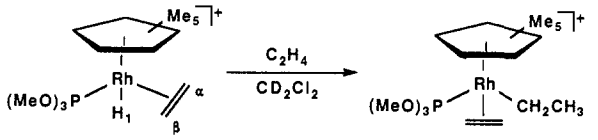
eq 3. By using standard spin saturation transfer techniques the rate constant for hydride migration was determined to be 28 s^{-1} at −39 °C which corresponds to $\Delta G^{\ddagger}$ = 12.0 kcal/mol.

Treatment of **7** in CD_2Cl_2 at −80 °C with 20–50 equiv of ethylene results in rapid trapping of **8** and formation of the ethyl ethylene complex **9**.[10,11] Warming **9** to 23 °C in the presence



7 **9**

of excess ethylene results in the catalytic dimerization of ethylene by **9** to butenes (1-butene:*cis*-2-butene:*trans*-2-butene = 7:1:1)[12] with *no change* in the spectral intensity of **9**. The rate of production of butenes is linear over more than 30 turnovers with a turnover rate of 1 equiv of C_2H_4/**9**/42 min.

The proposed mechanism for butene formation is shown in Scheme I. Migratory insertion of **9** generates the unsaturated rhodium–butyl complex **10** which, upon β-elimination, must give initially the 1-butene complex **11a**. The 2-butene isomers must arise by the well-established mechanism of migratory insertion of **11a** to the Rh-*sec*-butyl complex followed by reelimination. Whether equilibrium is established among isomers **11a–c** prior to butene displacement by ethylene is unknown. Since no other species are detectable in significant quantities[13] the turnover limiting step must be the migratory insertion reaction **9** → **10**. From the rate of production of butenes at 23 °C the rate constant for migratory insertion of **9** is calculated to be 2 × 10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 22.3 kcal/mol.

These experiments establish for the first time a quantitative measure of the relative migratory aptitudes of hydride and alkyl groups in the β-migratory insertion reaction. The difference in free energies of activation ($\Delta G^{\ddagger}_{Et\ mig} - \Delta G^{\ddagger}_{H\ mig}$) is 10.3 kcal/mol which corresponds to a rate ratio of $k_{H\ mig}/k_{Et\ mig}$ of ca. 10^7–10^8 at 25 °C.[14] This value is somewhat smaller than that observed for the relative rates of -H and -CH_3 α-migration in $Cp^*_2Ta(CH_2)(H)$ and $Cp^*_2Ta(CH_2)(CH_3)$ of (k_H/k_{Me} = 10^{10}) at 50 °C.[2d] The large difference in activation barriers for hydride versus alkyl migrations is consistent with the fact that alkyl migrations are unobserved in ethylene alkyl complexes where the analogous terminal hydride systems show barriers for migration of greater than 17–18 kcal/mol.[2d,5] Relative migratory aptitudes of hydride and alkyl groups may vary significantly from system to system. We are probing this point by examining other pairs of isoelectronic complexes, $L_nM(C_2H_4)H/L_nM(C_2H_4)R$.

Acknowledgment is made to the National Science Foundation (Grant No. CHE-8705534) for support of this research.

(10) **9**: ^1H NMR (−117 °C, CD_2Cl_2) δ 3.75 (d, J_{P-H} ≈ 11.2 Hz, P(OMe)3), δ 1.69 (d, J_{P-H} = 4.4 Hz, C_5Me_5), δ 1.17 (t, J_{C-H} = 7.2 Hz, CH_2CH_3), δ 2.4, 2.7, 2.8, 3.5 (multiplets, four inequivalent protons of C_2H_4). The CH_2 signal is obscured by the C_5Me_5 signal but was located by decoupling experiments: ^{13}C NMR (−108 °C, CD_2Cl_2), δ 104.3 (s, C_5Me_5), δ 8.4 (q, J_{C-H} = 129 Hz, C_5Me_5), δ 55.1 (dq, J_{P-C} = 10 Hz, J_{C-H} = 148 Hz, P(OMe)3), δ 55.1 (br, C_1 or C_2), δ 65.0 (br, C_1 or C_2), δ 18.9 (q, J_{C-H} = 127 Hz, CH_2CH_3), δ 16.2 (tdd, J_{C-H} = 144 Hz, J_{Rh-C} and J_{P-C} are either 10 and 15 Hz or 15 and 10 Hz, respectively, CH_2CH_3). From line shape analysis of the ^1H NMR spectrum an approximate barrier for olefin rotation of 7 kcal/mol at −110 °C can be calculated.

(11) An analogous reaction of $Cp(PMe_3)Rh(C_2H_4)(H)^+$ with C_2H_4 has been reported by Werner,[5b,c] but no further insertions of the alkyl species were observed.

(12) The equilibrium ratio of *trans*-2-butene:*cis*-2-butene:1-butene at 25 °C is 100:30:4. When **9** is exposed to a limited amount of ethylene, butenes are isomerized after ethylene dimerization has occurred.

(13) Two very low intensity doublets (<5%) in the pentamethylcyclopentadienyl region grow in rapidly when butene production begins after which their intensity remains constant throughout the dimerization reaction. It is likely that these are butene-hydride species (**11a–c**); experiments are in progress to identify them.

(14) In calculating this relative rate difference at 25 °C we have assumed that the free energy of activation for hydride migration is temperature independent. It is likely that for both intramolecular processes $\Delta S^{\ddagger}$ values are small and $\Delta G^{\ddagger}$ values will be nearly independent of temperature.

Chiral Lithium: Conformation and Dynamic Behavior of Monomeric Neopentyllithium–*N,N,N′,N′,N″*-Pentamethyldiethylenetriamine Complex

Gideon Fraenkel* and William R. Winchester

Department of Chemistry, The Ohio State University Columbus, Ohio 43210-1173

Received August 26, 1988

Organolithium[1] compounds exhibit an astonishing variety of structures[2-4] which undergo fast equilibrium carbon lithium[4-7] and lithium ligand bond exchange, respectively, as well as rapid conformational interconversions including inversions at C_αLi.[8] These processes are often fast enough even at very low temperature as to obviate the utility of NMR studies of RLi structure and dynamic effects. In this communication we report that neopentyllithium, **1**, monomer complexed to *N,N,N′,N′,N″*-pentamethyldiethylenetriamine, PMDTA, in diethyl ether, is a system in which the above exchange processes are slow enough at 160 K to provide unusually detailed information on its structure. Then, above 160 K NMR line shape analysis[9] enabled us to disentangle the different fast dynamic processes—internal rotation, N–Li coordination exchange, and monomer–dimer[7] interconversion.

Neopentyllithium, **1**, was prepared by cleavage of the mercury compound with ^6Li shavings in cyclopentane at 297 K over 7 days. This material was identical in all respects with material prepared by reaction of neopentyl chloride with lithium metal.[10]

In diethyl ether at all temperatures **1** consists entirely of dimers as evidenced by the $^{13}C_\alpha$ NMR multiplicity of 1:2:3:2:1 with $J(^{13}C_\alpha,^6Li)$ of 8.9 Hz and C_α shift at 34.4 δ.

A sample of **1**, 0.5 M with PMDTA, 0.30 M in diethyl ether at 166 K consists of monomeric **1** complexed to PMDTA as evidenced by $^{13}C_\alpha$ at 34.4 δ, 1:1:1, with $J(^{13}C_\alpha,^6Li)$ = 14.7 Hz[11] and a second species which exhibits the same ^{13}C NMR parameters just described for the dimeric etherate. There is no detectable free triamine in this solution up to 300 K. With PMDTA in excess of **1** free triamine is resolved from complexed triamine. The monomer–dimer ratio does not change significantly between 160 and 300 K.

Most interestingly at 146 K *all* but *two carbons* (methylenes) of complexed PMDTA are magnetically nonequivalent, see Figure 1. We can assume that the structure of **1**·PMDTA qualitatively resembles those of other RLi·PMDTA monomers studied crystallographically in the past, i.e., that Li is tridentately coordinated to PMDTA.[12] Then the NMR data at 146 K imply that our species, **1**·PMDTA, is conformationally locked about the C–Li internuclear axis, in the form of *one rotamer* within which the *tert*-butyl group is disymmetrically sited with respect to the tri-

(1) Reviewed, Kaiser, E. J. *J. Organomet. Chem.* **1982**, *227*, 1.
(2) Brown, T. L. *Pure Appl. Chem.* **1970**, *23*, 447–462.
(3) Crystal structures reviewed: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.
(4) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. Seebach, D.; Siegel, H.; Gabriel, J.; Hassig, R. *Helv. Chim. Acta* **1980**, *63*, 2046.
(5) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745. Fraenkel, G.; Henrichs, M.; Hewitt, M.; Geckle, M. J.; Su, B.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3345.
(6) Fraenkel, G.; Hsu, S.-P.; Su, B. M. In *Lithium Current Applications in Science, Medicine and Technology*; Bach, R., Ed.; John Wiley and Sons: New York, 1985; p 273.
(7) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848.
(8) Fraenkel, G.; Beckenbaugh, W.; Yang, P. P. *J. Am. Chem. Soc.* **1976**, *98*, 6878.
(9) Fraenkel, G.; Kaplan, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 2907. Fraenkel, G.; Kaplan, J. I. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980; Chapter 6.
(10) Schrock, P. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(11) Bauer, W.; Winchester, W. R.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371.
(12) Lappert, M. F.; Engelhardt, E. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323. Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Stamper, J. G.; Sullivan, A. C. *J. C. S. Chem. Commun.* **1986**, 969. Schumann, U.; Kopf, J.; Weiss, E. *Angew. Chem.* **1985**, *97*, 222; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 215.

0002-7863/88/1510-8720$01.50/0

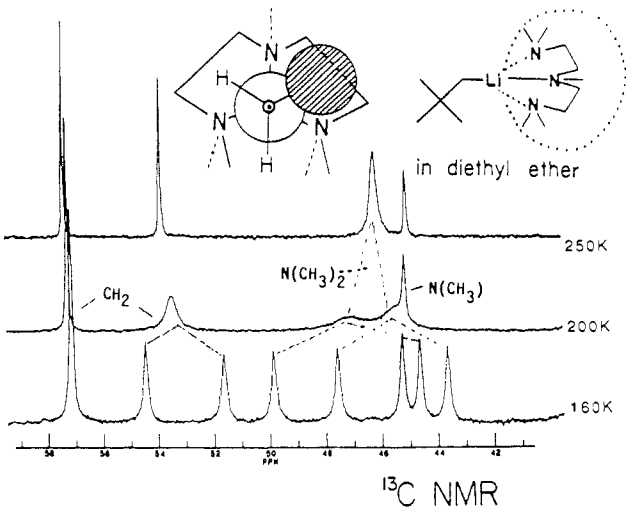
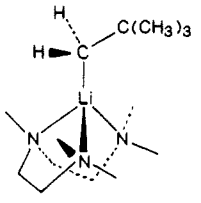


Figure 1. ^{13}C NMR, 75 MHz, ligand resonances of [^{6}Li]neopentyllithium M, in diethyl ether containing 1 equiv of *N,N,N',N',N''*-pentamethyldiethylenetriamine, different temperatures. Temperature calibrated by method of Van Geet.[14,15]

amine moiety and both lithium and the NCH_3 nitrogen are chiral centers, see **2**. This conclusion is supported by the results of a



2

fully optimized structure of **1** complexed to PMDTA, using MNDO.[13] The complex is unsymmetrical with the C-methyls closer to one terminal nitrogen (N_1) than the other, thus by steric repulsion forcing the N_1–Li distance to exceed that of N_3 to Li. Inspection of the model reveals minimum steric interactions between the *tert*-butyl methyls and the *N*-methyls compared to the other rotamers.

The NMR data for **1**·PMDTA at 146 K show inversion at nitrogen to be slow relative to the NMR time scale as is also rotation about the CH_2–Li axis and Li–N coordination exchange.

Further assignments of ^{13}C shifts in **1**·PMDTA and insight into dynamic effects come from NMR behavior observed above 146 K. With increasing temperature there is signal averaging which involves all the ^{13}C PMDTA resonances except the one at 45.38 δ, which must be due to N_2–CH_3. This assigns the peaks at 43.78, 44.75, 47.69, and 49.98 δ, respectively, to $N(CH_3)_2$ carbons, Figure 1. Between 166 and 216 K three pairs of resonances—all δ units, CH_2 at 54.58 and 51.74, $N(CH_3)_2$ methyls at 43.77 and 47.69 and a second pair at 44.76 and 49.97—each average to broad lines at their respective centers, Figure 1. NMR line shape analysis shows the process responsible for this low-temperature signal averaging is the same for all three collapsing doublets. But since the methylene doublet must come from CH_2's at opposite ends of the ligand, then the averaging mechanism is rotation about the CH_2–Li axis. In that case one can classify the $N(CH_3)_2$ resonances as 43.77 δ and 47.69 δ on one side and equidistant to Li and 44.76 δ and 49.97 δ on the other side.

A second dynamic process is seen in the ^{13}C NMR of **1**·PMDTA above 200 K, the averaging of all the ^{13}C $N(CH_3)_2$ resonances. We would like to propose this is the result of reversible N–Li coordination exchange, each dissociation being accompanied by one or more inversions. The process appears to be synchronous with the exchange of neopentyls and lithiums between monomer and dimer. For, above 200 K their respective ^{13}C and ^{6}Li resonances also signal average, and the rate constants derived from line shape analysis are closely similar to those for N–Li coordination exchange. We also observe qualitatively that the N–Li coordination exchange rate increases with the concentration of ether-solvated dimer. Taking account of both internal rotation about the CH_2–Li axis and N–Li coordination exchange in the ^{13}C NMR line shape analysis[9] of complexed PMDTA gives rise to $\Delta H_r^{\ddagger} = 7.7$ kcal and $\Delta S_r^{\ddagger} = -3.4$ eu for rotation and $\Delta H_e^{\ddagger} = 8.8$ kcal and $\Delta S_e^{\ddagger} = -8.3$ eu for the slower coordination exchange.

In sum we have been able to describe the structure of a chiral monomeric tridentately coordinated complex of **1** with PMDTA because at 160 K the species is conformationally locked into one rotamer, due to steric interactions, and all bond exchange processes (C, Li and N, Li) are slow relative to the NMR time scale. Then at higher temperatures a detailed dynamic picture of rotationand the just mentioned bond exchanges has been revealed by using our methods of NMR line shape analysis.

Acknowledgment. This research was supported by the National Science Foundation Grant No. CHE 8304636 and in part by the Goodyear Tire and Rubber Company. Purchase of high field NMR equipment was also financed in part by grants from the National Science Foundation. We thank Dr. Charles Cottrell, Central Campus Instrumentation Center, for technical consulting.

Supplementary Material Available: Coupled density matrix equations together with an exchange matrix, figures representing experimental and calculated line shapes and Eyring plots, and a table listing the shifts, line widths, and fitted rate constants (10 pages). Ordering information is given on any current masthead page.

(13) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4399. Thiel, W.; Clark, T. Quantum Chemistry Program Exchange, Indiana University, 1983; 438.

(14) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(15) These samples did not precipitate or freeze down to the lowest temperatures used, 146 K.

Structure of the 3Fe–4S Cluster in *Desulfovibrio gigas* Ferredoxin II

Charles R. Kissinger,* Elinor T. Adman, Larry C. Sieker, and Lyle H. Jensen

Department of Biological Structure, SM-20
School of Medicine, University of Washington
Seattle, Washington 98195

Received August 22, 1988

Since the discovery of 3-Fe clusters in proteins,[1] their structure and composition have been controversial. Recently in our laboratory, the structure of ferredoxin I from *Azotobacter vinelandii* was redetermined at 2.6 Å resolution.[2] It was demonstrated that the first reported structure[3] for this protein was in error and that the 3-Fe cluster in the molecule appears to be a 3Fe–4S cluster with a configuration much like the 4Fe–4S cubane-type clusters previously found in other proteins[4] but simply lacking one iron

(1) (a) Emptage, M. H.; Kent, T. A.; Huynh, B. H.; Rawlings, J.; Orme-Johnson, W. H.; Münck, E. *J. Biol. Chem.* **1980**, *255*, 1793–1796. (b) Huynh, B. H.; Moura, J. J. G.; Moura, I.; Kent, T. A.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1980**, *255*, 3242–3244.

(2) Stout, G. H.; Turley, S.; Sieker, L. C.; Jensen, L. H. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 1020–1022.

(3) (a) Stout, C. D.; Ghosh, D.; Patthabi, B.; Robbins, A. H. *J. Biol. Chem.* **1980**, *255*, 1797–1800. (b) Ghosh, D.; O'Donnell, S.; Furey, W., Jr.; Robbins, A. H.; Stout, C. D. *J. Mol. Biol.* **1982**, *158*, 73–109. (c) A reanalysis of this work subsequent to ref 2 has been published (Stout, C. D. *J. Biol. Chem.* **1988**, *263*, 9256–9260).

(4) (a) Carter, C. W., Jr. In *Iron–Sulfur Proteins*; Lovenberg, W., Ed.; Academic Press: New York, 1977; Vol. 3, pp 157–204. (b) Adman, E. T.; Sieker, L. C.; Jensen, L. H. *J. Biol. Chem.* **1973**, *248*, 3987–3996. (c) Fukuyama, K.; Nagahara, Y.; Tsukihara, T.; Katsube, Y.; Hase, T.; Matsubara, H. *J. Mol. Biol.* **1988**, *199*, 183–193.

0002-7863/88/1510-8721$01.50/0