

Structure Determination of Unsolvated Potassium, Rubidium, and Cesium Carbazolates

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The solid-state structures of unsolvated potassium, rubidium, and cesium carbazoles were determined using laboratory X-ray powder diffraction data. Potassium and rubidium carbazoles adopt a polymeric helical arrangement, whereas cesium carbazolate forms a polymeric twisted column structure.

Introduction

The alkali-metal salts of essential anionic ligands in organometallic chemistry, such as cyclopentadienyl, indenyl, and fluorenyl, are the standard precursors for the synthesis of related complexes.¹ Ten years ago the solid-state structures of these important precursors were unknown, because no sizable single crystals of the homoleptic alkali-metal compounds could be grown. Structure determinations could only be carried out on base adducts of these compounds or by introducing bulky substituents to the organic anions. In these cases single crystals were obtainable.² To get insights into the structures of the simple unsolvated organic alkali-metal salts, a program on structure determination from X-ray powder diffraction data was initiated. In 1997 we presented the solid-state structures of all alkali-metal cyclopentadienyls, followed by the structures of unsolvated (pentamethylcyclopentadienyl)lithium and -sodium, indenyllithium, and fluorenylsodium. All structures were determined by high-resolution powder diffraction using synchrotron radiation.³ The structure of fluorenyllithium could be solved by X-ray single-crystal diffraction.⁴

In this study, we present the solid-state structures of the unsolvated heavier alkali-metal carbazoles, the carbazolate anion being the nitrogen analogue of the important fluorenyl ligand (Figure 1). The structures of potassium (**1**), rubidium (**2**), and cesium carbazoles (**3**) were determined from laboratory X-ray powder diffraction data.

Results and Discussion

All unsolvated alkali-metal carbazoles were synthesized by deprotonation of the NH-acidic carbazole⁵ using *n*-butyllithium, sodium hexamethyldisilazide, potassium hydride, rubidium hexamethyldisilazide, and cesium hexamethyldisilazide, respectively. The alkali-metal salts could be precipitated directly from a tetrahydrofuran solution by adding *n*-hexane.⁶ It has to be pointed out that in this way no thf base adducts were obtained. The carbazoles form air-sensitive, white powders which are insoluble in diethyl ether, toluene, and *n*-hexane but soluble in tetrahydrofuran. ¹H and ¹³C NMR spectra were taken in deuterated tetrahydrofuran (for data see the Experimental Section). In the case of lithium and sodium carbazoles, the elemental analyses indicate impurities within the obtained crystal powders.

X-ray powder patterns were taken for all alkali-metal carbazoles at room temperature and for the Li, K, Rb, and Cs compounds at low temperature as well. The diffractograms of lithium and potassium carbazolate were different at both temperatures, indicating two different crystalline phases. The

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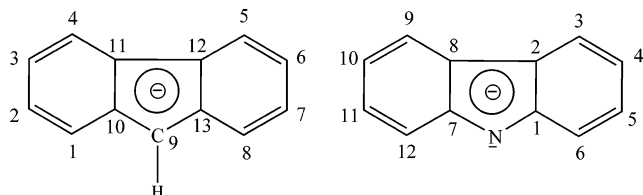


Figure 1. Fluorenyl anion (left) and carbazolate anion (right) with numbering scheme.

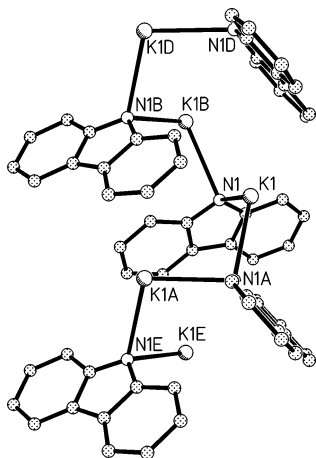


Figure 2. Part of the helix in $\text{KNC}_8\text{H}_{12}$ (**1**). Five units are shown with the hydrogen atoms omitted for clarity. $\text{RbNC}_8\text{H}_{12}$ (**2**) shows the same structure. Symmetry operations: (A) $-y + 2/3, x - y + 1/3, z + 1/3$; (B) $-x + y + 1/3, -x + 2/3, z - 1/3$; (D) $-y + 2/3, x - y + 1/3, z - 2/3$; (E) $-x + y + 1/3, -x + 2/3, z + 2/3$.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Potassium (1) and Rubidium Carbazolates (2)^a

Compound 1					
K1...K1A	4.293(1)	K1-N1	2.870(5)	K1-N1A	2.892(6)
K1-C9C	2.998(5)	K1-C9D	3.208(5)	K1-C12B	3.293(5)
K1-C11B	3.378(6)				
N1-K1-N1A	104.5(2)	K1-N1-K1A	96.3(2)		
Compound 2					
Rb1...Rb1A	4.403(1)	Rb1-N1	2.971(5)	Rb1-N1A	3.020(5)
Rb1-C9C	3.016(5)	Rb1-C9D	3.332(6)	Rb1-C12B	3.280(4)
Rb1-C11B	3.265(5)				
N1-Rb1-N1A	101.8(2)	Rb1-N1-Rb1A	94.6(2)		

^a Symmetry operations: (A) $-y + 2/3, x - y + 1/3, z + 1/3$; (B) $-x + y + 1/3, -x + 2/3, z - 1/3$; (C) $-y + 2/3, -x + 1/3, z - 1/6$; (D) $-y + 2/3, x - y + 1/3, z - 2/3$.

powder diagrams of potassium (**1**), rubidium (**2**), and cesium carbazolates (**3**) were excellent in quality at low temperature, so that the solid-state structures could be obtained directly from these data.

The solid-state structures of $\text{KNC}_{12}\text{H}_8$ (**1**) and $\text{RbNC}_{12}\text{H}_8$ (**2**) are isostructural at -173°C . The substances crystallize in the space group $R3c$ with one metal carbazolate forming the asymmetric unit. Table 1 gives selected bond lengths and angles. Both metal carbazolates adopt an interesting helical arrangement (Figure 2). One turn of the helix consists of three metal carbazolate units (K1A, K1, and K1B). The repeat distance between turns is the length of the crystallographic c axis (7.8355(2) Å (**1**) and 8.1932(4) Å (**2**)). There are equal numbers of right-handed and left-handed helices in the crystal, because of 3_1 and 3_2 screw axes in the space group. Therefore, each 3_1 helix is surrounded by three 3_2 helices and vice versa (Figure 3).

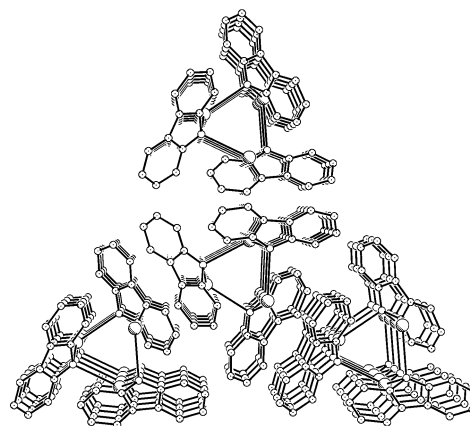


Figure 3. Drawing of four neighboring helices in $\text{KNC}_8\text{H}_{12}$ (**1**): perspective view along the crystallographic c axis.

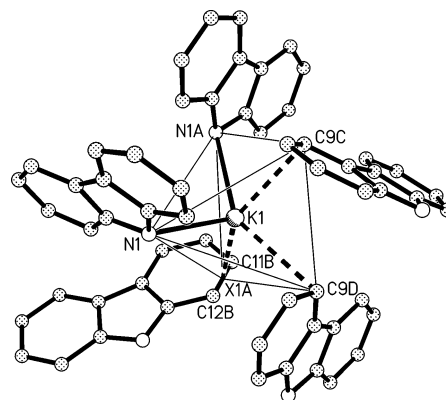


Figure 4. Coordination sphere of potassium in $\text{KNC}_8\text{H}_{12}$ (**1**) with the distorted-tetragonal-pyramidal polyhedron shown. Symmetry operations: (A) $-y + 2/3, x - y + 1/3, z + 1/3$; (B) $-x + y + 1/3, -x + 2/3, z - 1/3$; (C) $-y + 2/3, -x + 1/3, z - 1/6$; (D) $-y + 2/3, x - y + 1/3, z - 2/3$.

Each K^+ or Rb^+ cation is engaged in two almost identical bonds to the nitrogen atoms of two bridging carbazolate anions (**1**, 2.870(5), 2.892(6) Å; **2**, 2.971(5), 3.020(5) Å). The angle at the metal atom is slightly larger than 100° . The bridging carbazolate anions are practically planar within error limits. The bridging nitrogen centers are essentially tetrahedrally four-coordinated with M-N-C angles between 101.6(2) and 124.5(2)°. To satisfy the coordination sphere around the metal centers, K-C and Rb-C π interactions are obvious. Short M-C distances are found between neighboring helices (Figure 4) (**1**, K-C9C = 2.998(5) Å; **2**, Rb-C9C = 3.016(5) Å). Longer are the contacts between the metal atoms and three carbon atoms (C9D, C11B, and C12B) of adjacent carbazolate anions within the same helix (**1**, 3.208(5)–3.378(6) Å; **2**, 3.265(5)–3.332(6) Å). The metal atoms thus gain the coordination number 5 with a geometry of a distorted tetragonal pyramid, one nitrogen atom (N1) being in the apical position. The cation to plane distance (best plane through the atoms N1A, C9C, C9D, and X1A) is 0.887(3) Å for K^+ and 0.757(3) Å for Rb^+ (X1A = center between C11B and C12B; Figure 4). The description of the carbazolate anions can be given as a $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{:}\eta^2$ ligand.

Although the solid-state structures of $\text{KNC}_{12}\text{H}_8$ (**1**) and $\text{RbNC}_{12}\text{H}_8$ (**2**) are isostructural, as mentioned before, in **2** a more efficient packing of the helices can be observed. Because the Shannon radius⁷ of Rb^+ is 14 pm larger compared to that of K^+ (for coordination number 6), the Rb-N distances found are

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10 and 13 pm longer in **2** than the K–N distances in the potassium compound, leading to a longer *c* axis in **2** (*c* axis: 7.8355(2) Å (**1**); 8.1932(4) Å (**2**)). As described before, the M⁺ cations (M = K (**1**), Rb (**2**)) interact with five different carbazolate anions (Figure 4): two in a M–N manner and three as a M–C π -interaction. Interestingly, in RbNC₁₂H₈ two M–C π interactions are shorter (M–C11B; M–C12B) or have almost the same distance (M–C9C) compared to those in **1** (Figure 4 and Table 1). These stronger Rb–C π interactions between adjacent helices in **2** lead to a better packing of the structure and thus to a shorter *a* axis in RbNC₁₂H₈ (*a* axis: 25.0827(9) Å (**1**); 24.9084(11) Å (**2**)).

The solid-state structure of the important organic reagent lithium diisopropylamide (LDA) shows a certain similarity to the structures of **1** and **2**. LDA, too, adopts a helical arrangement, but with four turns per repeat distance.⁸ Finally, it should be mentioned that there are a number of solid-state structures of unsolvated, base-free lithium dialkylamides with two bulky substituents at the nitrogen atom where single crystals could be grown. Trimeric, tetrameric, and hexameric structures were found.⁹ Furthermore, the crystal structure of unsolvated sodium tetramethylpyrrolate is known, which forms a polymeric ladder structure with bridging σ - and π -bonded pyrrolate anions.¹⁰ Solid-state structures of solvated alkali-metal carbazates have been determined by us and others. Dimeric and monomeric complexes are found, along with compounds with uncoordinated carbazolate anions.^{6b,c,11}

The solid-state structure of cesium carbazolate (**3**) is completely different from those of **1** and **2**. The cesium salt crystallizes in the noncentrosymmetric space group *Ia* (non-standard setting of *Cc*, No. 9) with two cesium carbazates forming the asymmetric unit, which is shown in Figure 5. Table 2 gives selected bond lengths and angles.

In the asymmetric unit chosen, there are two closely arranged cesium cations (Cs1...Cs2 distance 4.439(2) Å) which are sandwiched by two carbazolate anions in such a way that both nitrogen atoms are in cis positions (Figure 5). The angle between both carbazolate anions (planar within errors) is 112.2(1)°. Within this dimeric (CsNC₁₂H₈)₂ unit each Cs⁺ ion is located asymmetrically above the six-membered rings of two anions. The distances of these interactions vary between 3.442(8) and 4.033(5) Å for Cs1 and between 3.337(7) and 4.056(7) Å for Cs2. In the crystal structure the asymmetric units are connected via strong Cs–N contacts (3.160(2) and 3.152(9) Å to N1; 3.283(9) Å to N2) to adjacent dinuclear units, forming a one-dimensional polymeric twisted column along the crystallographic *c* axis which is presented in Figure 6.

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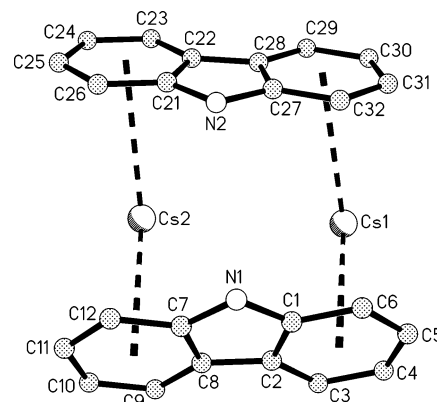


Figure 5. Asymmetric and dinuclear unit of cesium carbazolate (**3**).

Table 2. Selected Bond Lengths (Å) of Cesium Carbazolate (**3**)^a

Cs1...Cs2	4.439(2)	Cs1–N1A	3.160(2)	Cs1–C3	3.607(7)
Cs1–C1	3.818(4)	Cs1–C2	3.787(5)	Cs1–C6	3.661(5)
Cs1–C4	3.442(8)	Cs1–C5	3.470(5)	Cs1–C29	3.926(7)
Cs1–C27	3.868(5)	Cs1–C28	4.033(5)	Cs1–C32	3.583(6)
Cs1–C30	3.642(6)	Cs1–C31	3.462(7)	Cs1–C23B	3.473(5)
Cs1–C21B	3.528(6)	Cs1–C22B	3.338(5)	Cs1–C26B	3.820(6)
Cs1–C24B	3.770(8)	Cs1–C25B	3.933(7)		
Cs2–N1A	3.152(9)	Cs2–N2A	3.283(9)		
Cs2–C7	3.585(5)	Cs2–C8	3.624(5)	Cs2–C9	3.702(7)
Cs2–C10	3.740(6)	Cs2–C11	3.704(7)	Cs2–C12	3.627(7)
Cs2–C21	3.337(7)	Cs2–C22	3.627(6)	Cs2–C23	3.974(7)
Cs2–C24	4.056(7)	Cs2–C25	3.805(6)	Cs2–C26	3.441(8)

^a Symmetry operations (A) $x, -y + 3/2, z - 1/2$; (B) $x + 1/2, 2 - y, z$.

Each column is surrounded by four other columns. The Cs1⁺ ions within a stack are coordinatively unsatisfied and interact with neighboring columns. Between the stacks displayed in Figure 6 there are further contacts to adjacent one-dimensional entities via the Cs1⁺ ion in a Cs1– η^6 (NC₁₂H₈) manner, again asymmetric to a six-membered ring of an anion. The Cs1– η^6 –(C) distances between different columns are 3.338(5)–3.933(7) Å. In this way a complex three-dimensional assemble of cesium cations and carbazolate anions is established: a solid-state network. The Cs1⁺ ion is coordinated by four NC₁₂H₈ anions in an η^1 (N): η^6 (C₆): η^6 (C₆): η^6 (C₆) manner and a tetrahedral geometry (Figure 7), while Cs2⁺ interacts as well with four ligands in a tetrahedral geometry but in an η^1 (N): η^1 (N): η^6 (C₆): η^6 (C₆) manner (Figure 8). The two different carbazolate anions can be described as μ_4 - η^1 : η^6 : η^6 : η^6 and μ_4 - η^1 : η^1 : η^6 : η^6 ligands.

There is no crystal structure of an unsolvated organic cesium amide reported in the literature, except for three related cesium silazides: dimeric cesium hexamethyldisilazide,¹² dimeric cesium tetramethyldiphenyldisilazide,¹³ and tetrameric cesium trimethylsilazide.¹⁴ Two cesium carbazates with further Lewis bases at the metal atom have been characterized structurally: cesium carbazolate with pentamethyldiethylenetriamine^{6c} and cesium carbazolate with 18-crown-6.^{11d} They form molecular dimers with bridging aromatic amide anions.

Closely related to the solid-state structure of **3** are the crystal structures of [(KC₁₃H₉)₂thf]_n and [(CsC₁₃H₉)₂thf]_n (C₁₃H₉[−] =

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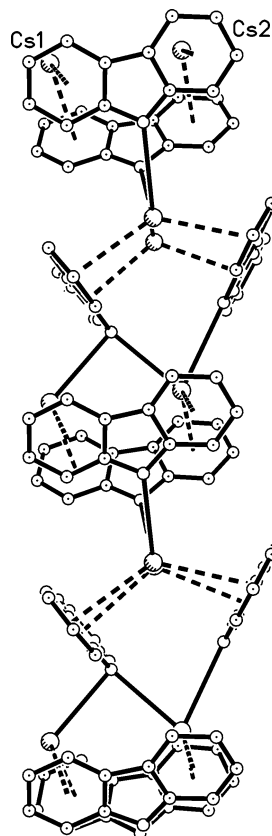


Figure 6. Part of the polymeric twisted column in base-free $\text{CsNC}_{12}\text{H}_8$ (**3**) along the c axis. Five dimeric $(\text{CsNC}_{12}\text{H}_8)_2$ units are shown (no H atoms).

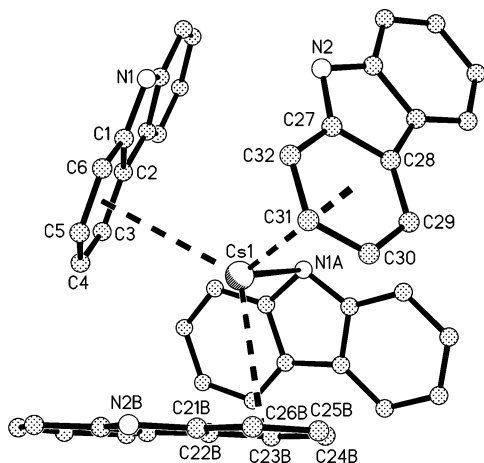


Figure 7. Coordination sphere of $\text{Cs}1^+$ in $\text{CsNC}_8\text{H}_{12}$ (**3**). Cesium distances to the center of the six-membered rings (Å): $\text{Cs}1-\eta^6\text{-(C1-C6)} = 3.351(3)$, $\text{Cs}1-\eta^6\text{-(C27-C32)} = 3.485(3)$, $\text{Cs}1-\eta^6\text{-(C21B-C26B)} = 3.369(3)$. Symmetry operations: (A) $x, -y + 3/2, z - 1/2$; (B) $x + 1/2, 2 - y, z$.

fluorenyl anion; Figure 1).¹⁵ These two compounds also crystallize as three-dimensional networks in which dinuclear units were found (i.e. $[(\text{CsC}_{13}\text{H}_9)_2\text{thf}]_n$; Figure 9).

Experimental Section

The chemicals used ($n\text{-BuLi}$, NaNH_2 , KH , hexamethyldisilazane, carbazole, toluene, tetrahydrofuran) were purchased from Merck,

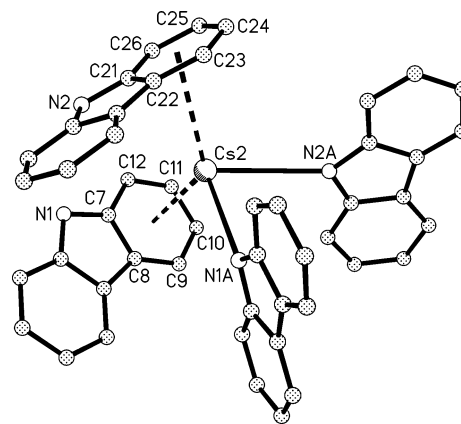


Figure 8. Coordination sphere of $\text{Cs}2^+$ in $\text{CsNC}_8\text{H}_{12}$ (**3**). Cesium distances to the center of the six-membered rings (Å): $\text{Cs}2-\eta^6\text{-(C7-C12)} = 3.384(3)$, $\text{Cs}2-\eta^6\text{-(C21-C26)} = 3.440(3)$. Symmetry operations: (A) $x, -y + 3/2, z - 1/2$; (B) $x + 1/2, 2 - y, z$.

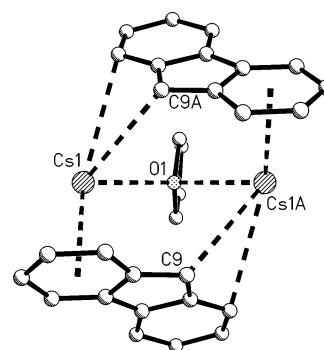


Figure 9. Dinuclear $(\text{CsC}_{13}\text{H}_9)_2\text{thf}$ unit as a part of the polymeric network of $[(\text{CsC}_{13}\text{H}_9)_2\text{thf}]_n$ (H atoms not shown).

except for Rb and Cs metal (ChemPur Feinchemikalien Co.). All manipulations were performed using conventional Schlenk techniques under an atmosphere of argon. Solvents were dried (K metal; benzophenone), distilled, and degassed before use. Instrumentation: infrared, Perkin-Elmer FT-IR PE 1720; NMR, samples were dissolved in dried $\text{THF-}d_8$ (Bruker Avance 400); X-ray powder diffraction, samples were measured in 0.3 mm glass capillaries (Debye-Scherrer mode) with $\text{Cu K}\alpha_1$ radiation using a Ge(111) primary beam monochromator (StadiP, Stoe & Cie GmbH).

The precursors sodium, rubidium, and cesium hexamethyldisilazides were prepared by standard literature methods.^{12,16}

Synthesis of Lithium Carbazolate. To a stirred solution of 0.35 g (2.1 mmol) of carbazole in 10 mL of toluene was added 0.46 mL of $n\text{-BuLi}$ (15% in $n\text{-hexane}$). After 10 min the white precipitate was collected, washed with hot toluene, dissolved in tetrahydrofuran, precipitated again by adding $n\text{-hexane}$, and dried under vacuum. Yield: 0.29 g (80%). Lithium carbazolate is insoluble in ether, toluene, and $n\text{-hexane}$ but soluble in tetrahydrofuran. Mp: 292 °C dec. $^1\text{H NMR}$ (400 MHz, $\text{THF-}d_8$): δ 7.98 (d, 2H), 7.43 (d, 2H), 7.22 (t, 2H), 6.98 (t, 2H) ppm.¹⁷ IR (Nujol): ν 1603, 1583, 1327, 1270, 1234, 1144, 888, 768, 729 cm^{-1} . Anal. Calcd (found) for $\text{C}_{12}\text{H}_8\text{LiN}$: C, 83.2 (78.1); H, 4.7 (4.6); N, 8.1 (7.2).

Synthesis of Sodium Carbazolate. To a stirred solution of 0.32 g (1.75 mmol) of sodium hexamethyldisilazide in 10 mL of toluene was added 0.26 g (1.6 mmol) of carbazole. After 10 min the white precipitate was collected, washed with hot toluene, dissolved in tetrahydrofuran, precipitated again by adding $n\text{-hexane}$, and dried under vacuum. Yield: 0.24 g (80%). Sodium carbazolate is insoluble in ether, toluene, and $n\text{-hexane}$ but soluble in tetrahy-

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(17) See also: Cox, R. H. *Can. J. Chem.* **1971**, *49*, 1377.

drofuran. Mp: 317 °C dec. ¹H NMR (400 MHz, THF-*d*₈): δ 7.95 (d, 2H), 7.46 (d, 2H), 7.12 (t, 2H), 6.79 (t, 2H) ppm.¹⁷ ¹³C NMR (50.3 MHz, THF-*d*₈): δ 126.1, 123.2, 120.1, 114.6, 114.1 ppm (signal for C1 not observed). IR (Nujol): ν 1602, 1583, 1239, 1116, 929, 749, 726 cm⁻¹. Anal. Calcd (found) for C₁₂H₈NNa: C, 76.2 (72.9); H, 4.3 (4.6); N, 7.4 (6.8).

Synthesis of Potassium Carbazolate (1). To a stirred suspension of 0.18 g (4.5 mmol) of potassium hydride in 10 mL of tetrahydrofuran was added 0.67 g (4.0 mmol) of carbazole. After 3 h the brownish solution was filtered; the white product precipitated by adding *n*-hexane and was dried under vacuum. Yield: 0.72 g (88%). Potassium carbazolate is insoluble in ether, toluene, and *n*-hexane but soluble in tetrahydrofuran. Mp: 279 °C dec. ¹H NMR (400 MHz, THF-*d*₈): δ 7.96 (d, 2H), 7.55 (d, 2H), 7.15 (t, 2H), 6.79 (t, 2H) ppm.¹⁷ ¹³C NMR (50.3 MHz, THF-*d*₈): δ 126.0 (weak), 123.4, 120.1, 114.5, 114.1 ppm (signal for C1 not observed). IR (Nujol) ν 1608, 1579, 1325, 1272, 1235, 1198, 1147, 993, 879, 769, 729 cm⁻¹. Anal. Calcd (found) for C₁₂H₈KN: C, 70.2 (69.4); H, 3.9 (4.3); N, 6.8 (6.2).

Synthesis of Rubidium Carbazolate (2). To a clear stirred solution of 0.97 g (3.9 mmol) of rubidium hexamethyldisilazide in 15 mL of tetrahydrofuran was added 0.85 g (5.1 mmol) of carbazole. After 10 min the white product was precipitated by adding *n*-hexane, washed with *n*-hexane, and dried under vacuum. Yield: 0.82 g (83%). Rubidium carbazolate is insoluble in ether, toluene, and *n*-hexane but soluble in tetrahydrofuran. Mp: 288 °C dec. ¹H NMR (400 MHz, THF-*d*₈): δ 7.95 (d, 2H), 7.53 (d, 2H), 7.13 (t, 2H), 6.78 (t, 2H) ppm.¹⁷ ¹³C NMR (50.3 MHz, THF-*d*₈): δ 152.3, 126.0, 123.3, 120.1, 114.8, 113.9 ppm. IR (Nujol): ν 1575, 1325, 1289, 1229, 1140, 995, 873, 777, 733 cm⁻¹. Anal. Calcd (found) for C₁₂H₈NRb: C, 57.3 (57.0); H, 3.2 (3.4); N, 5.6 (5.0).

Synthesis of Cesium Carbazolate (3). To a clear stirred solution of 1.28 g (4.4 mmol) of cesium hexamethyldisilazide in 20 mL of tetrahydrofuran was added 0.88 g (5.3 mmol) of carbazole. After 10 min the white product was precipitated by adding *n*-hexane, washed with *n*-hexane, and dried under vacuum. Yield: 1.24 g (95%). Cesium carbazolate is insoluble in ether, toluene, and *n*-hexane but soluble in tetrahydrofuran. Mp: 285 °C dec. ¹H NMR (400 MHz, THF-*d*₈): δ 7.93 (d, 2H), 7.53 (d, 2H), 7.12 (t, 2H), 6.75 (t, 2H) ppm. ¹³C NMR (50.3 MHz, THF-*d*₈): δ 126.0 (weak), 123.2, 120.1, 115.4, 113.6 ppm (signal for C1 not observed). IR (Nujol): ν 1617, 1573, 1326, 1296, 1237, 1143, 1117, 993, 875, 765, 726 cm⁻¹. Anal. Calcd (found) for C₁₂H₈CsN: C, 48.2 (48.1); H, 2.7 (2.8); N, 4.7 (4.4).

X-ray Crystallography. The crystal data of K, Rb, and Cs carbazolates were obtained using powder diffraction methods. For this purpose the colorless air-sensitive compounds were sealed in 0.3 mm capillaries under argon. The data were collected at -173 °C with a Stoe Stadi-P transmission diffractometer (Ge monochromator for Cu Kα₁ radiation). Data reduction was performed using the GUMI program.¹⁸ The powder patterns were indexed with the program ITO.¹⁹ Systematic absences and crystallographic consid-

Table 3. Selected Crystallographic Data of Potassium (1), Rubidium (2), and Cesium Carbazolates (3)

	1	2	3
formula	C ₁₂ H ₈ KN	C ₁₂ H ₈ NRb	C ₁₂ H ₈ CsN
fw	205.30	251.67	299.11
cryst syst	trigonal	trigonal	monoclinic
space group ^a	<i>R</i> 3 <i>c</i> (No. 161)	<i>R</i> 3 <i>c</i> (No. 161)	<i>I</i> a (No. 9)
<i>a</i> (Å)	25.0827(9)	24.9084(11)	15.3978(3)
<i>b</i> (Å)			12.7373(3)
<i>c</i> (Å)	7.8355(2)	8.1932(4)	11.3843(2)
β (deg)			103.503(1)
<i>V</i> (Å ³)	4269.2(2)	4402.3(3)	2171.04(8)
<i>Z</i>	18	18	8
density (g cm ⁻³)	1.437	1.709	1.830
2θ range (deg)	4–60	3–50	5–60
step width (deg)	0.01	0.01	0.01
time/step (s)	0.3/60	0.3/70	0.3/60
no. of rflns	138	90	305
no. of variables	69	77	149
R- <i>p</i> ^b	0.0442	0.0393	0.0464
R-w <i>p</i> ^b	0.0562	0.0502	0.0581
R- <i>F</i> ^b	0.0672	0.0613	0.0537
R- <i>F</i> ² ^b	0.0992	0.1011	0.0955

^a Refinement in the centrosymmetric space groups (*R*3*c* and *I*2/*a*, respectively) was not successful. ^b R-*p*, R-w*p*, R-*F*, and R-*F*² as defined in GSAS.¹⁶

erations led to the results provided in Table 3. The crystal structures were solved by global optimization in real space using the DASH structure solution package for laboratory data sets.²⁰ An internal coordinate description of the rigid carbazolate moiety was constructed using C–C bond lengths of 140 pm and C–C–C angles of 120° in the six-membered rings. The C–C bonds in the five-membered ring were fixed to 143 pm, both N–C bonds were fixed to 137 pm, and the C–N–C angle was fixed to 104°. These geometric data for the carbazolate anion were taken from the literature.^{11d} The hydrogen positions were calculated using a C–H distance of 96 pm. Final Rietveld refinements were carried out with the program package GSAS using soft constraints for bond lengths and widths within the carbazolate anion.²¹ The C and N atoms were refined using the same isotropic thermal parameter.

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Supporting Information Available: For 1–3, CIF files giving crystal data and tables, figures, and text giving crystallographic details, all bond lengths and angles, atomic coordinates, thermal parameters, and Rietveld plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060927T

(20) DASH: A structure solution package for X-ray powder diffraction, developed and distributed between the ISIS Facility of the Rutherford Appleton Laboratory and the Cambridge Crystallographic Data Centre. Version 3.0; CCDC, Cambridge, U.K., 2004.

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