Carbazole deprotonation by sodium metal mirror in various ethers: structures with Na$^+$-coordination numbers 3 and 4 to 7 [1]

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Abstract

Solutions of carbazole anions and sodium cations in aprotic ethers such as tetrahydrofuran, dimethoxyethane, diglyme, triglyme, tetraglyme, 15-crown-5 or 2.2.1-cryptand form a cation solvation system with a shallow potential and numerous local minima. Its experimental exploration allows to crystallize and structurally characterize contact ion multiples of Na$^+$-solvated carbazole anion M$^-$ salts comprising polyether-solvated monomers $[M^-Na_{solv}^+]_1$, solvent-shared dimers $[M^-Na_{solv}^+]_2$ and solvent-separated polyions $[(M^-)_n Na_{solv}^+]^{(n-1)-}[Na_{solv}^+]_{(n-1)}$. Their Na$^+$ coordination numbers stretch from 3 to 7. Series of compounds, shape-selected from the same crystallization batch such as 3- and 7-coordinate $[(M^-)_3Na^+]^{2-}[Na^+(2.2.1\text{-cryptand})]_2$, 4- and 7-coordinate $[(M^-)_2Na^+(THF)_2]^-[Na^+(2.2.1\text{-cryptand})]$ as well as solvent-separated $[M^-][Na^+(2.2.1\text{-cryptand})]$ suggest potential cation solvation equilibria in the reductive deprotonation mixtures. The seven different carbazolate sodium salts presented, therefore, demonstrate the delicate energy balance, by which cation solvation can influence the crystallization of individual molecular crystals. © 1997 Elsevier Science S.A.

Keywords: Carbazole deprotonation; Ether-dependent Na$^+$ solvation; Crystal structures

1. Solvation equilibria of sodium carbazolates in aprotic ether solutions

Cation solvation is a fascinating phenomenon (preceeding part: Ref. [1]) (selected reviews: Refs. [2–5]) of general importance, which controls the often thermodynamically delicately balanced redox equilibria in solution [6–11] including numerous geological [12] as well as biochemical [13] ones. In order to improve the still rather limited knowledge concerning the essential solvent-dependent metal ion complexation (for reviews, see Refs. [14,15]), we have selected the molecular anion of the three-ring heterocycle carbazole [2] and advanta-

geous Na$^+$ cations [3] [23–25] in aprotic ether solutions and prepared various, partly novel contact ion multiples around the same cationic center [23–27].

All of the O- and N-solvated Na$^+$ carbazolate salts presented (Fig. 1) have been prepared by sodium metal deprotonation of carbazole in aprotic solutions of the respective ethers:

(1)
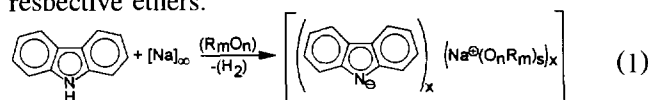
The air-sensitive single crystals grown are characterized by X-ray diffraction in a cooled N$_2$-flow [4], and their

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[1] Part 110 of Interactions in Molecular Crystals, see Ref. [1]. Dedicated to Professor Paul von Rague-Schleyer.
[2] For preceding structural investigations of carbazole and derivatives, see Refs. [16] (carbazole), [17] ($[Li^+(THF)_2carbazol^-]_2$), [18] ($[K^+(PMDTA)carbazole^-]_2$ and Cs$^+$ (PMDTA)carbazole$^-]_2$), [19] (monomeric[tetraalkylcarbazole$^-$ Mg$^{2+}(THF)_2C_2H_5]$). No crystal structure of a sodium carbazole salt can be detected in the most recent Cambridge Structural Data File.

[3] See e.g. Ref. [20]. The first vertical ionization energy of sodium metal Na, IE$_1^v$ = 5.13 eV, and the hydration enthalpy of $[Na^+(H_2O)_{17}]$ $\Delta Hf = -390$ kJ mol^{-1}, contribute both to the rather low first reduction potential, $E_{1/2}^{red}$ (Na) = -2.71 V. The ionic radius $r = 97$ pm, increasing to 113 pm for 30% covalent contribution [14,15] fits nicely into a benzene hexagon of 240 pm diameter as exemplified in Refs. [21,22].

[4] Crystal structures of all other carbazole anion sodium salts with Na$^+$ coordination numbers 5 to 7 (Fig. 1) cf. Ref. [28]. See also Section 2.
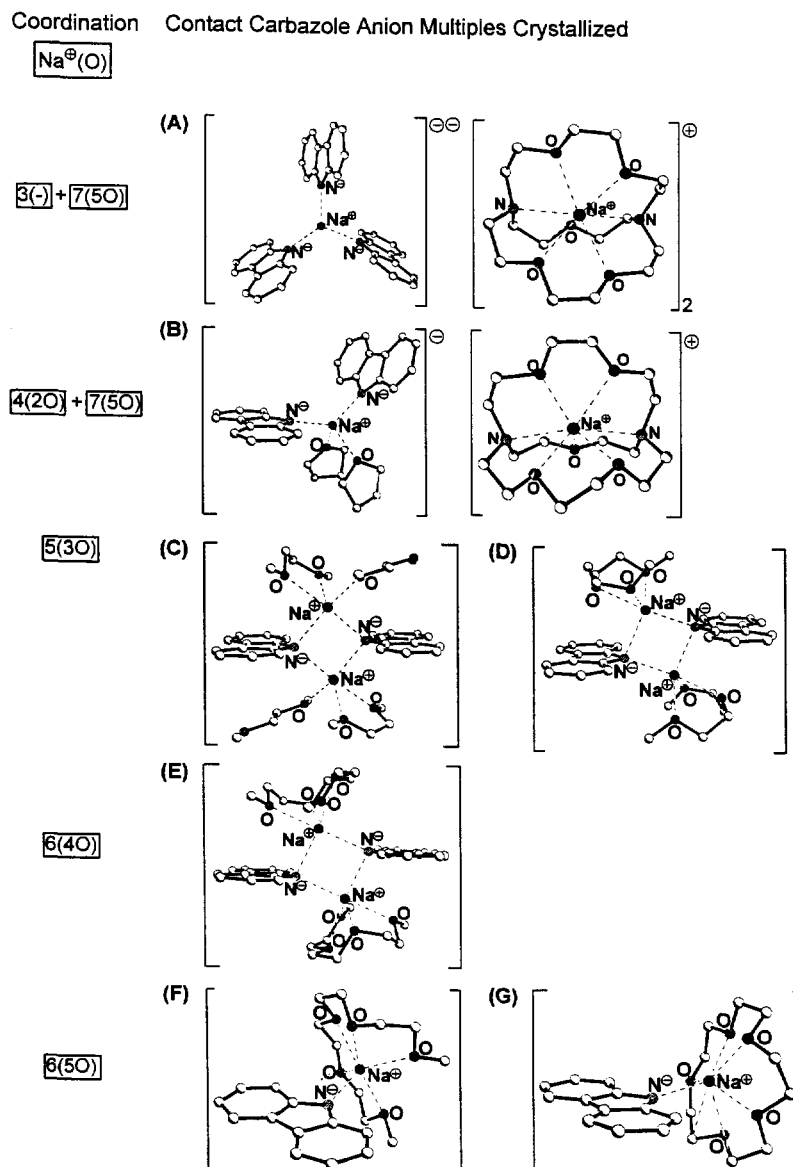
Fig. 1. Low-temperature single crystal structures of contact ion multiples, prepared by carbazole deprotonation (1) using sodium metal in various ether solvents, with increasing Na$^+$ coordination numbers (oxygen solvation in brackets): (A) tris(carbazolato)sodium-bis(2.2.1-cryptand-sodium) (triclinic P$\bar{1}$,. $Z = 2$); (B) bis(carbazolato)-bis(tetrahydrofuran)sodium-(2.2.1-cryptand-sodium) (triclinic, P$\bar{1}$,. $Z = 2$); (C) carbazole-sodium-1,5 dimethoxyethane (triclinic P$\bar{1}$,. $Z = 2$); (D) carbazole sodium-diglyme (triclinic P$\bar{1}$,. $Z = 2$); (E) carbazole-sodium-triglyme (monoclinic P2$_1$/n, $Z = 4$; (F) carbazole-sodium-tetraglyme (monoclinic P2$_1$/n, $Z = 4$) and (G) carbazole-sodium-15 crown 5 (monoclinic, P2$_1$/c (Nr. 14), $Z = 8$).

structures are discussed by comparison of the different Na$^+$ coordination numbers stretching from 3 and 4 to 7 (Fig. 1) based on results of MNDO calculations.

2. Experimental section

2.1. General

Carbazole (Aldrich, 99%) as well as 2.2.1.-cryptand are both dried for 1 d at 10^{-2} mbar. Ethers tetrahydrofuran and dimethoxyethane are refluxed for 2 d over Na/K alloy and distilled under argon into carefully dried Schlenk traps. All other ether solvents are dried over molecular sieve.

2.2. Carbazole deprotonation using sodium metal mirrors

The crystallization solutions (1) are prepared by transferring 4 to 10 mmoles sodium metal, freshly cut under n-hexane, under argon into a Schlenck trap, in which at 10^{-5} mbar a sodium metal mirror is generated using a hot air vent. Stoichiometric amounts of car-

bazole are weighed in and the carefully dried ($c_{H^+} < 1$ ppm) solvent is added with its amount determined by the concentration needed for optimum crystallization. On standing of the reaction mixture at room temperature under argon, the sodium metal mirror disappears in about 2 d.

For the deprotonation of carbazole in THF solution by a sodium metal mirror discussed in detail, 590 mg (2.2 mmol) carefully decrusted sodium are distilled at 10^{-5} mbar to the wall of a Schlenk trap and under Ar are added 50 mg (0.3 mmol) carbazole, 10 ml THF (dried over Na/K alloy) as well as 0.09 ml (0.3 mmol) 2.2.1.-cryptand. After the H_2 evolution ceases, the solution is covered by a layer of 5 ml n-hexane (dried over $LiAlH_4$) and within a day a crystal mixture deposits, from which the following three carbazole anion sodium salts $[M^- Na^+_{solv}]$ could be isolated by shape-selecting individual specimens of $[(M^-)_3 Na^+][Na^+(2.2.1)]_2$ with Na^+ counter cations of both coordination numbers 3 and 7 (Fig. 1A), of $[(M^-)_2 Na^+ (THF)_2][Na^+(2.2.1)]$ with four- and seven-fold Na^+ coordination (Fig. 1B) and of solvent-separated $[M^-][Na^+(2.2.1)]$ with again sevenfold coordinated sodium cation (Fig. 1: due to heavy disordering (cf. 2.5), see iso(valence)electronic (G)).

The dimers $[M^- Na^+ (H_3CO(CH_2CH_2O)_n CH_3)]_2$ with Na^+ solvated by dimethoxyethane ($n = 1$), diglyme ($n = 2$) or triglyme ($n = 3$) ligands are crystallized from sodium metal reduction solutions (1) in the respective ethers [28] (Fig. 1C–E) and contain five- and six-coordinate Na^+ counter cations solvated by three or four ether oxygen centres (Fig. 1: (3 O) and (4 O)). The monomeric carbazole anion sodium salts, $[M^- Na^+ (RO(CH_2CH_2O)_4 R)]_1$ and $[M^- Na^+ (CH_2CH_2O)_5]_1$ (Fig. 1F, G), crystallized from solutions in tetraglyme or in THF with added 15-crown-5 [28].

2.3. Crystal structure of tris(carbazolato)sodium-bis(2.2.1-cryptand sodium)

Colourless prisms, $(C_{12}H_8N)Na \cdot 2 NaC_{16}H_{32}N_2O_5$ (M.W. = 1232.42), $a = 13.024$ (1), $b = 13.757$ (1), $c = 21.233$ (1) Å, $\alpha = 90.92$ (1)°, $\beta = 105.12$ (1)°, $\gamma = 116.82$ (1)°, $V = 3237.8$ Å^3 ($T = 150$ K), $\rho_{ber} = 1.264$ g cm^{-3}, triclinic, P$\bar{1}$ (Nr. 2), $Z = 2$, Siemens P4 four-circle diffractometer, MoK α-radiation, $\mu = 0.10$ mm^{-1}, 11491 measured reflections with $3° \leq 2\Theta \leq 50°$, of which 10964 are independent and 10964 used for refinement ($R_{int} = 0.0202$), extinction-correction. Structure solution by direct methods (SHELXTL-PC), structure refinement against F^2 (SHELXTL-PC), 812 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0358 \cdot P)^2 + 1.85 P]$, R for 8475 Fo > 4σ (Fo) = 0.0421, wR2 for all 10964 data = 0.1061, GOOF = 1.019. Residual electron density 0.46/ − 0.47 e/Å^3. C, N, O and Na centers are refined anisotropically, hydrogen centers are positioned ideally and refined isotropically using individual displacement parameters within the riding model. Two carbons of the cryptand molecule were disordered and refined using a split model.

2.4. Crystal structure of bis(carbazole)-bis(tetrahydro-furan)sodium-2.2.1-cryptand-sodium)

Colourless prisms, $(C_{12}H_8N)_2 Na \cdot 2C_4H_8O_2 \cdot NaC_{16}H_{32}N_2O_5$ (M.W. = 855.01), $a = 11.857$ (1), $b = 11.946$ (1), $c = 18.793$ (1) Å, $\alpha = 89.98$ (1)°, $\beta = 75.53$ (1)°, $\gamma = 68.95$ (1)°, $V = 2313.1$ Å^3 ($T = 150$ K), $\rho_{ber} = 1.228$ g cm^3, triclinic, P$\bar{1}$(Nr. 2), $Z = 2$, Siemens P4 four-circle diffractometer, MoK α-radiation, $\mu = 0.10$ mm^{-1}, 10706 measured reflections within $3° \leq 2\Theta \leq < 50°$, of which are 7705 independent and 7704 used for refinement ($R_{int} = 0.0210$), extinction-correction. Structure solution by direct methods and difference-Fourier-technique (SHELXTL-PC), structure refinement against F^2 (SHELXL-93), 575 parameters, $w = 1/[\sigma^2(F_o^2) + (0.0618 \cdot P)^2 + 2.08 P]$, R for 6093 Fo > 4σ (Fo) = 0.0410, wR2 for all 7704 data = 0.1536, GOOF = 1.022, residual electron density 0.49/ − 0.40 e/Å^3. C, N, O and Na centers are refined anisotropically, hydrogen centers are positioned ideally and refined isotropically using isotropic displacement parameters within the riding model. Each two carbon as well as two oxygen centers of one cryptand molecule were disordered and refined using a split model.

2.5. Crystal structure of carbazole-sodium (2.2.1 cryptand)

Due to severe disordering, refinement to a comparable level of precision ($wR_2 < 0.2$) could not be accomplished. All other structure determinations (Fig. 1) are reported in Ref. [28].

2.6. MNDO calculations

Starting from the experimentally determined structure coordinates, the calculations have been performed using optimised sodium parameters [29,30] in the program package SCAMP IV/1 (Dr. T. Clark, University Erlangen) on our work station IBM RISC 6000/320.

3. Results and discussion

3.1. Structures of ether-solvated sodium salts of carbazole anions and their calculated charge distributions

The seven differently ether solvated sodium salts of the carbazole anion prepared (see footnote 4), are advantageously characterized by both the total and the
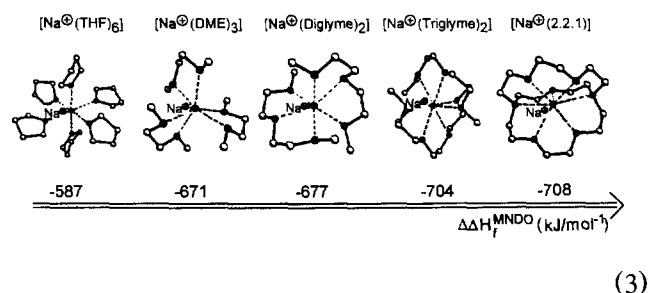
oxygen coordination numbers CN and CN(O) of their Na^+ counter cations (Fig. 1).

The crystal structures of the carbazole sodium salts crystallized (Fig. 1) can be typified as solvent-separated ion multiples $[M^- Na_{solv}^+]^{(n-1)-} \ [Na_{solv}^+]_{(n-1)}$, as solvent-shared contact ion pair dimers $[M^- Na_{solv}^+]_2$ or as solvent-shared monomeric contact ion pairs $[M^- Na_{solv}^+]_1$. Their structural data (see footnote 4) are expectedly partly comparable: All carbazole anions exhibit constant bond lengths, only the angles change in their charge-distorted five-membered rings with angles ⊀ CNC decreasing from 109° by 5° to 104° and ⊀ CCN widened from 109° by +4° to 113°. Contact distances Na^+ ... N vary between 2.30 and 2.53 Å around a mean value of 2.39 Å and Na^{+1} ⋯ O between 2.35 and 2.59 Å around 2.43 Å. The largest structural differences are observed for the deviation of the Na^+ cation from the idealized carbazole planes, which varies for the monomers between 0.38 and 0.66 Å and for the dimers between 0.80 and 2.30 Å [28] (Fig. 1).

Based on the structural data, the following charge distributions and enthalpies of formation are predicted.

$q_{Na^\oplus}$	+.34	+.43	+.48
$q_{N^\ominus}$	-.35	-.32	-.29
q_O	-.28	-.25	-
ΔH_f^{MNDO}	-365	-647	-817 kJ/mol^{-1}

$$(2)$$
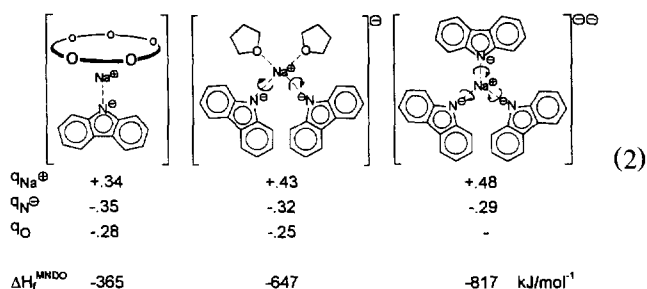
The positive charge at the Na^+ cation increases with the number of anion ligands, whereas the negative charge of the carbazole anion nitrogen centre decreases. The ether solvation of the sodium cations can be rationalized by increasing enthalpy contributions predicted by MNDO calculations based on the experimentally determined structural coordinates [23–25] for the sequence:

$[Na^\oplus (THF)_6]$ $[Na^\oplus (DME)_3]$ $[Na^\oplus (Diglyme)_2]$ $[Na^\oplus (Triglyme)_2]$ $[Na^\oplus (2.2.1)]$

-587   -671   -677   -704   -708

$\Delta\Delta H_f^{MNDO}$ (kJ/mol^{-1})

$$(3)$$

Accordingly, the structures of the complexes (2) selected for discussion are dominated by the extremely advantageous Na^+ cation solvation by the 15-crown-5

ligand or by the rather poor competing donor properties of the space-filling ether tetrahydrofuran [23–25]. The sodium cation solvation sequence (3), unexpected only at first sight, is substantiated and confirmed by numerous recent reports, e.g. on the crystallization of $Na^+[^-(C(NO_2)_3]$ from 18-crown-6/THF solutions as ion pair $[(18-K-6)Na^+(THF)_2][(18-K-6)Na^+(C(NO_2)_3)_2]^-$ [29,30] or of a tripeldecker-disodium salt $[(18-K-6)Na^+(18-K-6)Na^+(18-K-6)][M^-]_2$ [31]. Two THF ligands can be replaced by one carbazolate anion to generate the sterically shielded contact quadruple ion dianion $[(M^-)_3Na^+]^{2-}$ (2) with an Na^+ center of the rather rare coordination number 3 [5].

3.2. Na^+ solvation equilibria in solution suggested by the structures of the carbazole anion salts crystallized

The reductive deprotonation mixtures (1), generated from their components carbazole, sodium metal, ether solvent and sometimes a multidentate complexing ligand such as 2.2.1-cryptand or 15-crown-5, are multiparameter systems [8–11,14,15]. Even if all controllable reaction conditions from stoichiometry, aprotic conditions ($c_{H^-} < 0.1$ ppm) to temperature are kept as constant as possible, compound-specific networks of interdependent equilibria will be activated comprising electron transfer [1,8,9], contact ion formation [6,7,10,11] as well as aggregation [6,7,11,14,15] and, above all, cation solvation [14,15,23–27]. Often, well-chosen sensitive methods of measurement such as cyclic voltammetry [8–10,35,36], UV/VIS spectroscopy [36] or ENDOR signal patterns [10,14,15] provide some 'snap-shot' insights into the rather complex multitude of interrelated processes in solution [14,15]. Here it will be pointed out in addition, that also the crystallization and structural characterization of various chemically related contact ion multiples from one multiparameter system (Fig. 1) - such as especially the 'handpicked' specimens of carbazole anion sodium salts from a 'one batch crystallization' (see Section 2) - allow to rationalize some facets of the equilibria network and its numerous local minima (Fig. 2).

The tentative scheme (Fig. 2) for sodium carbazolate formation in solution is based on the structure of the crystals isolated (Fig. 1). It begins with the metal mirror deprotonation of carbazole and the formation of optimally ether-solvated Na^+ counter cations (3) [23–25]: addition of 2.2.1-cryptand to the ether solution of an initially generated solvent-separated contact ion pair

[5] Examples for threefold coordinate Na^+ centers in the Cambridge Structural Database: (a) sodium(tert-butoxide) [32], (b) cation $[Na^+ (THF)_2]$ in Rh complex [33], or (c) dianion $[Na^+ (NCBH_3)_3]^{2-}$ in Ni complex [34].

$[M^-] + [Na^+(OR_2)_6]$, therefore, should yield $[M^-]$ + $[Na^+ 2.2.1]$ as the energetically more favorable one [23–25]. According to the one batch-crystallization (cf. Section 2), the nucleophilic carbazole anion $[M^-]$ can replace two THF ether solvate ligands and form the contact ion triple anion $[(M^-)_2 Na^+ (OR_2)_2]^-$ (Fig. 2B and Fig. 1B). The replacement of the remaining two THF ligands by another carbazole anion M^- finally produces the threefold carbazolate substituted contact ion quadruple dianion $[(M^-)_3 Na^+]^{2-}$ (Figs. 1 and 2A) with a Na^+ center of rare (see footnote 5) coordination number 3 (cf. Section 2). For the heavily disordered, solvent-separated sodium carbazolate $[M^-][Na^+(2.2.1)]$ (cf. Section 2) related salts such as $[M^- Na^+(15\text{-}K\text{-}5)]$ (Fig. 1G) [28] have to serve as substitutes.

From sodium carbazolate solutions in various polyethers $RO(CH_2 CH_2 O)_n R$ containing $n = 2$, 3 or 4 oxygen coordination centers, obviously, the crystallization of dimers $[(M^-)_2 Na^+(O_n R_m)]_2$ is favored (Figs. 1 and 2C–E). On further increase of the solvation, $Na^+ \leftarrow$ O to five oxygen centers (Fig. 2: $n = 5$) such as with tetraglyme or 15-crown-5, monomer ether-solvated Na^+ counter cations are preferred again (Fig. 1F, G).

Summarizing, the different solvation of the Na^+ counter cations (3) according to their total and especially their oxygen coordination number (Fig. 1), which is well-documented in the literature [14,15,23–27,29–31], preferentially stabilizes either solvent-shared or solvent-separated ion multiples. Therefore, even a simplified qualitative scheme of potential crystallization pathways (Fig. 2) as suggested by structural comparison, allows to rationalize the manifold of carbazole anion sodium salts, which are formed in a network of equilibria after its activation by sodium metal mirror deprotonation of carbazole in various ethers.
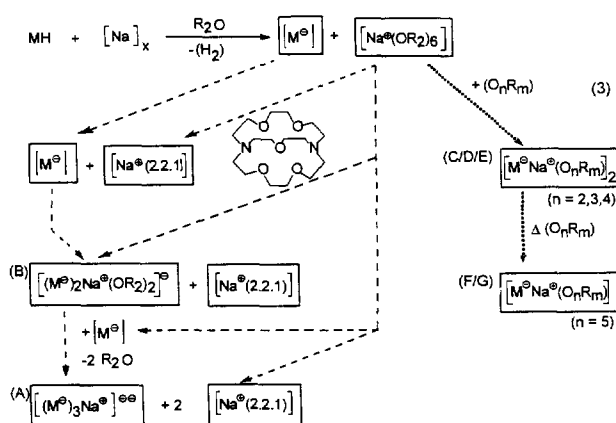

Fig. 2. Potential crystallization pathways for carbazole anion $[M^-]$ salts with various ether-solvated Na^+ cations after metal mirror deprotonation under aprotic conditions (1) as suggested by comparison of their crystal structures (Fig. 1).

References

[1] H. Bock, K. Gharagozloo-Hubmann, C. Näther, N. Nagel, Z. Havlas, Angew. Chem. 108 (1996) 720; Angew. Chem. Int. Ed. Engl. 36 (1996) 631.
[2] M. Szwarc (Ed.), Ions and Ion Pairs in Organic Reactions, vols. 1 and 2, Wiley-Interscience, New York, 1972 and 1974.
[3] Y. Marcus, Ion Solvation, Wiley, Chichester, 1985.
[4] J.M. Lehn, Angew. Chem. 100 (1988) 91; Angew. Chem. Int. Ed. Engl. 27 (1988) 89.
[5] Y. Inoue, G.W. Gokel (Eds.), Cation Bonding by Macrocycles, Marcel Dekker, New York, 1990.
[6] S.W. Mao, K. Nakamura, N. Hirota, J. Am. Chem. Soc. 96 (1974) 5341.
[7] W. Lubitz, M. Plato, K. Möbius, R. Biehl, J. Phys. Chem. 83 (1979) 3401.
[8] H. Bock, Polyhedron 7 (1988) 2429.
[9] H. Bock, Angew. Chem. 101 (1989) 1659; Angew. Chem. Int. Ed. Engl. 28 (1989) 1627.
[10] H. Bock, H.-F. Herrmann, J. Am. Chem. Soc. 111 (1989) 7622.
[11] H. Bock, H.-F. Herrmann, D. Fenske, H. Goesmann, Angew. Chem. 100 (1988) 1125; Angew. Chem. Int. Ed. Engl. 27 (1988) 1967.
[12] A.F. Wells, Structural Inorganic Chemistry, 5th ed., Oxford University Press, Oxford, 1987.
[13] W. Kaim, B. Schwederski, Bioanorganische Chemie, Teubner, Stuttgart, 1991.
[14] H. Bock, K. Ruppert, C. Näther, Z. Havlas, H.-F. Herrmann, C. Arad, I. Göbel, A. John, J. Meuret, S. Nick, A. Rauschenbach, W. Seitz, T. Vaupel, B. Solouki, Angew. Chem. 104 (1992) 564; Angew. Chem. Int. Ed. Engl. 31 (1992) 550.
[15] H. Bock, Mol. Cryst. Liq. Cryst. 240 (1994) 155.
[16] R.E. Gerkin, W.J. Reppart, Acta Crystallogr. C 42 (1986) 480.
[17] R. Hacker, E. Kaufmann, P.v.R. Schleyer, W. Mahdi, H. Dietrich, Chem. Ber. 120 (1987) 1533.
[18] K. Gregory, M. Bremer. P.v.R. Schleyer, P.A.A. Klusener, L. Brandsma, Angew. Chem. 101 (1989) 1261; Angew. Chem. Int. Ed. Engl. 28 (1989) 1224.
[19] N. Kuhn, M. Schulten, R. Boese, D. Bläser, J. Organomet. Chem. 421 (1991) 1.
[20] N. Wiberg, Hollemann/Wiberg: Lehrbuch der Anorganischen Chemie, de Gruyter, Berlin, 1995.
[21] H. Bock, K. Ruppert and D. Fenske, Angew. Chem. 101 (1989) 1717; Angew. Chem. Int. Ed. Engl. 28 (1989) 1685.
[22] H. Bock, K. Ruppert, Z. Havlas and D. Fenske, Angew. Chem. 102 (1990) 1095; Angew. Chem. Int. Ed. Engl. 29 (1990) 1042.
[23] H. Bock, C. Näther, Z. Havlas, A. John, C. Arad, Angew. Chem. 106 (1994) 931; Angew. Chem. Int. Ed. Engl. 33 (1994) 875.
[24] H. Bock, A. John, C. Näther, Z. Havlas, Z. Naturforsch. B 49 (1994) 1339.
[25] H. Bock, A. John, C. Näther, Z. Havlas, E. Mihokava, Helv. Chim. Acta 77 (1994) 41.
[26] H. Bock, C. Näther, Z. Havlas, J. Am. Chem. Soc. 117 (1995) 3869.
[27] H. Bock, C. Näther, K. Ruppert, Z. Havlas, J. Am. Chem. Soc. 114 (1994) 6907.

[28] H. Bock, C. Arad, C. Näther, Z. Havlas, Helv. Chim. Acta 80 (1997) 606.

[29] H. Bock, T. Hauck, C. Näther, Z. Havlas, Z. Naturforsch. 49 (1994) 1012.

[30] W.S. Sheldrick, J. Kroner, F. Zwaschka, A. Schmidpeter, Angew. Chem. 91 (1979) 998; Angew. Chem. Int. Ed. Engl. 18 (1979) 934.

[31] H. Bock, T. Hauck, C. Näther, Z. Havlas, Angew. Chem. 109 (1997), 650; Angew. Chem. Int. Ed. Engl. 36 (1997), 638.

[32] Th. Greiser, E. Weiss, Chem. Ber. 110 (1977) 3388.

[33] A.S.C. Chan, H.-S. Shieh, J.R. Hill, J. Organomet. Chem. 279 (1985) 151.

[34] G. Ferguson, M.C. Jennings, H.A. Mirza, R.J. Puddephatt, Organometallics 9 (1990) 1576.

[35] H. Bock, A. John, C. Näther, Z. Havlas, I. Göbel, A. John, M. Kleine, Helv. Chim. Acta 78 (1995) 866.

[36] H. Bock, C. Arad, C. Näther, I. Göbel, Helv. Chim. Acta 79 (1996) 92.