

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.

Received: November 24, 2000

Revised: January 10, 2001 [Z16173]

- [1] J. S. Thorson, T. J. Hosted, Jr., J. Jiang, J. B. Biggins, J. Ahlert, M. Ruppen, *Curr. Org. Chem.* **2001**, 5, 89–111, and references therein.
- [2] P. J. Solenberg, P. Matsushima, D. R. Stack, S. C. Wilkie, R. C. Thompson, R. H. Baltz, *Chem. Biol.* **1997**, 4, 195–202.
- [3] J. Jiang, J. B. Biggins, J. S. Thorson, *J. Am. Chem. Soc.* **2000**, 122, 6803–6804; for recent reviews see: K. M. Koeller, C.-H. Wong, *Nat. Biotechnol.* **2000**, 18, 835–841; J. M. Elhalabi, K. G. Rice, *Curr. Med. Chem.* **1999**, 6, 93–116; M. M. Palcic, *Curr. Opin. Biotechnol.* **1999**, 10, 616–624; H. J. M. Gijzen, L. Qiao, W. Fitz, C.-H. Wong, *Chem. Rev.* **1996**, 96, 443–473; C.-H. Wong, *Pure Appl. Chem.* **1995**, 67, 1609–1616; C.-H. Wong, R. L. Halcomb, Y. Ichikawa, T. Kajimoto, *Angew. Chem.* **1995**, 107, 569–593; *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 521–546; Y. Ichikawa, G. C. Look, C.-H. Wong, *Anal. Biochem.* **1992**, 202, 215–238.
- [4] This enzyme (E.C. 2.7.7.24) is also known as dTDP-glucose synthase, dTDP-glucose pyrophosphorylase, thymidine diphosphoglucose pyrophosphorylase, and thymidine diphosphate glucose pyrophosphorylase. The name “E_p” historically derives from the original pyrophosphorylase designation.
- [5] V. Maunier, P. Boullanger, D. Lafont, Y. Chevalier, *Carbohydr. Res.* **1997**, 299, 49–57.
- [6] W. A. Greenberg, E. S. Priestley, P. S. Sears, P. B. Alper, C. Rose-nbohm, M. Hendrix, S.-C. Hung, C.-H. Wong, *J. Am. Chem. Soc.* **1999**, 121, 6527–6541.
- [7] P. J. Garegg, I. Kvarnstrom, A. Niklasson, G. Niklasson, S. C. T. Svensson, *J. Carbohydr. Chem.* **1993**, 12, 933–953.
- [8] E_p was purified as described in ref. [3] from a *rmlA* expression strain (L. Lindquist, R. Kaiser, P. R. Reeves, A. A. Lindberg, *Eur. J. Biochem.* **1993**, 211, 763–770) and this homogeneous preparation was utilized for the present study. The expression strain for this enzyme was provided by Professor Hung-wen Liu (Medicinal Chemistry, University of Texas, Austin).
- [9] The inorganic pyrophosphatase was included to drive the reaction forward. For examples, see: a) D. C. Crans, R. J. Kazlauskas, B. L. Hirschbein, C.-H. Wong, O. Abril, G. M. Whitesides, *Methods Enzymol.* **1987**, 136, 263–280; b) S. L. Haynie, G. M. Whitesides, *Appl. Biochem. Biotechnol.* **1990**, 23, 155–170; c) Y. Ichikawa, R. Wang, C.-H. Wong, *Methods Enzymol.* **1994**, 247, 107–124.
- [10] The reaction of a mixture containing NTP (2.5 mM), sugar phosphate (5.0 mM), MgCl₂ (5.5 mM), and inorganic pyrophosphatase (10 U; 1 U = the amount of protein needed to produce 1 μmol min⁻¹ of TDP-D-glucose) in potassium phosphate buffer (pH 7.5, 50 mM, 50 μL) at 37 °C was initiated by the addition of E_p (3.52 U). The reaction was incubated with slow agitation for 30 min at 37 °C, quenched with MeOH (50 μL), centrifuged (5 min, 14000 × g), and the supernatant was stored at –20 °C until analysis by HPLC. Samples (30 μL) were resolved on a Spherclone 5 μ SAX column (150 × 4.6 mm) fitted with a SecurityGuard cartridge (Phenomenex, Torrance, CA) by using a linear gradient (potassium phosphate buffer, pH 5.0, 50–200 mM, 1.5 mL min⁻¹, A_{275nm}).
- [11] HPLC product fractions from the assay described in ref. [10] were lyophilized and submitted directly for HR-MS (fast-atom bombardment (FAB)) analysis.
- [12] Allosteric activation is common for the nucleotidyltransferase family. For examples, see: a) M. X. Wu, J. Preiss, *Arch. Biochem. Biophys.* **1998**, 358, 182–188; b) D. A. Bulik, P. van Ophem, J. M. Manning, Z. Shen, D. S. Newburg, E. L. Jarroll, *J. Biol. Chem.* **2000**, 275, 14722–14728. However, data is not yet available pertaining to the allosteric effectors of E_p.
- [13] The product of this reaction, thymidine 5'-(4-amino-4,6-dideoxy-α-D-glucopyranosyl diphosphate), is a critical intermediate in the forma-

tion of the calicheamicin aryltetrasaccharide. See: a) J. S. Thorson, B. Shen, R. E. Whitwam, W. Liu, Y. Li, J. Ahlert, *Bioorg. Chem.* **1999**, 27, 172–188; b) R. E. Whitwam, J. Ahlert, T. R. Holman, M. Ruppen, J. S. Thorson, *J. Am. Chem. Soc.* **2000**, 122, 1556–1557; c) J. B. Biggins, J. R. Prudent, D. J. Marshall, M. Ruppen, J. S. Thorson, *Proc. Natl. Acad. Sci. USA* **2000**, 97, 13537–13542; d) J. S. Thorson, E. L. Sievers, J. Ahlert, E. Shepard, R. E. Whitwam, K. C. Onwueme, M. Ruppen, *Curr. Pharm. Des.* **2000**, 6, 1841–1879).

Note added in proof: The three-dimensional structure of E_p and the structure-based engineering of E_p to expand the methodology reported here have recently been reported (W. A. Barton, J. Lesniak, J. B. Biggins, P. D. Jeffrey, J. Jiang, K. R. Rajashankar, J. S. Thorson, D. B. Nikolov, *Nat. Struct. Biol.* **2001**, in press).

[Ru(N₂)(PiPr₃)(‘N₂Me₂S₂’)]⁺: Coordination of Molecular N₂ to Metal Thiolate Cores under Mild Conditions**

Dieter Sellmann,* Barbara Hautsch, Annette Rösler, and Frank W. Heinemann

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 N₂ fixation has remained as unknown as low-molecular weight compounds catalyzing the reduction of N₂ 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 N₂ reduction. This includes the first stage, the synthesis of N₂ complexes.

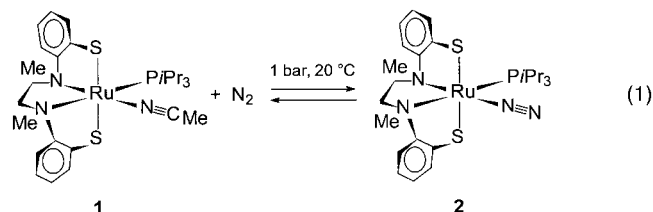
All mechanisms postulated for biological N₂ fixation consider the coordination of N₂ to the metal sulfur core of the Fe₇MoS₉ cofactors as the first key step.^[1] However, *metal sulfur complexes* that bind N₂ under mild conditions are unknown, in spite of numerous intensive efforts.^[2] There are only 12 N₂ complexes with sulfur coligands,^[3] only two of which could be prepared directly from molecular N₂.^[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

[*] Prof. Dr. D. Sellmann, Dipl.-Chem. B. Hautsch, Dipl.-Chem. A. Rösler, Dr. F. W. Heinemann
Institut für Anorganische Chemie
Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax: (+49)9131-852-7367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

[**] Transition Metal Complexes with Sulfur Ligands, Part 150. This work was supported by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. Part 149: D. Sellmann, F. Geipel, F. W. Heinemann, *Z. Anorg. Allg. Chem.*, in press. ‘N₂Me₂S₂²⁻’ = 1,2-ethanediamine-*N,N'*-dimethyl-*N,N'*-bis(2-benzenethiolate)(2–).

have now led to a N_2 reaction that transforms the acetonitrile complex $[Ru(MeCN)(PiPr_3)(N_2Me_2S_2)]$ (**1**) under mild conditions into the N_2 complex $[Ru(N_2)(PiPr_3)(N_2Me_2S_2)]$ (**2**) [Eq. (1)].



The precursor MeCN complex **1** was obtained from $[Ru(Cl)_2(MeCN)_4]$ and $Li_2[N_2Me_2S_2]$ in the presence of $PiPr_3$. Complexes **1** and **2** have been completely characterized. Figure 1 shows their molecular structures.^[4]

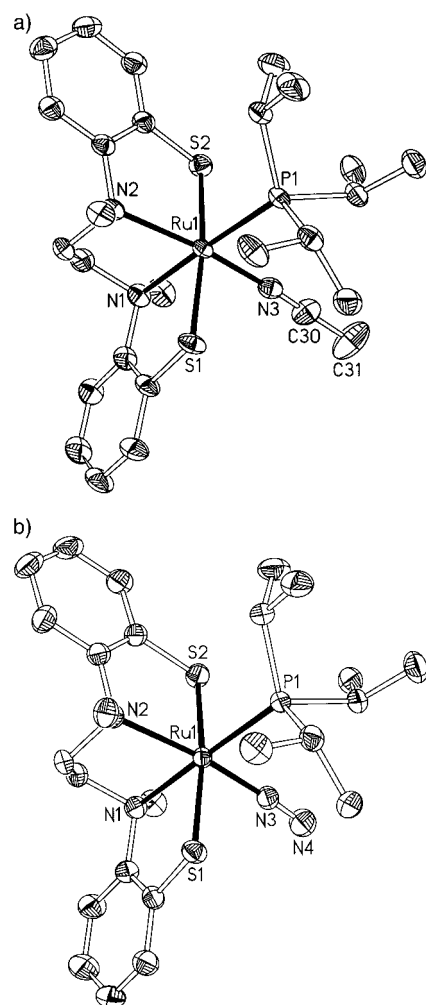


Figure 1. Molecular structures of a) **1**·MeOH and b) **2** (50% probability ellipsoids, C-bound H atoms and solvate molecules omitted). Selected distances [pm] and angles [°]: **1**·MeOH: Ru1-S1 238.52(9), Ru1-S2 237.54(9), Ru1-P1 232.84(9), Ru1-N1 225.6(3), Ru1-N2 221.9(3), Ru1-N3 199.0(3), N3-C30 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 $[Ru(PiPr_3)(N_2Me_2S_2)]$ 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 $[Ru(CO)(PiPr_3)(N_2Me_2S_2)]$ (**3**) (229.2(4) pm).^[5] They indicate a practically identical *trans* influence of N_2 and MeCN, and explain the ready MeCN $\rightarrow N_2$ exchange of **1**. In this context, two important functions of the methyl substituents at the amine donors need to be mentioned. A comparison of $[Ru(L)(L')(N_2Me_2S_2)]$ and their analogous $[Ru(L)(L')(N_2H_2S_2)]$ 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 $[Ru(L)(L')(N_2H_2S_2)]$ complexes is their spontaneous self-oxidation to give $[Ru^{IV}(L)(N_2S_2)]$ complexes with $N_2S_2^{4-} = 1,2$ -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 $P(p\text{-tolyl})_3$ 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 $[Ru(H)(PiPr_3)(N_2Me_2S_2-H)]$.

Experimental Section

All manipulations were carried out in absolute solvents under nitrogen or argon. $[RuCl_2(MeCN)_4]$ ^[9] and $N_2Me_2S_2 \cdot H_2$ ^[10] were prepared as described in the literature.

1: A solution of 'N₂Me₂S₂-H₂' (696 mg, 2.29 mmol) in MeOH (35 mL) and 1*N* LiOMe in MeOH (9.16 mL, 9.16 mmol) was added dropwise to a boiling MeOH suspension of [RuCl₂(MeCN)₄] (768 mg, 2.29 mmol) and *PiPr*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; ¹H NMR (269.7 MHz, CD₂Cl₂): δ = 7.53–6.70 (m, 8H; C₆H₄), 3.33 (s, 3H; CH₃), 3.28 (s, 3H; CH₃), 3.30–2.20 (m, 4H; C₂H₄), 2.20 (s, 3H; CH₃CN), 2.19–2.09 (m, 3H; P(CH₃)), 1.36–1.24 (m, 18H; (CH₃)); ¹³C{¹H} NMR (67.7 MHz, CD₂Cl₂): δ = 157.7 (CH₃CN), 154.3, 153.9, 153.1, 151.7, 131.5, 131.2, 126.0, 125.7, 123.4, 122.0, 120.3, 119.9 (C₆H₄), 68.4, 62.0 (C₂H₄), 50.3, 47.8 (CH₃), 27.6 (d, *J*(P,C) = 18 Hz), 20.8, 19.5 (P(C₃H₇)); ³¹P{¹H} NMR (161.7 MHz, CD₂Cl₂): δ = 50 (s); FD-MS (CH₂Cl₂, ¹⁰²Ru, rel. intensity): *m/z* (%): 564 (100) [Ru(*PiPr*₃)(N₂Me₂S₂)]⁺, 605 (12) [Ru(MeCN)(*PiPr*₃)(N₂Me₂S₂)]⁺.

2: A stream of N₂ 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 N₂ through the solution. Yellow-green **2** precipitated, was separated, washed with Et₂O (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; ¹H NMR (269.7 MHz, THF): δ = 7.47–6.77 (m, 8H; C₆H₄), 3.42 (s, 3H; CH₃), 3.38 (s, 3H; CH₃), 3.37–2.30 (m, 4H; C₂H₄), 2.30–2.23 (m, 3H; P(CH₃)), 1.38–1.30 (m, 18H; (CH₃)); ¹³C{¹H} NMR (67.7 MHz, THF): δ = 155.8, 155.0, 153.6, 153.4, 134.0, 133.9, 128.9, 128.8, 124.4, 123.6, 123.5, 123.0 (C₆H₄), 70.7, 64.5 (C₂H₄), 54.2, 50.1 (CH₃), 30.1 (d, *J*(P,C) = 18 Hz), 23.0, 21.8 (P(C₃H₇)); ³¹P{¹H} NMR (161.7 MHz, THF): δ = 48 (s); FD-MS (THF, ¹⁰²Ru, rel. intensity): *m/z* (%): 564 (100) [Ru(*PiPr*₃)(N₂Me₂S₂)]⁺, 592 (8) [Ru(N₂)(*PiPr*₃)(N₂Me₂S₂)]⁺.

Received: November 27, 2000 [Z16177]

a saturated boiling MeCN/MeOH (2:1) solution of **1** was slowly cooled to room temperature. C₂₈H₄₆N₃OPRuS₂, crystal size 0.70 × 0.60 × 0.40 mm, monoclinic, space group *P*₂₁/*n*, *a* = 1044.6(2), *b* = 1019.6(1), *c* = 2832.7(4) pm, β = 94.43(1)°, *V* = 3.0080(8) nm³, *Z* = 4, ρ_{calcd} = 1.406 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.74 mm⁻¹, *T* = 200 K, ω scans (10° min⁻¹); 8523 measured reflections (4.0 < 2 θ < 54.0°), 6569 unique reflections, 5350 observed reflections (*F*_o ≥ 4 σ (*F*)); 461 parameters, *wR*₂ = 0.1105, *R*₁ = 0.0446 (*F*_o ≥ 4 σ (*F*)). b) [Ru(N₂)(-*PiPr*₃)(N₂Me₂S₂)] (**2**). Yellow-green single crystals were grown by layering a saturated THF solution of **2** with MeOH. C₂₅H₃₉N₄PRuS₂, crystal size 0.52 × 0.46 × 0.36 mm, orthorhombic, space group *Pbca*, *a* = 1207.7(1), *b* = 1442.2(1), *c* = 3108.1(2) pm, *V* = 5.4135(7) nm³, *Z* = 8, ρ_{calcd} = 1.452 g cm⁻³, $\mu(\text{MoK}\alpha)$ = 0.81 mm⁻¹, *T* = 220 K, ω scans (12° min⁻¹); 8713 measured reflections (4.2 < 2 θ < 58.0°), 7194 unique reflections, 5106 observed reflections (*F*_o ≥ 4 σ (*F*)); 416 parameters, *wR*₂ = 0.0886, *R*₁ = 0.0396 (*F*_o ≥ 4 σ (*F*)). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153362 (**1**·MeOH) and CCDC-153363 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

- [5] A. Rösler, Dissertation, Universität Erlangen-Nürnberg, 2001.
[6] D. Sellmann, R. Ruf, F. Knoch, M. Moll, *Inorg. Chem.* **1995**, *34*, 5963–5972.
[7] D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460–469.
[8] J. Chatt, D. P. Melville, R. L. Richards, *J. Chem. Soc. A* **1969**, 2841–2844.
[9] D. Rose, G. Wilkinson, *J. Chem. Soc. A* **1970**, 2765–2769.
[10] D. Sellmann, R. Ruf, F. Knoch, M. Moll, *Z. Naturforsch. B* **1995**, *50*, 791–801.

- [1] a) J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965–2982; b) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983–3011; c) R. N. F. Thorneley, D. J. Lowe, *J. Biol. Inorg. Chem.* **1996**, *1*, 576–580; d) C. J. Pickett, *J. Biol. Inorg. Chem.* **1996**, *1*, 601–606; e) G. J. Leigh, *Eur. J. Biochem.* **1995**, *229*, 14–20; f) D. Sellmann, J. Sutter, *J. Biol. Inorg. Chem.* **1996**, *1*, 587–593.
[2] M. Hidai, Y. Mizobe, *Chem. Rev.* **1995**, *95*, 1115–1133.
[3] The known examples are: a) [Mo(N₂)₂(Me₈-16[ane]S₄)]: T. Yoshida, T. Adachi, M. Kaminaka, T. Ueda, *J. Am. Chem. Soc.* **1988**, *110*, 4872–4873; b) [Mo(N₂)₂(PMe₂Ph)₂(Ph₂PC₂H₄SM₂)]: R. H. Morris, J. M. Rössner, J. F. Sawyer, M. Shiralian, *J. Am. Chem. Soc.* **1984**, *106*, 3683–3684; c) [Mo(N₂)₂(PMe₂Ph)₂(PhSC₂H₄SPh)]: M. Aresta, A. Sacco, *Gazz. Chim. Ital.* **1972**, *102*, 755–759; d) [Re(N₂)(S₂CNR₂)(PMe₂Ph)₃]: J. Chatt, R. H. Crabtree, J. R. Dilworth, R. L. Richards, *J. Chem. Soc. Dalton Trans.* **1974**, 2358–2362; e) [Os(N₂)(Cl)(SC₂F₅)(PMe₂Ph)₃]: D. Cruz-Garrits, S. Gelover, H. Torrens, J. Leal, R. L. Richards, *J. Chem. Soc. Dalton Trans.* **1988**, 2393–2396; f) [Re(N₂)(SAR)₃(PPh₃)]: J. R. Dilworth, J. Hu, R. M. Thompson, D. L. Hughes, *J. Chem. Soc. Chem. Commun.* **1992**, 551–553; g) [N₂[M(S₂CNEt₃)₃]] (M = Nb, Ta): J. R. Dilworth, R. H. Henderson, A. Hills, D. L. Hughes, C. Macdonald, A. N. Stephens, D. R. M. Walton, *J. Chem. Soc. Dalton Trans.* **1990**, 1077–1085; h) [N₂[WCp*(Me)₂(SAR)₂]]: M. B. O'Regan, A. H. Liu, W. C. Finck, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1990**, *112*, 4331–4338; i) [N₂[Ta(SAR)₃(thf)₂]]: R. R. Schrock, M. Wesolek, A. H. Liu, K. C. Wallace, J. C. Dewan, *Inorg. Chem.* **1988**, *27*, 2050–2054.
[4] X-ray structure analyses: Suitable single crystals were embedded in perfluoropolyether oil; data were collected on a Siemens P4 four-circle diffractometer using MoK α radiation (λ = 71.073 pm, graphite monochromator). Structures were solved by direct methods and refined on *F*² using full-matrix least squares (SHELXTL NT 5.10), all non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in a difference Fourier map and refined with a common fixed isotropic displacement parameter. a) [Ru(MeCN)(*PiPr*₃)(N₂Me₂S₂)]·MeOH (**1**·MeOH). Yellow single crystals formed when

Synthesis and Characterization of RbLi₇Ge₈ with Isolated *closo*-[Li₄Ge₁₂]⁸⁻ Ions, Lithium-Capped Truncated Tetrahedra of Ge₁₂^{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

[*] Prof. S. C. Sevov, S. Bobev
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 219-631-6652
E-mail: ssevov@nd.edu

[**] We thank the Petroleum Research Fund, administered by the ACS, for the financial support of this research.