexes with sulfur coligands,[3] only two of which could be prepared directly from molecular N_2.[3a,f] Their preparation, however, required strong reductants or precursors prepared by use of strong reductants. None of these complexes meets the severe constraints with regard to mild conditions.

Our attempts to tackle this problem have focussed on sulfur ligand complexes of iron and its congener ruthenium. They

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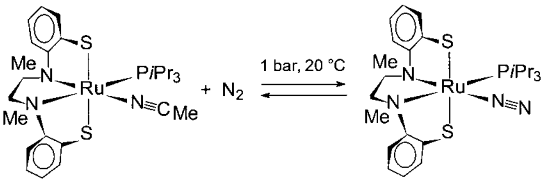
have now led to a N$_2$ reaction that transforms the acetonitrile complex [Ru(MeCN)(P*i*Pr$_3$)(‘N$_2$Me$_2$S$_2$’)] (**1**) under mild conditions into the N$_2$ complex [Ru(N$_2$)(P*i*Pr$_3$)(‘N$_2$Me$_2$S$_2$’)] (**2**) [Eq. (1)].



(1)

1 **2**

The precursor MeCN complex **1** was obtained from [Ru(Cl)$_2$(MeCN)$_4$] and Li$_2$[‘N$_2$Me$_2$S$_2$’] in the presence of P*i*Pr$_3$. Complexes **1** and **2** have been completely characterized. Figure 1 shows their molecular structures.[4]

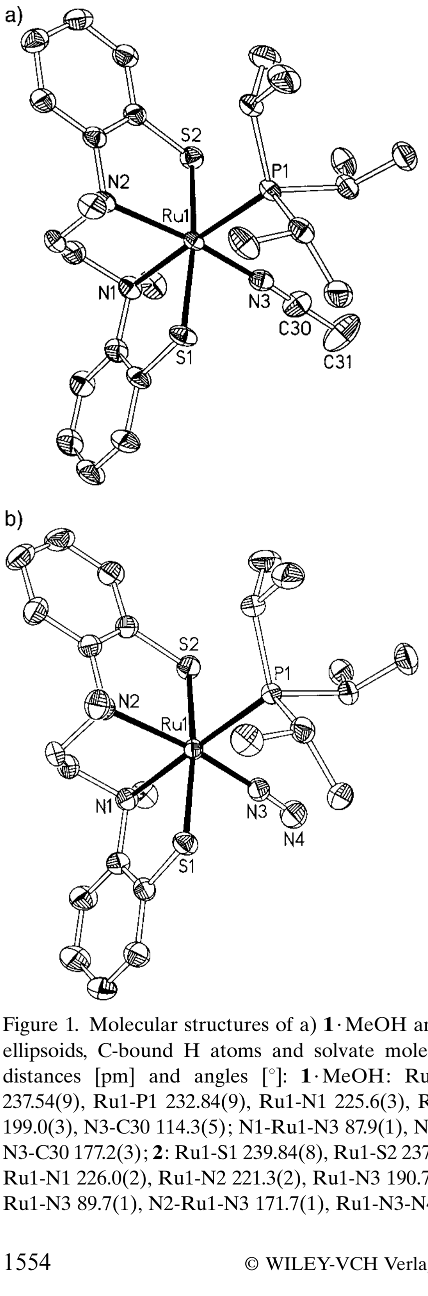


Figure 1. Molecular structures of a) **1**·MeOH and b) **2** (50% probability ellipsoids, C-bound H atoms and solvate molecules omitted). Selected distances [pm] and angles [°]: **1**·MeOH: Ru1-S1 238.52(9), Ru1-S2 237.54(9), Ru1-P1 232.84(9), Ru1-N1 225.6(3), Ru1-N2 221.9(3), Ru1-N3 199.0(3), N3-C30 114.3(5); N1-Ru1-N3 87.9(1), N2-Ru1-N3 170.0(1), Ru1-N3-C30 177.2(3); **2**: Ru1-S1 239.84(8), Ru1-S2 237.94(8), Ru1-P1 235.72(8), Ru1-N1 226.0(2), Ru1-N2 221.3(2), Ru1-N3 190.7(3), N3-N4 111.0(4); N1-Ru1-N3 89.7(1), N2-Ru1-N3 171.7(1), Ru1-N3-N4 176.9(3).

The [Ru(P*i*Pr$_3$)(‘N$_2$Me$_2$S$_2$’)] core distances and angles of **1** and **2** are nearly identical. This holds true, in particular, for the distances Ru1–N2 *trans* to the coligands MeCN and N$_2$, which are 221.9(3) pm in **1** and 221.3(2) pm in **2**. These distances are relatively short, and considerably shorter than the corresponding distance in [Ru(CO)(P*i*Pr$_3$)(‘N$_2$Me$_2$S$_2$’)] (**3**) (229.2(4) pm).[5] They indicate a practically identical *trans* influence of N$_2$ and MeCN, and explain the ready MeCN → N$_2$ exchange of **1**. In this context, two important functions of the methyl substituents at the amine donors need to be mentioned. A comparison of [Ru(L)(L′)(‘N$_2$Me$_2$S$_2$’)] and their analogous [Ru(L)(L′)(‘N$_2$H$_2$S$_2$’)] parent complexes shows that the methyl substituents cause a slight elongation of the Ru–N distances and stabilize the Ru^{II} oxidation state towards oxidation.[5] A characteristic property of [Ru(L)(L′)(‘N$_2$H$_2$S$_2$’)] complexes is their spontaneous self-oxidation to give [Ru^{IV}(L)(‘N$_2$S$_2$’)] complexes with ‘N$_2$S$_2$$^{4-}$’ = 1,2-ethanediamido-*N*,*N*′-bis(2-benzenedithiolate) (4 –).[6]

The N$_2$ ligand binds end-on to the Ru center of **2**, the $\nu(N_2)$ frequency (2113 cm^{-1}, KBr) reflects a normal N$_2$ activation in **2** when compared with other N$_2$ complexes or the $\nu(CO)$ frequency of **3** (1930 cm^{-1}, KBr).[2] In this respect, **2** looks like a regular N$_2$ complex. Unique for **2**, and unprecedented, however, are the mild conditions under which N$_2$ binds to yield metal thiolate N$_2$ complexes.

This raises the question why the attempts to synthesize such complexes have remained unsuccessful for such a long time. There are two major reasons. 1) It is well established that the coordination of N$_2$ can depend on triflingly minor looking subtleties. For example, exchange of PPh$_3$ for P(*p*-tolyl)$_3$ causes instability of the Ir–N$_2$ bond in [Ir(N$_2$)(Cl)(PPh$_3$)$_2$].[7] In other words, metal and N$_2$ orbitals have to match precisely in order to warrant binding of N$_2$. 2) Thiolate (and also sulfide) donors are principally adverse to the coordination of N$_2$. Binding N$_2$ to a metal center requires a vacant site of coordination. Metal thiolate (or sulfide) complexes, however, are notorious for saturating vacant sites by formation of M-S-M bridges and oligo- to polynuclear complexes. In nitrogenase, such N$_2$ binding sites at the FeMoco may be kept vacant through steric strain and shielding provided by the enzyme protein. Low-molecular-weight thiolate complexes, however, need to achieve simultaneously the electronic “fine-tuning” of the vacant site and the delicate balance between the competing reactions of blocking this site either by N$_2$ or by a sulfur donor from another metal thiolate complex fragment. As yet, there is no other way than carrying out the experiments to elucidate the conditions necessary for meeting these constraints.

Preliminary experiments show that the thiolate donors of **2** are Brønsted-basic and can be protonated by HBF$_4$. This constitutes an essential requirement for 2H$^+$/2e$^-$ reductions of N$_2$ complexes.[8] In addition, replacement of N$_2$ by H$_2$ yields the hydride–thiol species [Ru(H)(P*i*Pr$_3$)(‘N$_2$Me$_2$S$_2$-H’)].

Experimental Section

All manipulations were carried out in absolute solvents under nitrogen or argon. [RuCl$_2$(MeCN)$_4$][9] and ‘N$_2$Me$_2$S$_2$-H$_2$’[10] were prepared as described in the literature.

1: A solution of '$N_2Me_2S_2$-H_2' (696 mg, 2.29 mmol) in MeOH (35 mL) and 1N LiOMe in MeOH (9.16 mL, 9.16 mmol) was added dropwise to a boiling MeOH suspension of $[RuCl_2(MeCN)_4]$ (768 mg, 2.29 mmol) and P*i*Pr$_3$ (0.89 mL, 4.57 mmol). The resulting yellow solution was heated for another 45 min under reflux, filtered while hot, and stored at −20 °C for 12 h. The precipitated yellow crystals were separated at −20 °C, washed with MeOH (50 mL), and dried in vacuo for 12 h (980 mg, 69 %). Correct elemental analyses. IR (KBr): $\tilde{\nu} = 2245$ (ν_{CN}) cm^{-1}; ^{1}H NMR (269.7 MHz, CD_2Cl_2): $\delta = 7.53-6.70$ (m, 8H; C_6H_4), 3.33 (s, 3H; CH_3), 3.28 (s, 3H; CH_3), 3.30–2.20 (m, 4H; C_2H_4), 2.20 (s, 3H; CH_3CN), 2.19–2.09 (m, 3H; P(CH)), 1.36–1.24 (m, 18H; (CH_3)); $^{13}C\{^1H\}$ NMR (67.7 MHz, CD_2Cl_2): $\delta = 157.7$ (CH_3CN), 154.3, 153.9, 153.1, 151.7, 131.5, 131.2, 126.0, 125.7, 123.4, 122.0, 120.3, 119.9 (C_6H_4), 68.4, 62.0 (C_2H_4), 50.3, 47.8 (CH_3), 27.6 (d, *J*(P,C) = 18 Hz), 20.8, 19.5 ($P(C_3H_7)$); $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): $\delta = 50$ (s); FD-MS (CH_2Cl_2, ^{102}Ru, rel. intensity): *m/z* (%): 564 (100) $[Ru(PiPr_3)('N_2Me_2S_2')]^+$, 605 (12) $[Ru(MeCN)(PiPr_3)('N_2Me_2S_2')]^+$.

2: A stream of N_2 was passed through a solution of **1** (1.58 g, 2.6 mmol) in toluene (50 mL), until the ν_{N_2} IR band of **2** showed maximum intensity (ca. 30 min). At the end of the reaction, the solution was gently heated to 40–50 °C to remove liberated MeCN. After filtration, *n*-hexane (200 mL) was added precipitating unreacted **1**, which was removed after 30 min. The remaining *n*-hexane/toluene solution was reduced in volume to about 100 mL by passing a stream of N_2 through the solution. Yellow-green **2** precipitated, was separated, washed with Et_2O (3 mL), and dried in vacuo for 3 h (720 mg, 46 %). Correct elemental analyses. IR (KBr): $\tilde{\nu} = 2113$ (ν_{N_2}) cm^{-1}; ^{1}H NMR (269.7 MHz, THF): $\delta = 7.47-6.77$ (m, 8H; C_6H_4), 3.42 (s, 3H; CH_3), 3.38 (s, 3H; CH_3), 3.37–2.30 (m, 4H; C_2H_4), 2.30–2.23 (m, 3H; P(CH)), 1.38–1.30 (m, 18H; (CH_3)); $^{13}C\{^1H\}$ NMR (67.7 MHz, THF): $\delta = 155.8$, 155.0, 153.6, 153.4, 134.0, 133.9, 128.9, 128.8, 124.4, 123.6, 123.5, 123.0 (C_6H_4), 70.7, 64.5 (C_2H_4), 54.2, 50.1 (CH_3), 30.1 (d, *J*(P,C) = 18 Hz), 23.0, 21.8 ($P(C_3H_7)$); $^{31}P\{^1H\}$ NMR (161.7 MHz, THF): $\delta = 48$ (s); FD-MS (THF, ^{102}Ru, rel. intensity): *m/z* (%): 564 (100) $[Ru(PiPr_3)(N_2Me_2S_2)]^+$, 592 (8) $[Ru(N_2)(PiPr_3)(N_2Me_2S_2)]^+$.

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Synthesis and Characterization of $RbLi_7Ge_8$ with Isolated *closo*-$[Li_4Ge_{12}]^{8-}$ Ions, Lithium-Capped Truncated Tetrahedra of Ge_{12}^{12-}[**]

Svilen Bobev and Slavi C. Sevov*

Zintl phases with isolated clusters of more than four atoms were very rare fifteen years ago, when only a few examples were known.[1] Since then, however, this number has skyrocketed with many examples of Groups 13 (Tr = Triels) and 14 (Tt = Tetrels) as well as some heteroatomic species.[2] Furthermore, many compounds in the A–Tt systems (A = alkali metal) were found to contain isolated deltahedral clusters, often referred to as Zintl ions, that were previously either unknown[3] or could be crystallized from solutions only.[4] Understanding the electronic structure and bonding in Zintl phases with deltahedral clusters combines both the assumption for complete electron transfer from the alkali metal atoms to the clusters (the Zintl–Klemm concept)[1, 5] with the Wade's rules for electron counting in deltahedral boranes.[6] Our interest has focused especially on clusters of

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