11604 *J. Am. Chem. Soc.* **1994,** *116,* 11604–11605

First Spectroscopic Evidence for Complex Bases: A ^{23}Na NMR Study of Solid $NaNH_2$–*t*-BuONa

P. Palmas,[†] P. Tekely,[†] B. Jamart-Grégoire,[‡]
P. Caubère,*,[‡] and D. Canet*,[†]

Laboratoire de Méthodologie RMN
URA CNRS 406 (LESOC) and
Laboratoire de chimie Organique I, URA CNRS 457
INCM FU CNRS 0008, Université H. Poincaré, Nancy I
BP 239, F-54506 Vandoeuvre-lès-Nancy, France

Received July 20, 1994

Two of the most important consequences of aggregative activation[1] was to reveal the existence of "complex bases" [2] and "complex reducing agents," [2b,3] which are two families of useful reagents in organic synthesis. The several hypotheses which were formulated about the structure of these reagents[1,2,4] were deduced mainly from chemical results as well as from the aggregative activation principles.

Two years ago, we undertook the physical study of these reagents. Thus, we recently confirmed that the complex reducing agent $Ni(OAc)_2$–NaH–*t*-AmONa possesses subnanometer Nickel clusters[5] and contains $Ni^{(0)}$ species.[6] Until now, no physical information had been obtained for a complex base. In the present paper, we wish to report the first spectroscopic evidence for the existence of such reagents. We chose to study aggregates formed when 1 equiv of *t*-BuOH was added to 3 equiv of $NaNH_2$ to obtain the complex base of $NaNH_2$–*t*-BuONa (2/1). We found this complex base composition to be one of the most useful for organic synthesis[1,2] particularly in promoting syn eliminations.[7] It should be noted that studies of complex base-promoted syn eliminations reported by others[8] have utilized a complex base of $NaNH_2$–*t*-BuONa (1/1) which may give differing results. We continue to believe that a unique species was formed during the preparation of the complex base of $NaNH_2$–*t*-BuONa (2/1). This hypothesis is supported by the present study of central transition line shapes of ^{23}Na MAS (magic angle spinning) NMR spectra for the complex base $NaNH_2$–*t*-BuONa (2/1),[9] compared to spectra of individual species *t*-BuONa[10] and $NaNH_2$.[11]

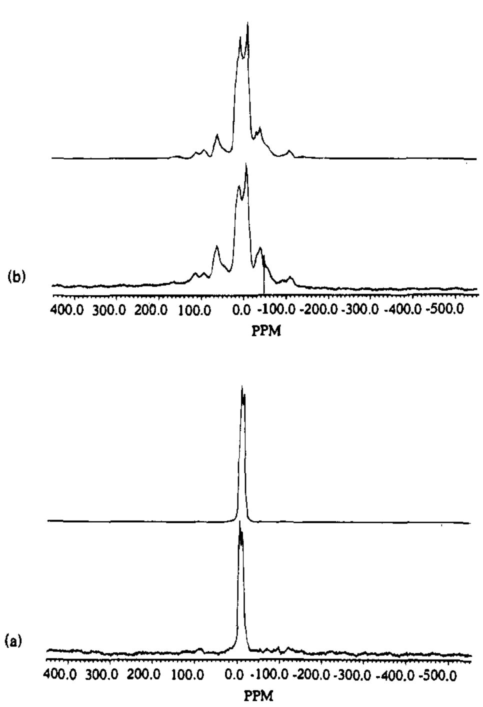

Figure 1. Experimental (bottom) and simulated (top) ^{23}Na MAS NMR spectra at 79.4 MHz of (a) *t*-BuONa at a spinning speed of $\nu_r = 8$ kHz and (b) $NaNH_2$ at a spinning speed of $\nu_r = 4$ kHz. Refined values for the quadrupolar parameters and isotropic chemical shifts used in the simulations are given in the text.

Nuclei with spins greater than $^1/_2$, like ^{23}Na with spin $^3/_2$, experience quadrupolar coupling leading to very broad lines in the solid state NMR spectrum due to the very strong interaction between the electric quadrupole and the electric field gradient at the nuclear site.[12] Primarily, this broadening affects the lateral transitions and to a lesser extent the central transition ($^1/_2 \rightarrow -^1/_2$) which exists for half-integer nuclear spins. Therefore, a sharper signal is observed for the central portion in comparison with the remainder of the spectrum.[13] However, in the case of strong quadrupolar coupling, second-order quadrupolar effects influence this central transition and produce an extra broadening and usually a characteristic pattern which may be split into sidebands under the MAS conditions. Under such conditions, the central part of the spectrum contains structural information imparted by the quadrupolar interaction,[14,15] i.e. the quadrupolar coupling constant $\chi = eq_{zz}Q/h$ and the asymmetry parameter $\eta = (q_{yy} - q_{xx})/q_{zz}$, where Q is the quadrupolar moment, q_{xx}, q_{yy}, and q_{zz} are the electric field gradient tensor components in its principal axis system (PAS), and the other symbols have their usual meanings. These parameters can be derived from spectral simulations along with an iterative procedure (SIMPLEX) for refining their values. A general computer program has been developed for this purpose and will be described elsewhere.[16] It is essentially based on the irreducible spherical representation of the spin Hamiltonian and on the first- and second-order perturbation theory approach.

Figure 1 shows the experimental and calculated ^{23}Na MAS NMR spectra for *t*-BuONa and $NaNH_2$. In Figures 2 and 3 are presented the spectra of the complex base $NaNH_2$–*t*-BuONa

---

[†] Laboratoire de Méthodologie RMN.

[‡] Laboratoire de chimie Organique I.

(1) Caubère, P. *Rev. Heteroatom. Chem.* **1991**, *4*, 78.

(2) (a) Caubère, P. *Acc. Chem. Res.* **1974**, *7*, 301. (b) Caubère, P. *Top. Curr. Chem.* **1978**, *73*, 50. (c) Caubère, P. Crown Ethers and Phase Transfer Catalysis. In *Polymer Science*; Mathias, L. J., Carraher, C. E., Jr., Eds.; Plenum Publishing Corp.: New York, 1984; p 139. (d) Caubère, P. *Chem. Rev.* **1993**, *93*, 2317.

(3) Caubère, P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 599. Caubère, P. *Pure Appl. Chem.* **1985**, *57*, 1875.

(4) Caubère, P.; Loubinoux, B. *Bull. Soc. Chim. Fr.* **1969**, 2483.

(5) Gallezot, P.; Leclercq, C.; Fort, Y.; Caubère, P. *J. Mol. Catal.*, in press.

(6) Fox, M. A.; Merkert, J. W.; Caubère, P. *New J. Chem.* **1994**, *18*, 447.

(7) Caubère P.; Coudert, G. *J. Chem. Soc., Chem. Commun.* **1972**, 1289. Guillaumet, G.; Lemmel, V.; Coudert, G.; Caubère, P. *Tetrahedron* **1974**, *30*, 1289. Caubère, P.; Coudert, G. *Bull. Soc. Chim. Fr.* **1973**, 3067.

(8) (a) Lee, J. G.; Bartsch, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 228. (b) Croft , A. P.; Bartsch, R. A. *J. Org. Chem.* **1983**, *48*, 876. (c) Croft, A. P.; Bartsch, R. A. *Tetrahedron Lett.* **1983**, *24*, 2737. (d) Bartsch, R. A.; Cho, B. R.; Pugia, M. J. *J. Org. Chem.* **1987**, *52*, 5494. (e) Hudlicky, M. *J. Fluorine Chem.* **1986**, *32*, 441. (f) Lee, J. G.; Kaug, K. T.; Lee E.-S. *J. Korean Chem. Soc.* **1984**, *28*, 20. (g) Croft A. P.; Bartsch, R. A. *J. Org. Chem.* **1994**, *59*, 1930.

(9) Preparation of the complex base $NaNH_2$–*t*-BuONa (2/1). To a suspension of $NaNH_2$ powder (MERCK) (150 mmol) in THF (20 mL) was added dropwise a solution of *t*-BuOH (50 mmol) in THF (10 mL) under nitrogen. The mixture was stirred at 45 °C for 2 h. Most of the solvent was removed by distillation under reduced pressure. The solid complex base was warmed at 60 °C in a vacuum oven for a period of 6 h.

(10) The *t*-BuONa was prepared by the procedure described in ref 9 with 1 equiv of $NaNH_2$ and 1 equiv of *t*-BuOH.

(11) $NaNH_2$ powder was obtained commercially (MERCK).

(12) Engelhardt, G.; Michel, D. *High Resolution Solid State NMR of Silcates and Zeolites*; Wiley: Chichester, U.K., 1987.

(13) Skibsted, J.; Nielsen, N. C.; Bildsoe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1991**, *95*, 88.

(14) Koller, H.; Engelhardt, G.; Kentgens, A. P. M.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 1544.

(15) Skibsted, J.; Jakobsen, H. J. *Solid State NMR* **1994**, *3*, 29.

(16) Palmas, P. Thesis, University Henri Poincaré, Nancy I, 1994.

0002-7863/94/1516-11604$04.50/0

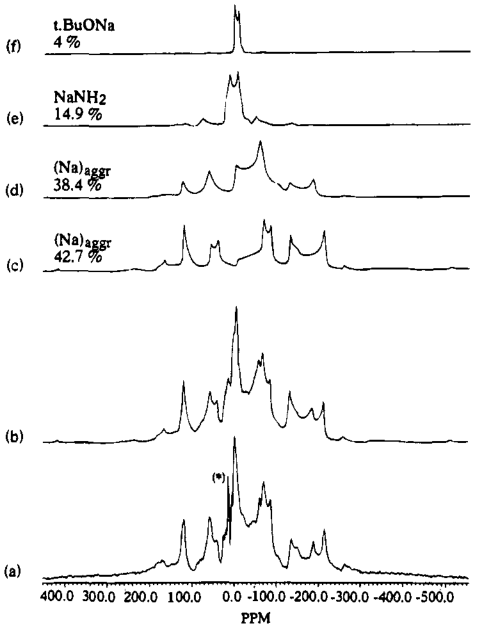

Figure 2. (a) Experimental ^{23}Na MAS NMR spectrum of the complex base NaNH$_2$–*t*-BuONa (2/1) (sample 1) spinning at 5 kHz. The small narrow signal indicated by an asterisk probably resulted from a liquid component. (b) Composite simulated spectrum which resulted from the superposition of the four simulated spectra c, d, e, and f, which are labeled according to the chemical species ((Na)$_{aggr}$ means a sodium atom in the complex base) and to their relative proportions (in percent).

(2/1). The experimental spectra were obtained with short excitation pulses to prevent spectral distortion and high-power proton decoupling to suppress potential broadening from ^{1}H–^{23}Na dipolar couplings. For *t*-BuONa and NaNH$_2$, each spectrum contains only one type of ^{23}Na nucleus and consequently exhibits relatively simple features. Theoretical analysis performed on several spectra obtained at different spinning speeds yields perfectly consistent results. Accurate values for the quadrupolar parameters as well as the isotropic chemical shifts (with *t*-BuONa as the chemical shift reference) were determined to be, for NaNH$_2$, ν_{iso} = 21.9 ppm, χ = 2.48 MHz, and η = 0.32 and, for *t*-BuONa, ν_{iso} = 0 ppm, χ = 1.54 MHz, and η = 0.1.

The experimental and calculated ^{23}Na NMR spectra of sample 1 (Figure 2) of the NaNH$_2$–*t*-BuONa complex base are much more complicated than those shown for NaNH$_2$ and for *t*-BuONa in Figure 1. It is clear that the experimental spectra shown in Figure 2 cannot be described only by the superposition of the spectra for *t*-BuONa and NaNH$_2$. Thus, the presence of a third compound is unambiguously established by this experiment. In fact, the fitting procedure reveals the existence of at least two new ^{23}Na species approximately in equal proportions and which represent 80% of the total integration of the spectrum. These species have very different quadrupolar parameters from those for *t*-BuONa and NaNH$_2$, indicating drastic changes in the crystalline structure as compared with those of pure compounds. In fact, a recent study[14] showed, both experimentally and theoretically, that quadrupolar parameters are very sensitive to any change in the coordination number and symmetry within the first ^{23}Na coordination sphere, leading to values for χ ranging from 0.77 to 5.90 MHz and from 0 to 1 for η. In the present study, quadrupolar coupling constants of 3.53 and 4.15 MHz, an asymmetry parameter near 0, and isotropic chemical shifts of 9.9 and 12.6 ppm, respectively, were determined from the fit to experimental data. An improved fit of the experimental and calculated spectra was obtained when 4% of *t*-BuONa which had been formed during the complex base preparation and 15% of the initial NaNH$_2$ were included. The quadrupolar parameters and isotropic chemical shifts for the *t*-BuONa and NaNH$_2$ contaminants were found to be unchanged with respect to those of the pure compounds.

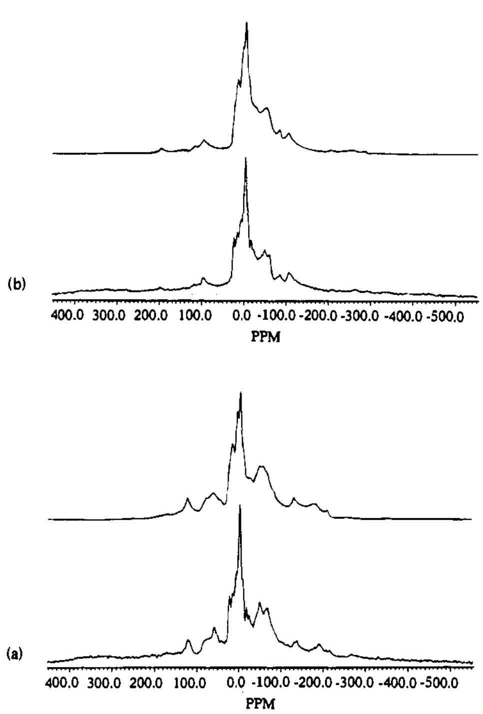

Figure 3. Experimental (bottom) and simulated (top) ^{23}Na MAS NMR spectra of NaNH$_2$–*t*-BuONa (2/1) (sample 2) spinning at (a) 5 kHz and (b) 8 kHz. In the fitting procedure, only percentages and linewidths were adjusted for each species; the other parameters were introduced as constants.

To confirm these results, independent measurements were performed with another sample (sample 2) of the complex base NaNH$_2$–*t*-BuONa at two spinning speeds, 5 and 8 kHz. All the parameters listed above, except proportions and line widths, which may vary from one sample to another, were included in the fitting procedure. The result is shown in Figure 3. Small discrepancies which are noted in the spectrum recorded at a spinning speed of 5 kHz may be attributed to residual chemical shift anisotropy effects which disappear at a higher spinning speed (Figure 3b). However, the spectrum recorded at the low spinning rate has better defined quadrupolar spinning sidebands, which allows for an easier separation of species possessing different quadrupolar coupling constants. This is because the intensity of spinning sidebands is directly related to the quadrupolar coupling value.

These preliminary results demonstrate unambiguously the existence of a specific molecular entity (the complex base) which includes at least two sodium atoms in electronic environments definitely different from those in *t*-BuONa and NaNH$_2$. This confirms our hypothesis and should be considered as a starting point toward the determination of the structure of these solid complex bases and a correlation with structural models. The experimental evidence for the presence of new species obtained in the present work and that found for complex reducing agents[5,6] strongly support our theory of aggregative activation.[1]

Acknowledgment. We are very grateful to a reviewer for his suggestions and improvements of the manuscript. We thank the CEE (SCI*-CT910657) for financial support.