Homo- and Heterocomplexes of Sodium and Lithium Amides—Structures in Solution

Anna Johansson*[a] and Öjvind Davidsson*[b]

Abstract: Addition of the chiral amine (*S*)-methyl(1-phenyl-2-pyrrolidinoethyl)-[^{15}N]amine (**1**) to a large excess of *n*BuNa resulted in the formation of a mixed sodium amide/*n*BuNa complex. This is the first observation of such a complex. Addition of *n*BuLi to the chiral sodium amide dimer **3** gave a new mixed lithium/sodium amide **5**. The use of ^{15}N,^{6}Li coupling constants showed that the lithium in **5** occupied the tetracoordinated site. The use of chiral sodium amide **3** in the desymmetrization of cyclohexene oxide gave a modest enantiomeric excess (*ee*) of 37%. The corresponding lithium amide gave an *ee* of 70% of the same enantiomer. This is the first example of the comparison of asymmetric induction by sodium as cation with that of lithium.

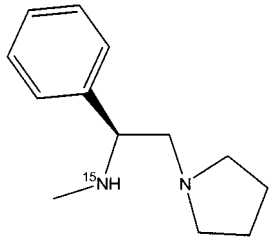
Keywords: amides · asymmetric synthesis · lithium · NMR spectroscopy · sodium

Introduction

The most widely utilized achiral reagent for deprotonation, rearrangement and functionalisation is lithium diisopropylamide (LDA). Its structure in solution and in the solid state are well covered in the literature.[1] Other research groups have investigated the crystal structure of its sodium analogue, sodium diisopropylamide (NDA), and their conclusions were that in reactions in which a high degree of reactivity was required, the use of heavier alkali metal organyls or amides can be advantageous due to their higher basicity.[2] Another recent area of extensive development is the preparation and use of the so-called super bases.[3] These hetero mixtures are considerable more basic than the corresponding homo alkali metal amides and alkoxide complexes. The use of lithium amides as organometallic reagents in asymmetric transformations, deprotonation of conformationally locked prochiral cyclic ketones,[4] rearrangement of epoxides to allylic alcohols,[5] and aromatic and benzylic functionalization of tricarbonyl (η^6-arene)chromium complexes has been successful.[6] It is commonly known that there is a difference in degree of kinetic versus thermodynamic control when the heavier alkali metals are used instead of lithium. However, there are to the best of our knowledge no examples of the comparison the enantiomeric outcome in a reaction with heavier organo alkali metal amide reagents with respect to the more common lithium amide reagents. In the literature there are only some examples of amides of the heavier alkali metals found in the solid state.[7] Investigations in solution are thus very sparse.[8] The organo alkali metal amide formed from hexamethyl disillylazide with lithium or/and potassium in THF is dimeric. Furthermore mixed dimers were also observed in which one lithium and one potassium metal cation constitute the dimeric metal core. Addition of TMEDA resulted in the appearance of monomers. However, in all cases found in the literature there are no publications that deal with chiral amides with internal coordinating groups. This encouraged us to investigate the solution structures of chiral alkali metal amides with internal coordinating groups and their use in asymmetric synthesis.

The lithium salt of the chiral amine *(S)*-methyl(1-phenyl-2-pyrrolidinoethyl)[^{15}N]amine (**1**) forms trimers as well as symmetrically and asymmetrically solvated dimers depending on solvent used. Trimers are observed in hydrocarbon solvents, such as toluene, and asymmetric and symmetric dimers are observed in coordinating solvents as diethyl ether (DEE) and THF, respectively.[9]

Our choice of sodium source for the preparation of the corresponding sodium amide was *n*-butyl sodium. The reason for using *n*-butyl sodium is the possibility to observe the formation of mixed alkyl sodium/sodium amide complexes.



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Results and Discussion

A NMR tube was loaded with an *n*-butyl sodium[10] (500 μL) hexane slurry, and the hexane was removed at a vacuum line. The *n*-butyl sodium was dissolved in diethyl ether ([D_{10}]DEE; 0.5 mL). A signal from the α protons on the carbanionic carbon in *n*-butyl sodium was observed at $\delta = -0.83$ in the ^{1}H NMR spectrum at $-90\,^\circ$C. When 0.25 equivalents of amine were added, two triplets were observed in the ^{1}H NMR spectra at $\delta = -0.83$ and -0.87 (Figure 1). The

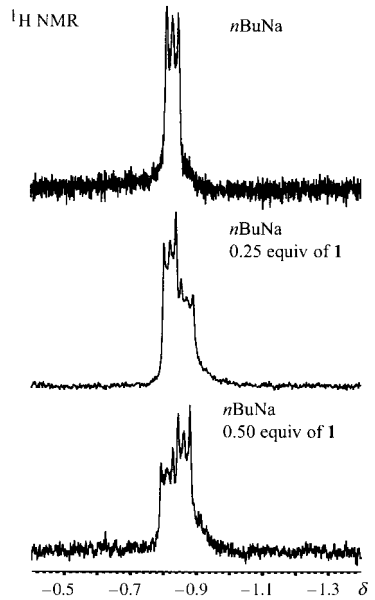
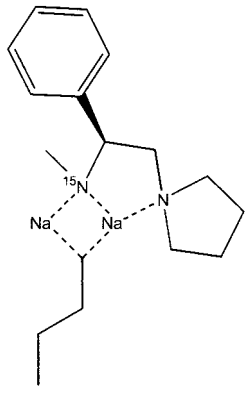


Figure 1. ^{1}H NMR spectra at $-90\,^\circ$C of *n*BuNa in [D_{10}]DEE with different amounts of **1** added, showing the carbanionic α-protons from *n*BuNa.

concentration of the *n*-butyl sodium hexane slurry was determined by titration with amine **1** until the ^{1}H NMR signal originating from the α-carbanionic carbon protons, which was observed at δ −0.83, disappeared totally (55 μL, 0.27 mmol of the amine **1**).

The signal at $\delta = -0.87$ was assigned to derive from a mixed dimer (**2**) that consists of one molecule of *n*-butyl sodium and one molecule of sodium amide. In the ^{13}C NMR spectra, two signals at $\delta = 152.40$ and 150.89 were observed in a 2:1 ratio at $-90\,^\circ$C. The signal at $\delta = 150.89$ was assigned to the quaternary carbon in the mixed dimer complex **2**, as this signal decreased upon further addition of amine (see Figure 2).



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The ^{13}C NMR signal at $\delta = 152.40$ was assigned to be the quaternary carbon in a dimer complex, **3a** or **3b**, since the amides preferably forms dimers in solvents like DEE, and this signal increased in intensity when further amine was added.

Mixed dimer complexes have previously been observed to be easily formed when lithium was used as counterion, but to the

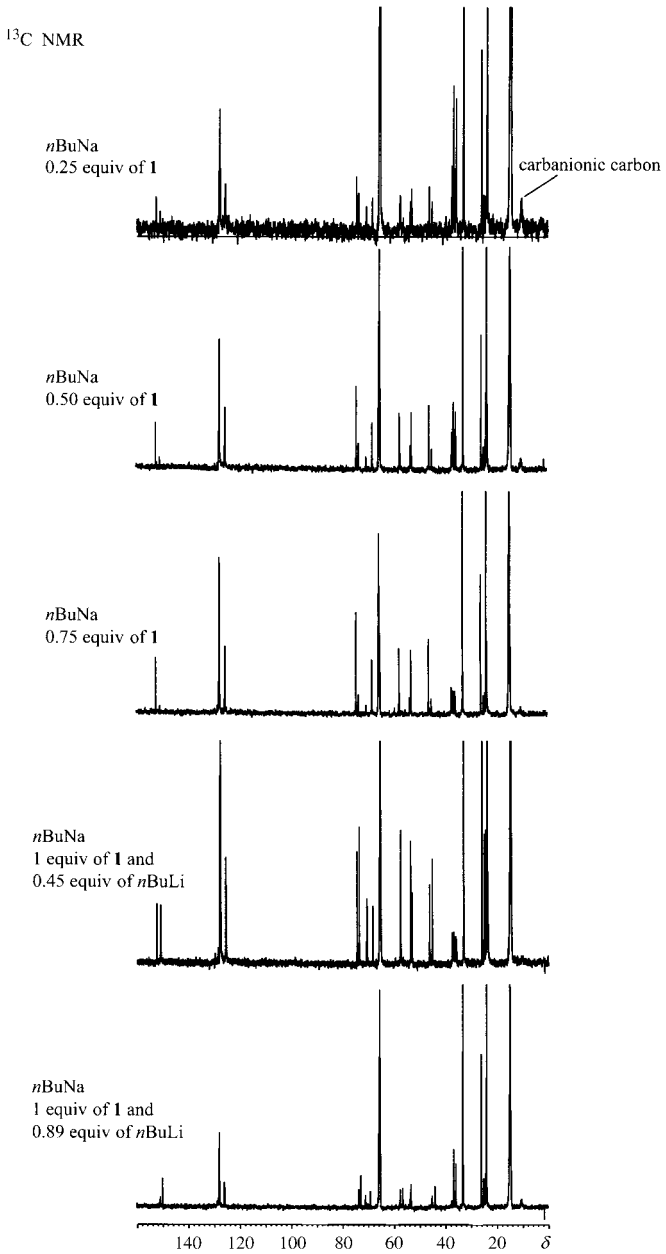
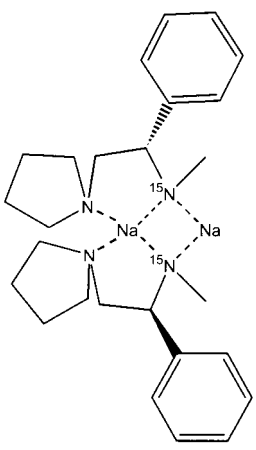
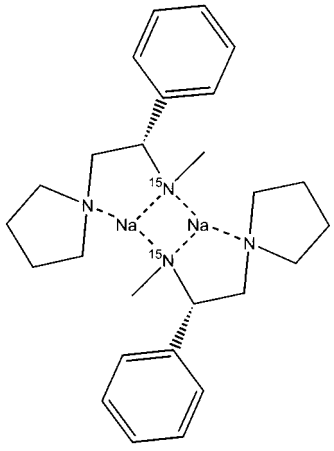


Figure 2. ^{13}C NMR spectra at $-90\,^\circ$C of *n*BuNa in [D_{10}]DEE with different amounts of **1** added and with different additions of *n*BuLi.



3a



3b

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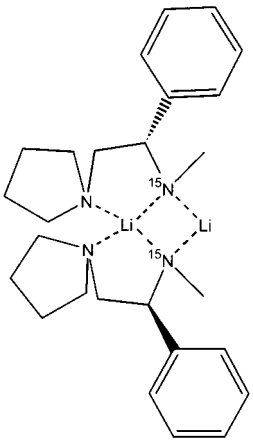
best of our knowledge there exists no reports of mixed butyl sodium/sodium amide complexes.[11] This observation indicates that it might be possibile to use sodium mixed complexes as asymmetric addition reagents to carbonyl carbon atoms.

When equimolar amounts of amine had been added to the *n*-butyl sodium, there was only one ^{13}C NMR quartenary signal seen at $\delta = 152.40$ (see Figure 2). No α protons from *n*-butyl sodium was observed in the ^{1}H NMR spectra. There are two possible indistinguishable structures available for this dimer, either an unsymmetrical internal coordination (**3a**) or a symmetrical internal coordination (**3b**). There is a small preference for structure **3a** as the lithium analogue in DEE exclusively forms asymmetrically internally coordinated dimers (**4**). The 1:1 solution of the amine and *n*BuNa was then titrated with *n*-butyl lithium, and when 0.45 equivalents of *n*BuLi was reached one triplet was observed at $\delta = 2.22$ ($J(^{6}Li,^{15}N) = 4.36$ Hz) in the ^{6}Li NMR spectra at $-90\,^{\circ}C$. This shows that structure **5a**, **5b**, or **5c** is formed (see Figure 3).

In the ^{1}H NMR spectra one observes the α-carbanionic carbon protons from **5** at $\delta = -0.83$ and a new α-carbanionic carbon proton signal at $\delta = -0.87$ from the *n*-butyl sodium formed. The reason for the appearance of *n*-butyl sodium is that the more electropositive metal is directed to the more acidic carbon atom; this results in metal–metal exchange (see Figure 4).



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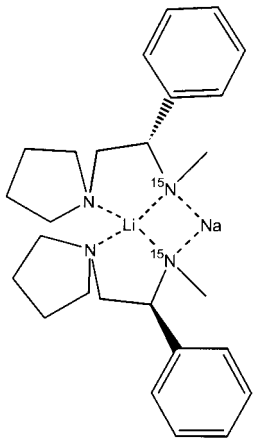
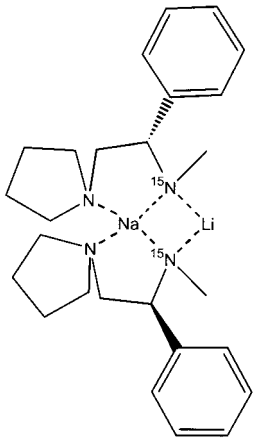
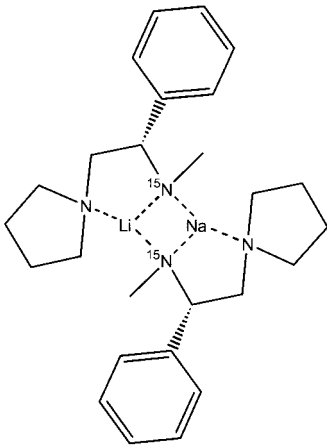
The magnitude of the coupling constant indicates that the lithium is tetracoordinated (one solvent molecule included), that is, it is coordinated by the two pyrrolidine nitrogen atoms and the two amide nitrogens.[12] This indicates that the sodium cation preferably is found in the tricoordinated site (one or two additional solvent molecules included) in the asymmetrically solvated dimer **5a**. This coordinative arrangement of the cations in a lithium/sodium mixed amide has previously been observed in only a few cases.[13]



5a



5b



5c

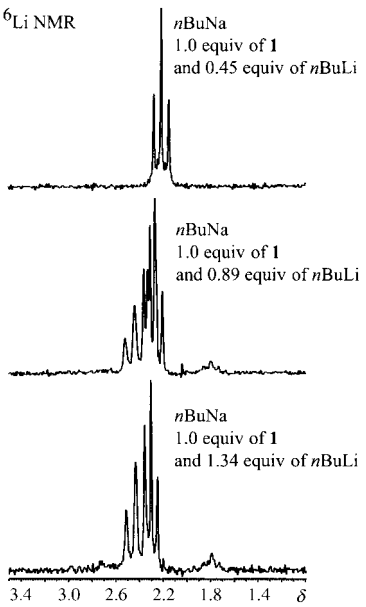


Figure 3. ^{6}Li NMR spectra at $-90\,^{\circ}C$ of **3** in $[D_{10}]$DEE with different additions of *n*BuLi.

Further addition of *n*BuLi results in the disappearance of the triplet at $\delta = 2.22$ and two new triplets appear at $\delta = 2.29$ and 2.28 with $J(^{6}Li,^{15}N) = 5.90$ and 4.11 Hz, respectively. These two new triplets show the same chemical shifts and coupling constant magnitudes as observed for the unsymmetrically solvated lithium dimer **4**.[9] Altogether these observations show that sodium has to be situated in the tricoordinate site, as shown in **5a**. The addition of *n*BuLi expels sodium from the sodium amide to form *n*BuNa; this is clearly seen in the ^{1}H NMR spectra in which α protons from *n*-butyl sodium start to appear upon increased addition of *n*BuLi, due to metal exchange.

The reactivity of the amine was measured by enantioselective deprotonation of a symmetrical epoxide, cyclohexene oxide, to give the optically active allylic alcohol, *(S)*-cyclohexanol. A NMR tube with **3** in DEE was prepared the same way as above, and one equivalent of cyclohexene oxide was added to the solution at room temperature. The enantiomeric excess (*ee*), determined by using chiral gas chromatography, was 37% *ee* of the *S* enantiomer. The corresponding lithium amide gave an *ee* of 70% of the same enantiomer. A NMR tube with **5** in DEE was prepared the same way, and the enantiomeric excess was 10% *ee* for the *S* enantiomer. The reason for the large difference in enantiomeric excess is probably to be found in the difference of the ionic radii and the coordination number at the alkali metals; the lithium cation coordinates the substrate to a larger extent both in the initial as in the transition state. In the case of lithium a

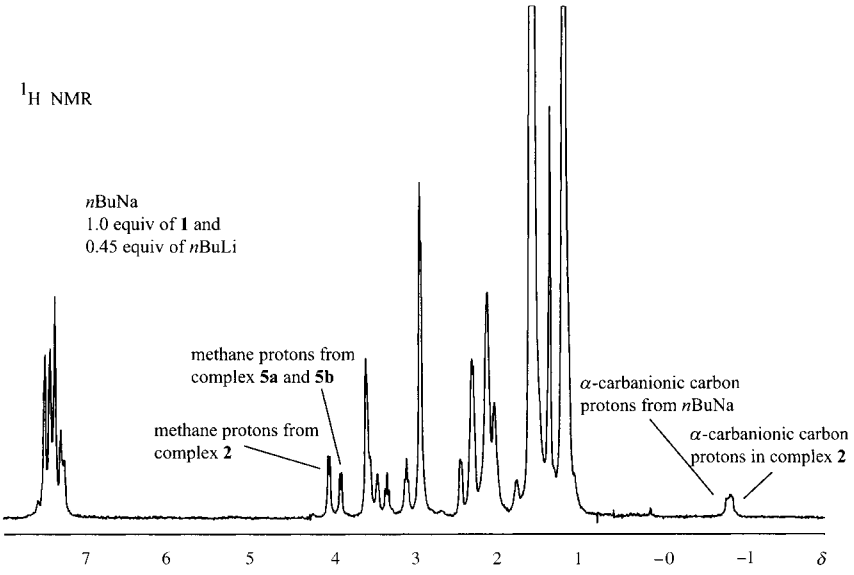


Figure 4. ^{1}H NMR spectra at $-90\,^\circ$C of *n*BuNa with 1 equivalent of **1** and 0.45 equivalents of *n*BuLi added.

tighter transition state is formed, and the substituents on the amide play a more important role in directing the stereochemistry of the reaction. The coordination number may also have an importance as the rates of ligand exchange are faster at a tetracoordinated site relative to a tricoordinated one.

The difference in *ee* is indeed reflected in the coordination status of the lithium and sodium cations in the alkali metal amide; in this case, the substrate coordinates to the tricoordinated sodium and therefore the *ee* decreases due to less interactions from substituents.

Experimental Section

General: All glassware and syringes used for the NMR studies and epoxide-opening reactions were dried at 50 °C in a vacuum oven before transferred into a glove box (Mercaplex GB80 equipped with a gas purification system that removes oxygen and moisture) that contained a nitrogen atmosphere. Chromatographic analyses were carried out on a Varian Star 3400 CX gas chromatograph. All GC analyses were run on a chiral stationary phase column (CP-Chirasil-DEX CB, 25 m, 0.32 mm) from Chrompack. All analyses were performed at 135 °C (injector: 225 °C; detector: 250 °C) with He (2 mL min^{-1}) as carrier gas. The NMR analysis were recorded on a Varian Unity 500 spectrometer with a 5 mm ^{1}H, ^{13}C, ^{6}Li, ^{15}N quad resonance probe head custom built by Nalorac.

Synthesis of the chiral amine 1: The amine **1** was synthesized by using published procedures.[14]

Preparation of NMR samples: The ^{6}Li-labeled lithium amides, and the NMR samples were prepared according to procedures published in previous papers.[15]

The reaction of enantioselective deprotonation of cyclohexene oxide: The reaction of enantioselective deprotonation of cyclohexene oxide was performed by using published procedures.[16]

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[1] a) A. S. Galiano-Roth, D. B. Collum, *J. Am. Chem. Soc.* **1989**, *111*, 6722; b) A. S. Galiano-Roth, Y-J. Kim, J. H. Gilchrist, A. T. Harrison, D. J. Fuller, D. B. Collum, *J. Am. Chem. Soc.* **1991**, *113*, 5053; c) P. L. Hall, J. H. Gilchrist, A. T. Harrison, D. J. Fuller, D. B. Collum, *J. Am. Chem. Soc.* **1991**, *113*, 9575; d) J. H. Gilchrist, D. B. Collum, *J. Am. Chem. Soc.* **1992**, *114*, 794; e) P. G. Williard, M. J. Hintze, *J. Am. Chem. Soc.* **1987**, *109*, 5539; f) W. Zarges, M. Marsch, K. Harms, G. Boche, *Angew. Chem.* **1989**, *101*, 1412; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1392; g) K. Gregory, P. v. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 48.

[2] a) L. Lochmann, J. Pospísil, D. Lim, Czech. Pat. 132.254, application date December 30, **1964** [*Chem. Abstr.* **1970**, 73, 25642f]; b) P. C. Andrews, N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O'Neil, D. Barr, L. Cowton, A. J. Dawson, B. J. Wakefield, *J. Organomet. Chem.* **1996**, *518*, 85; c) E. Pasquinet, P. Rocca, F. Marsais, A. Godard, G. Quéguiner, *Tetrahedron* **1998**, *54*, 8771; d) B. Renger, H. Hügel, W. Wykypiel, D. Seebach, *Chem. Ber.* **1978**, *111*, 2630; e) S. Raucher, G. A. Koolpe, *J. Org. Chem.* **1978**, *43*, 3794.

[3] a) A. Mordini, *Advances in Carbanion Chemistry, Vol. 1* (Ed.: V. Snieckus), JAI, Greenwich, CT (USA), **1992**, p. 1; b) A. Mordini, E. Ben Rayana, C. Margot, M. Schlosser, *Tetrahedron* **1990**, *46*, 2401; c) F. Gualtieri, A. Mordini, S. Pecchi, S. Scapecchi, *Synlett.* **1996**, 447; d) P. A. A. Klusener, L. Tip, L. Brandsma, *Tetrahedron* **1991**, *47*, 2041; e) D. Barr, A. J. Dawson B. J. Wakefield, *J. Chem. Soc. Chem. Commun.* **1992**, *2*, 204; f) P. C. Andrews, N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O'Neil, D. Barr, L. Cowton, A. J. Dawson, B. J. Wakefield, *J. Organomet. Chem.* **1996**, *518*, 85; g) A. Ricci, A. Guerrini, G. Secondi, A. Mordini, T. Constantieux, J.-P. Picard, J.-M. Aizpurua, C. Palomo, *Synlett* **1994**, 955; h) T. Kremer, S. Harder, M. Junge, P. von R. Schleyer, *Organometallics* **1996**, *15*, 585.

[4] a) N. S. Simpkins, *Chem. Commun.* **1986**, 88; b) C. M. Cain, R. P. C. Cousins, G. Coumbarides, N. S. Simpkins, *Tetrahedron* **1990**, *46*, 523; c) K. Koga, *Pure Appl. Chem.* **1994**, *66*, 1487; d) R. Shirai, M. Tanaka, K. Koga, *J. Am. Chem. Soc.* **1986**, *108*, 543; e) R. Shirai, D. Sato, K. Aoki, M. Tanaka, H. Kawasaki, K. Koga, *Tetrahedron* **1997**, *53*, 5963; f) T. Yamashita, D. Sato, T. Kiyoto, A. Kumar, K. Koga, *Tetrahedron Lett.* **1996**, *37*, 8195; g) T. Yamashita, D. Sato, T. Kiyoto, A. Kumar, K. Koga, *Tetrahedron* **1997**, *53*, 16987.

[5] a) P. O'Brien, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1439; b) D. M. Hodgson, J., Witherington, B. A. Moloney, *Tetrahedron: Asymmetry* **1994**, *5*, 337; c) D. M. Hodgson, J., Witherington, B. A. Moloney, *Tetrahedron: Asymmetry* **1994**, *4*, 1649; d) D. M. Hodgson, A. R. Gibbs, G. P. Lee, *Tetrahedron* **1996**, *52*, 14361; e) P. O'Brien, P. Poumellec, *Tetrahedron Lett.* **1996**, *37*, 8057; f) A. Bigi, A. Mordini, A. Thurner, F. Faigl, G. Poli, L. Toke, *Tetrahedron: Asymmetry* **1998**, *9*, 2293; g) J. K. Whitesell, S. W. Felman, *J. Org. Chem.* **1980**, *45*, 755; h) D. Bhuniya, A. DattaGupta, V. K. Singh, *J. Org. Chem.* **1996**, *61*, 6108; i) D. M. Hodgson, A. R. Gibbs, *Tetrahedron Lett.* **1997**, *38*, 8907; j) J. P. Tierny, A. Alexakis, P. Mangeney, *Tetrahedron: Asymmetry* **1997**, *8*, 1019; k) M. J. Södergren, P. Andersson, *J. Am. Chem. Soc.* **1998**, *120*, 10760; l) M. J. Södergren, P. S. K. Bertilsson, P. Andersson, *J. Am. Chem. Soc.* **2000**, *122*, 6610; m) D. Milne, P. J. Murphy, *J. Chem. Soc. Chem. Commun.* **1994**, 675; n) M. Asami, *J. Synth. Org. Chem. Jpn.* **1996**, *54*, 188; o) M. Asami, S. Inoue, *Tetrahedron* **1995**, *51*, 11725; p) M. Asami, T. Suga, K. Honda, S. Inoue, *Tetrahedron Lett.* **1997**, *38*, 6425.

[6] a) D. A. Price, N. S. Simpkins, A. M. McLeod, A. P. Watt, *J. Org. Chem.* **1994**, *59*, 1961; b) R. A. Ewin, N. S. Simpkins, *Synlett* **1996**, 317; c) S. E. Gibson, P. C. V. Potter, M. H. Smith, *Chem. Commun.*

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1996, 2757; d) S. E. Gibson, P. Ham, G. R. Jefferson, M. H. Smith, *J. Chem. Soc. Perkin Trans. 1* **1997**, 2161; e) E. L. M. Cowton, S. E. Gibson, M. J. Schneider, M. H. Smith, *Chem. Commun*. **1996**, 839.

[7] a) C. Schade, P. von R. Schleyer, *Adv. Organomet. Chem*. **1987**, *27*, 169; b) E. Weiss, *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem. Int. Ed. Engl*. **1993**, *11*, 1501; c) P. Gantzel, P. J. Walsh, *Inorg. Chem*. **1998**, *37*, 3450; d) P. B. Hitchcock, M. F. Lappert, W-P. Leung, L. Diansheng, T. Shun, *J. Chem. Soc. Chem. Commun*. **1993**, 1386; e) S. Harder, M. Lutz, T. Kremer, *Organometallics* **1995**, *14*, 2133; f) D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, *J. Chem. Soc. Chem. Commun*. **1989**, 57; g) D. R. Armstrong, W. Clegg, L. Dunbar, S. T. Liddle, M. MacGregor, R. E. Mulvey, D. Reed, S. A. Quinn, *J. Chem. Soc. Dalton Trans.* **1998**, 3431; h) F. Antolini, P. B. Hitchcock, M. F. Lappert, P. Merle, *Chem. Commun*. **2000**, 1301; i) P. C. Andrews, W. Clegg, R. E. Mulvey, *Angew.* Chem. **1990**, *102*, 1480; Angew. *Chem. Int. Ed. Engl*. **1990**, *29*, 1440; j) M. Driess, H. Pritzkow, M. Skipinski, U. Winkler, *Organometallics* **1997**, *16*, 5108; k) K. Gregory, M. Bremer, W. Bauer, P. v. R. Schleyer, N. P. Lorenzen, J. Kopf, E. Weiss, *Organometallics* **1990**, *9*, 1485; l) B. Gemünd, H. Nöth, H. Sachdev, M. Schmidt, *Chem. Ber*. **1996**, *129*, 1335; m) W. Clegg, K. W. Henderson, L. Hornsburgh, F. M. MacKenzie, R. E. Mulvey, *Chem. Eur. J.* **1998**, *4*, 53; n) D. Barr, W. Clegg, L. Cowton, L. Horsburgh, F. M. MacKenzie, R. E. Mulvey, *J. Chem. Soc. Chem. Commun*. **1995**, 891; o) P. C. Andrews, D. R. Armstrong, W. Clegg, M. MacGregor, R. E. Mulvey, *J. Chem. Soc. Chem. Commun*. **1991**, 497; p) I. Cragg-Hine, M. G. Davidson, A. J. Andrews, P. R. Raithby, R. Snaith, *J. Chem. Soc. Dalton Trans.* **1994**, 2901; q) J. Knizek, I. Krossing, H. Nöth, H. Schwenk, T. Seifert, *Chem. Ber*. **1997**, *130*, 1053; r) P. C. Andrews, D. R. Armstrong, D. B: Baker, R. E. Mulvey, W. Clegg, L. Horsburgh, P. A. O'Neil, D. Reed, *Organometallics* **1995**, *14*, 427; s) M. Veith, J. Böhnlein, V. Huch, *Chem. Ber*. **1989**, *122*, 841; t) R. E. Mulvey, *Chem. Soc. Rev*. **1991**, *20*,167; u) M. Veith, *Angew. Chem.* **1987**, *99*, 1; *Angew. Chem. Int. Ed. Engl*. **1987**, *26*, 1; v) D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, J. Wright, *J. Chem. Soc. Chem. Commun*. **1987**, 716; w) W. Clegg, M. MacGregor, R. E. Mulvey, P. A. O'Neil, *Angew. Chem.* **1991**, *104*, 74; *Angew. Chem. Int. Ed. Engl*. **1992**, *31*, 93; x) N. P. Lorentzen, J. Kopf, F. Olbrich, U. Schümann, E. Weiss, *Angew. Chem.* **1990**, *102*, 1481; *Angew. Chem. Int. Ed. Engl*. **1990**, *29*, 1441; y) R. Hacker, E. Kaufmann, P. von R. Schleyer, W. Mahdi, H. Dietrich, *Chem. Ber.* **1987**, *120*, 1533; z) F. Pauer, D. Stalke, *J. Organomet. Chem*. **1991**, *418*, 127; aa) S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc. Dalton Trans.* **1993**, 3479; ab) F. Pauer, D. Stalke, *J. Organomet. Chem*. **1991**, *418*, 127; ac) S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc. Dalton Trans.* **1993**, 3479; ad) P. C. Andrews, P. J. Duggan, G. D. Fallon, T. D. McCarthy, A. C. Peatt, *J. Chem. Soc. Dalton Trans.* **2000**, 2505; ae) J. D. Smith, *Adv. Organomet. Chem*. **1999**, *43*, 267; af) J. Eppinger, E. Herdtweck, R. Anwander, *Polyhedron* **1998**, *17*, 1195.

[8] a) D. R. Baker, R. E. Mulvey, W. Clegg, P. A. O'Neil, *J. Am. Chem. Soc.* **1993**, *115*, 6472; b) M. A. Nichols, D. Waldmüller, P. G. Williard, *J. Am. Chem. Soc*. **1994**, *116*, 1153; c) S. G. Sakharov, N. I. Pakuro, A. A. Arest-Yakubovich, L. V. Shcheglova, P. V. Petrovskii, *J. Organomet. Chem*. **1999**, *580*, 205.

[9] P. I. Arvidsson, Ö. Davidsson, *Angew. Chem.* **2000**, *112*, 1527; *Angew. Chem. Int. Ed.* **2000**, *39*, 1467.

[10] *n*-Butyl sodium was prepared according to published procedures, see C. Schade, W. Bauer, P. v. R. Schleyer, *J. Organomet. Chem*. **1985**, *295*, C25.

[11] a) G. Hilmersson, Ö. Davidsson, *J. Organomet. Chem*. **1995**, *489*, 175; b) P. G. Williard, C. Sun *J. Am. Chem. Soc*. **1997**, *119*, 11693; c) C. Sun, P. Williard, *J. Am. Chem. Soc*. **2000**; d) A. Corruble, J.-Y. Valnot, J. Maddaluno, Y. Prigent, D. Davoust, P. Duhamel, *J. Am. Chem. Soc.* **1997**, *119*, 10042; e) A. Corruble, J.-Y. Valnot, J. Maddaluno, P. Duhamel, *Tetrahedron: Asymmetry* **1997**, *8*, 1519; f) A. Corruble, J.-Y. Valnot, J. Maddaluno, P. Duhamel, *J. Org. Chem.* **1998**, *63*, 8266; g) Y. Prigent, A. Corruble, J.-Y. Valnot, J. Maddaluno, P. Duhamel, D. Davoust, *J. Chim. Phys.* **1998**, *95*, 401; h) P. I. Arvidsson, G. Hilmersson, Ö. Davidsson, *Chem. Eur. J.* **1999**, *5*, 2348; i) A. Thompson, E. G. Corley, M. F. Huntington, E. J. J. Grabowski, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc*. **1998**, *120*, 2028.

[12] K. B. Aubrecht, B. L. Lucht, D. B. Collum, *Organometallics* **1999**, *18*, 2981; see also ref. [9].

[13] a) P. G. Williard, M. A. Nichols, *J. Am. Chem. Soc* **1991**, *113*, 9671; b) see ref. [8a)] and [7aa)].

[14] The chiral amine **1** was synthesized by following the published procedures according to B. E. Rossiter, M. Eguchi, G. Miao, N. M. Swingle, A. E. Hernández, D. Vickers, E. Fluckiger, R. G. Patterson, K. V. Reddy, *Tetrahedron* **1993**, *49*, 965.

[15] a) G. Hilmersson, Ö. Davidsson, *J. Organomet. Chem.* **1995**, *489*, 175; b) G. Hilmersson, P. I. Arvidsson, M. Håkansson, Ö. Davidsson, *Organometallics* **1997**, *16*, 3352; c) G. Hilmersson, Ö. Davidsson, *J. Org. Chem.* **1995**, *60*, 7660.

[16] R. I. Olsson, P. Ahlberg, *Tetrahedron*: *Asymmetry* **1999**, *10*, 3991.

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