(Cyanocyclopentadienyl)potassium and -cesium

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(Cyanocyclopentadienyl)potassium and -cesium have been synthesized and subsequently characterized by single-crystal X-ray structure determinations, ^{1}H and ^{13}C NMR spectroscopy in solution as well as by ^{133}Cs NMR spectroscopy in solution and the solid-state. Both salts crystallize in zigzag chains which are crosslinked differently through the cyano substituents. There is significant distortion of the cyanocyclopentadienide ion toward a fulvalene-like structure because the alkali-metal ions do not only interact with the five-membered ring but also with the cyano groups. The ^{133}Cs NMR spectra reflect the bending of the [CpCsCp]$^{-}$ fragments of the chains.

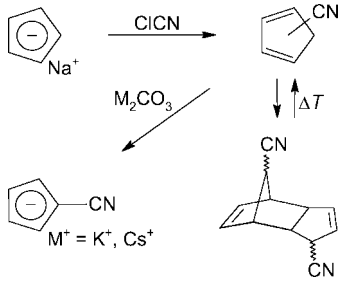
Introduction

The cyclopentadienyl (Cp) ligand is ubiquitous in organometallic chemistry and substitution has been widely used for generating special properties of its (transition) metal compounds such as better solubility, increased stability and asymmetry.[1] More recently, donor substituents have been introduced[2] mainly for providing (planar-)chiral[2b,2c] or C_2-symmetric[2a,2d] catalysts. For the latter derivatives, the substituted Cp groups have been designed such that intramolecular coordination of the Cp-attached donor occurs owing to dangling substituents. If intermolecular or bridging coordination is to be achieved, a donor function bonded directly to the Cp ring is advantageous. An example is the cyanocyclopentadienyl ligand (CpCN) which has been synthesised by various routes.[3] As for alkali-metal cyclopentadienides, these may be assumed to be simple compounds but, in fact, there is surprising structural diversity among them[4] and this might be particularly true for structural implications of the cyano substituent in the solid and liquid state. Therefore, we synthesized the title compounds CpCNK and CpCNCs and investigated them by techniques including X-ray diffraction and solid-state ^{133}Cs NMR spectroscopy.

Results and Discussion

Synthesis

When choosing Webster's synthetic approach,[3b] (see Scheme 1) special attention is warranted. Thus, the reaction between CpNa and ClCN is clean if the latter has been freshly prepared. The resultant isomeric cyanocyclopentadienes react almost instantaneously to give dimers (not only those in Scheme 1) which must be cracked thermally just before the reaction with an alkali carbonate. The overall yield (5–6%) of the alkali-metal cyanocyclopentadienides, CpCNK and CpCNCs, according to the sequence in Scheme 1 is mainly limited by interfering polymerization of cyanocyclopentadiene. Both compounds are colorless to brown powders which are air-sensitive and soluble in donor solvents such as propionitrile, DMSO and THF. The ^{1}H and ^{13}C NMR spectra of both salts in solution show similar signal patterns and confirm the expected structure of the anion. An example is the AA′BB′ spin system of the five-membered ring protons which gives rise to two pseudo-triplets. These and other signals of the nuclei in positions 2/5 and 3/4 of the ring could be distinguished by considering the contribution of a fulvene-type limiting structure (cf. discussion below and Figure 2b) and the fact that in fulvenes and the related cyclopentadienones the signal of C-3/4 is always more shifted than that of C-2/5.[5] Nevertheless, this assignment is tentative. The new cesium derivative was characterised in addition by mass spectrometry and IR spectroscopy, and its purity was checked.



Scheme 1.

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Crystal Structures of CpCNK and CpCNCs

An issue which arises during structural work on solid-state alkali-metal cyclopentadienides is whether solvent molecules are incorporated into the lattice or not. Because of the low solubilities of these salts, only few solvent-free structures are known[6] and most of them have been determined from powders. It is, therefore, unsurprising that the rich structural chemistry of alkali cyclopentadienides stems from crystals usually containing solvating amines or ethers. In contrast, the potassium and cesium salts of cyanocyclopentadiene form solvent-free crystals from THF or propionitrile because the anion contains its own donor.

The potassium salt CpCNK forms monoclinic crystals in which the anions and cations are arranged in zigzag chains running almost parallel to the *a* axis as illustrated in Figure 1. The chains can be broken down into inverse sandwich cations $[K(CpCN)K]^+$ highlighted by the broken frame and separated by $CpCN^-$ anions. The corresponding solvated and hence isolated lithium species $[(TMEDA)Li(MeCp)Li(TMEDA)]^+$ has been established previously.[7] Alternatively, the chains may be broken down into bent metallocene anions (solid frame in Figure 1) separated by potassium anions thereby enabling a structural analogy with bent metallocenes such as $[Cp_2Ti(NCCH_3)_2]^+$[8] which are well known in transition-metal organometallic chemistry. As for titanium in $[Cp_2Ti(NCCH_3)_2]^+$, the coordination sphere of potassium in CpCNK is completed by two neutral ligands, i.e. the cyano groups of adjacent CpCN anions. The metallocene bending angles (D–K1–D′ 135.86° and D–K2–D′ 135.14°) are very similar to that in $[Cp_2Ti(NCCH_3)_2]^+$ [134.8(5)°] but the angles N–K–N′ [90.00(4)° for K1 and 88.84(4)° for K2] and N–Ti–N′ [80.6(5)°] are somewhat different. It follows that the cyano groups of CpCNK force bent chains while for the cyclopentadienides of other alkali-metal ions, the chains may be linear or bent[6c–e] depending on the radius of the cation.[4a] When crystallizing with one molecule of diethyl ether, CpK also forms bent chains in which the angle is about 10° wider.[9]

The CpCN···K interaction links neighbouring chains to give a 3D network through slightly distorted squares K1,N,K2,N′ lying approximately in the *bc* plane as shown in Figure 2a. The angles between the best plane of K1,N,K2,N′ and the Cp groups on the left and the right are 22.6°. Unlike in $[Cp_2Ti(NCCH_3)_2]^+$, the metal–Cp bonding in CpCNK should be almost purely ionic as in all alkali-metal cyclopentadienides.[4] This implies a polarisation of the $CpCN^-$ anion in such a way that the negative charge is not only localised in the Cp π system but also at the N atom. Therefore, it can be expected that the limiting electronic structure B in Figure 2b plays a significant role. The crystal structure confirms this in two ways. Firstly, the

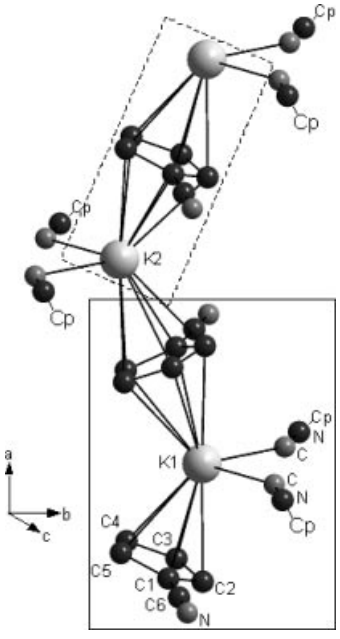

Figure 1. Inverse sandwich motif (broken frame) and bent-metallocene motif (solid frame) within the polymeric chains of CpCNK (detail with three formula units complemented by full coordination at the potassium ion); hydrogen atoms have been omitted for clarity; selected bond lengths [Å]: K1–C1 3.036(1), K1–C2 3.092(2), K1–C3 3.125(2), K1–C4 3.100(2), K1–C5 3.049(2), K2–C1 3.008(1), K2–C2 3.079(2), K2–C3 3.133(2), K2–C4 3.115(2), K2–C5 3.043(2), K1–D 2.840, K2–D 2.835, where D is the centre of gravity of the five-membered ring.

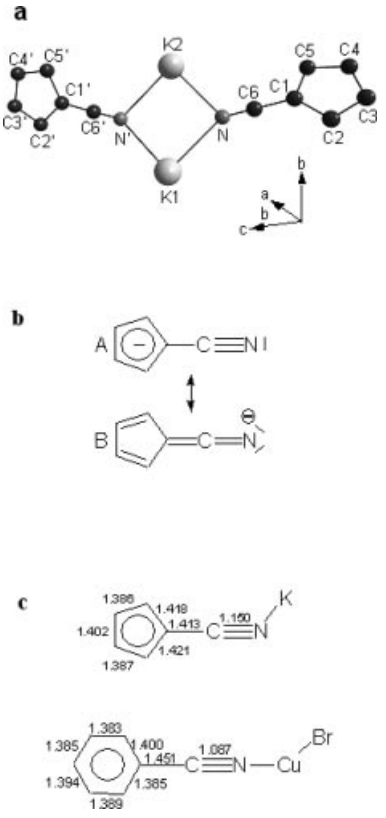

Figure 2. (a) Detail of the structure of CpCNK showing the K1, N, K2, N′ interactions between adjacent chains shown in Figure 1; selected bond lengths [Å] and angles [°]: C1–C2 1.418(2), C2–C3 1.386(2), C3–C4 1.402(2), C4–C5 1.387(2), C5–C1 1.421(2), C1–C6 1.413(2), C6–N 1.150(2), N–K1 2.7760(12), N–K2 2.8045(12), C1–C6–N 179.51(15), C6–N–K1 149.01(11), C6–N–K2 119.71(10), N–K1–N′ 90.00(4), N–K2–N′ 88.84(4); (b) limiting electronic structures of the CpCN anion; (c) bond lengths [Å] in CpCNK and $C_6H_5CNCuBr$.

CNK fragments in Figure 2a are bent rather than linear and secondly, the $CpCN^-$ anion is distorted toward a fulvene-type structure. A comparison of the bond lengths of CpCNK with those of the benzonitrile complex of CuBr[10] in Figure 2c shows that the C–C bond lengths of the phenyl group are very similar, whereas in CpCNK the bonds C3–C2 and C4–C5 are significantly shorter than C1–C2, C3–C4 and C5–C1. Also, compared with $C_6H_5CNCuBr$, C1–C6 of CpCNK is shorter while C6–N is longerand both are towards double bonds. It is worth noting that structure B in Figure 2b is the deprotonation product of the transient species 6-iminofulvene.[11]

The cesium salt CpCNCs forms orthorhombic crystals again featuring zigzag chains (along the *c* direction of the unit cell) which may also be decomposed into inverse sandwich cations (Figure 3, broken frame) or bent sandwich anions (Figure 3, solid frame). However, compared with the potassium salt, there are remarkable differences. The mean metal–Cp distance in CpCNCs is 0.37 Å longer than in CpCNK which is more than the difference of the coordination number adjusted radii of Cs^+ and K^+ (0.23 Å[12]) and which, therefore, points to additional factors contributing to that distance. There is a striking decrease in the sandwich bending angles from 135.14° and 135.86° to 107.3° when passing from CpCNK to CpCNCs. While in the latter salt the angle is still 8.3° smaller than in the isolated anion $[Cp_3Cs_2]^-$[13] and 22.4° smaller than in CpCs,[6c] the bending of the alkali-metal cyclopentadienides is most pronounced for Cs. Bending of Cp sandwich compounds as an intrinsic molecular property has been addressed for main-group element derivatives.[14] In particular, the salts CpCNK and CpCNCs correspond to the general tendency that the deviation from linearity in main-group compounds MX_2 increases when M becomes heavier.[15] In mostly ionic solids, another driving force is the need to optimise coulombic interactions and to complete the coordination spheres of the ions. Incomplete coordination of alkali-metal–organic compounds becomes more critical when the radius of the metal ion increases.[16] In the present case this means that upon additional coordination of the cyano groups, the Cp_2Cs^- fragment bends more strongly than Cp_2K^-.

The linkage of the chains in CpCNCs is also different from that in CpCNK. As can be seen in Figure 4, the CpCN···Cs interaction occurs in such a way that the $CpCN^-$ anions on both sides of the cation chain bridge different pairs of cations, whereas in CpCNK they bridge the same pair (Figure 2a). This does not prevent the CN group of CpCNCs from interacting with two cesium ions, thereby stretching the anion toward a fulvene limiting structure (Figure 2) much in the same way as in the case of CpCNK. An additional linkage between adjacent chains of CpCNCs occurs between one edge of the cyclopentadienyl and Cs′ (see inset of Figure 4). This is indicated by the large angle between the plane formed by C2,C3,Cs and the Cp plane (152.0°), and by the distances Cs′–C2 [3.654(3) Å] and Cs′–C3 [3.654(3) Å] which are only slightly longer than the Cs–C distances within the chains. The contribution of the η^2 interaction to the overall bonding energy of CpCNCs is probably substantial because, for the Cp^- and Li^+ pair, it has been calculated that such η^2 interactions are only about 1.4 times smaller than η^5 interactions.[4a]

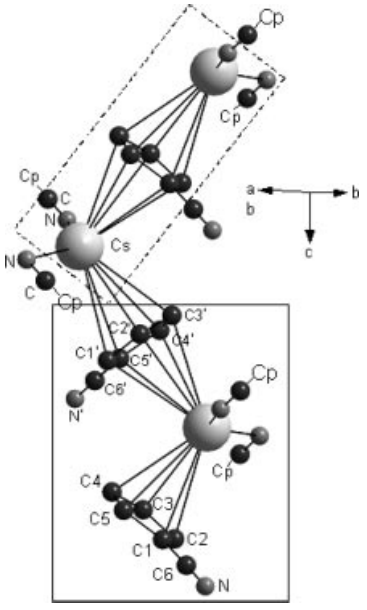

Figure 3. Inverse sandwich motif (broken frame) and bent-metallocene motif (solid frame) within the polymeric chains of CpCNCs (detail with three formula units complemented by full coordination at the potassium ion); hydrogen atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Cs–C1 3.541(3), Cs–C2 3.436(3), Cs–C3 3.309(3), Cs–C4 3.334(3), Cs–C5 3.486(3), Cs–C1′ 3.426(3), Cs–C2′ 3.464(3), Cs–C3′ 3.438(3), Cs–C4′ 3.403(3), Cs–C5′ 3.389(3), C1–C6–N 179.4(3), C6–N–Cs 117.7(3), C6′–N′–Cs 149.0(3), Cs–D 3.207, Cs–D′ 3.209, D–Cs–D′ 107.32, where D is the centre of gravity of the five-membered ring.

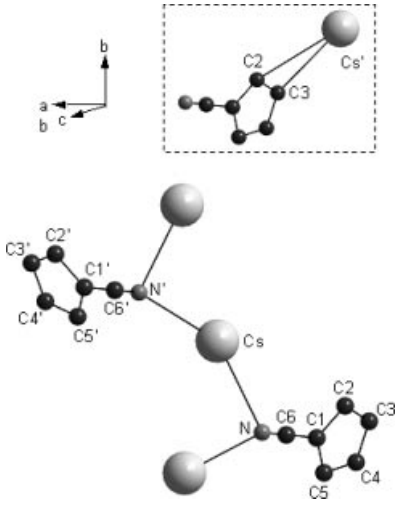

Figure 4. Detail of the structure of CpCNCs showing the Cs···N interactions between adjacent chains shown in Figure 3; inset: η^2 interaction between $CpCN^-$ and Cs^+; selected bond lengths [Å] and angles [°]: C1–C2 1.417(5), C2–C3 1.390(5), C3–C4 1.406(5), C4–C5 1.389(5), C5–C1 1.418(5), C1–C6 1.428(5), C6–N 1.151(5), N–Cs 3.236(3), N′–Cs 3.292(3), Cs′–C2 3.654(3), Cs′–C3 3.654(3), N–Cs–N′ 145.48(8), Cs–N–Cs 87.21(7), C2–Cs′–C3 21.93(7).

^{133}Cs NMR Spectroscopy

Since crystal structures of alkali-metal–organic compounds are sometimes difficult to obtain, we wanted to find out whether ^{133}Cs NMR spectroscopy would be a useful method of characterization. Alkali-metal ions have neither p nor d valence electrons and this makes qualitative signal shift interpretation as straightforward as for proton signals because simple electron density arguments can be used. The disadvantage is that the signal shift range of an alkali-metal nucleus is much smaller than that of its neighbours in the same row of the periodic table. For instance, ^{7}Li NMR signal shifts are much smaller than those of ^{11}B which are in turn smaller than those of ^{19}F. The disadvantage is partly compensated for by the fact that the shift range increases rapidly when passing from a light to a heavy nucleus in a given group. Therefore, ^{133}Cs should be the nucleus of choice for studying small changes of the bonding in alkali-metal cyclopentadienides. Figure 5 shows the ^{133}Cs MAS NMR spectra of microcrystalline samples of CpCNCs and CpCs. The envelope of the spinning sideband pattern corresponds to the typical signal shape of a spin nucleus with low chemical shift anisotropy.[17] At the given spinning frequency, the six satellite transitions flanking the central m = ±½ transition are best seen in the case of CpCs from the modulation of the sideband intensities. At lower spinning frequencies, some chemical shift anisotropy and its orientation relative to the quadrupolar interaction leads to additional spectroscopic features as has been worked out in detail previously.[18] In this study we were interested in the isotropic signal shifts which turned out to be rather different for solid CpCNCs (δ = –128.2 ppm) and CpCs (δ = –247.6 ppm). Similar shifts were found in solution for CpCNCs (δ = –50.7 ppm in MeCN) and CpCs (δ = –253.7 ppm in THF). One may think of attributing the shift difference of both salts to additional CN coordination in CpCNCs. This would be equivalent to solvation which has been shown to actually shift ^{133}Cs NMR signals to high frequency when the solvent is acetonitrile.[19] However, these shifts are much smaller even for fully solvated ions. Another reason for the low-frequency signal shift is the fact that Cs^+ sits above the center of the Cp ring and hence experiences the additional field induced by the π electrons of the aromatic ligand. This scenario applies to mapping protons of transition-metal compounds[20] and to determining the interaction of Li^+ with Cp and Cp-like anions.[21] In fact, for $^{6/7}$Li, as for ^{133}Cs in this work, the metal resonance is shifted to a lower frequency upon interacting with Cp anions and these shifts are much larger than solvation-induced shifts. In the case of ^{133}Cs NMR spectroscopy, the Cp-induced signal shift is so large that structural changes of CpCs derivatives should be visible. On this basis we suggest that the ^{133}Cs NMR signal shift depends on the bending angle α of the $[Cp_2Cs]^-$ fragment (see Figure 1 and Figure 3). When adding the field vectors induced at both Cp groups, the ^{133}Cs NMR signal shift can be expected to behave as cos(180 – α). A linear sandwich fragment can thus be expected to give the largest ^{133}Cs signal shift. Upon bending the sandwich, the angle α decreases and the signal should move to high frequency. This is true for CpCNCs [α = 107.3°, δ(^{133}Cs) = –128.2 ppm] and CpCs [α = 129.7°, δ(^{133}Cs) = –247.6 ppm] although the correlation is not perfect. The reason is that the signal shift also depends on other factors such as the Cp–Cs distance, additional ligands such as the CN groups and the neighbors in the lattice. In solution, the structural parameters may be different and solvation cannot be neglected.

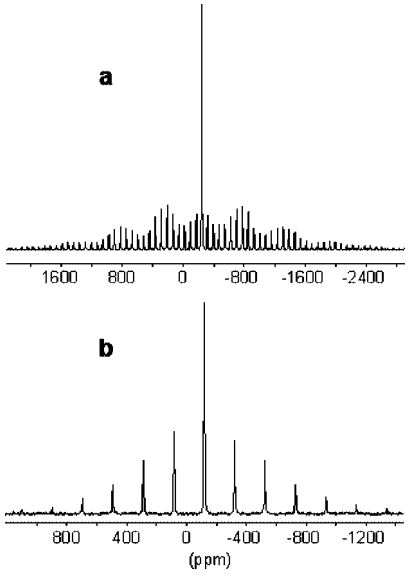

Figure 5. ^{133}Cs MAS NMR spectra of CpCNCs (a) and CpCs (b) at a spinning frequency of 8 kHz and a temperature of 301 K.

Conclusions

The potassium and cesium salts of cyanocyclopentadiene are soluble compounds and yet they do not form solid-state solvates. The arrangement of CpCN anions and alkali-metal cations in the lattice may be viewed as chains or *n*-decker sandwiches which are bent and which consist of linear inverse sandwich (M–Cp′–M) fragments and bent sandwich $[Cp'_2M(NCCp)_2]$ fragments. The chains are crosslinked through CN···M interactions which at the same time polarize the CpCN anion such that it is distorted from a cyclopentadienyl- toward a fulvene-type geometry. Different crosslinking patterns exist for CpCNK and CpCNCs and the latter features an additional η^2 interaction between Cs^+ and $CpCN^-$. ^{133}Cs NMR spectroscopy proved to be a sensitive probe for structural changes of the $[Cp_2Cs]^-$ fragment.

Experimental Section

Caution: *Cyanogen chloride used as reagent in this work is a very toxic gas at room temperature and should be handled with proper precautions!* All manipulations involving alkali-metal cyclopentadienides were carried out under nitrogen using Schlenk tech-

niques and dry, oxygen-free solvents. Cesium cyclopentadienide was synthesized as described by Harder.[13] The spectroscopic results were obtained with a Varian Mat 50 mass spectrometer, a Perkin–Elmer IR spectrometer 1600 FTIR as well as Jeol JNM GX 400 and Bruker Avance 300 NMR spectrometers for solution and solid-state NMR spectra, respectively. The solid samples were packed in ZrO_2 rotors and sealed with Kel-F caps in a glovebox. All referencing was done relative to TMS except for the ^{133}Cs NMR spectroscopic data which are relative to external CsCl as a solid or highly diluted in water for MAS and solution spectra, respectively. The sample temperature under MAS conditions was obtained from a previous calibration.[22]

Dicyanotricyclo[5.2.1.0^{2,6}]deca-4,8-diene Isomers: By modifying Webster's procedure,[3b] freshly prepared cyanogen chloride[23] (30.0 g, 0.488 mol) was dissolved at –78 °C in THF (150 mL). The colourless solution was warmed to 0 °C and a THF solution of sodium cyclopentadienide (208 mL, 2.35 M, 0.49 mol) was added dropwise while cooling with an ice bath. The reaction was apparent from the immediate formation of a colourless precipitate and colour changes first to yellow and subsequently to red-brown. The reaction mixture was allowed to warm to room temperature and was then stirred for 2 h. After removing the solvent at 10^{-4} bar, the brown solid was dissolved in water (100 mL), the pH was adjusted to 7 using a solution of 0.1 N hydrochloric acid and the product was extracted with diethyl ether (4 × 100 mL). The combined organic phases were dried with sodium sulfate, the solvent was removed under reduced pressure and the resultant deep red oil of cyanocyclopentadiene dimers (60.2 g, 67% yield relative to cyanogen chloride) was subjected immediately to further reaction.

Potassium Cyanocyclopentadienide: Similar to the procedure described previously,[3b] a mixture of dicyanotricyclo[5.2.1.0^{2,6}]deca-4,8-dienes (20.0 g, 0.110 mol) was cracked to cyanocyclopentadienes by heating to 170–180 °C and distilled at 15 mbar by using a short bridge directly into a suspension of potassium carbonate (11.1 g, 0.110 mol) in propionitrile (200 mL). The resultant pink suspension was stirred for 2 h and the solid removed by filtration. The solvent was then removed at 10^{-4} bar leaving behind microcrystalline CpCNK. Yield 1.71 g, yield 6%. Colourless crystals suitable for X-ray analysis were obtained by covering a solution of the solid in THF with hexane at room temperature. ^1H NMR (400 MHz, [D$_6$]DMSO, 305 K): δ = 5.51 (pseudo-t, $^{2+4}J_{H,H}$ = 5.6 Hz, 2 H, 2/5-H), 5.92 (pseudo-t, $^{2+4}J_{H,H}$ = 5.6 Hz, 2 H, 3/4-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 305 K): δ = 80.7 (C-1), 107.7 (C-2/5), 111.4 (C-3/4), 126.4 (CN) ppm.

Cesium Cyanocyclopentadienide: The procedure described for the potassium analogue was carried out with dicyanotricyclo[5.2.1.0^{2,6}]deca-4,8-dienes (9.11 g, 50 mmol) and cesium carbonate (16.3 g, 50 mmol) in propionitrile (100 mL). Crystallization of the resultant powder from acetonitrile at room temperature gave CpCNCs as brown crystals which were analytically pure and suitable for X-ray analysis. Yield 1.11 g, 5%. M.p. 170–175 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3037, 3095 [m, ν(CH)], 2191 [s, ν(CN)] cm^{-1}. CI$^+$ MS: *m*/*z* (%) = 223 (75) [M]$^+$, 196 (10) [M – CHN]$^+$, 133 (78) [M – C_6H_4N]$^+$. ^1H NMR (400 MHz, [D$_6$]DMSO, 305 K): δ = 5.67 (pseudo-t, $^{2+4}J_{H,H}$ = 5.6 Hz, 2 H, 2/5-H), 6.07 (pseudo-t, $^{2+4}J_{H,H}$ = 5.6 Hz, 2 H, 3/4-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO, 305 K): δ = 84.1 (C-1), 110.3 (C-2/5), 114.0 (C-3/4), 126.5 (CN) ppm. C_6H_4CsN (223.0): calcd. C 32.32, H 1.81, N 6.28; found C 32.79, H 1.91, N 6.18.

Single Crystal X-ray Structure Determination of CpCNK and CpCNCs

CpCNK: Crystal data and details of the structure determination are presented in Table 1. Suitable single-crystals for the X-ray diffraction study were grown from THF/hexane. A clear colorless fragment was stored under perfluorinated ether, transferred to a Lindemann capillary, fixed and sealed. Preliminary examinations and data collection were carried out with an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit-cell parameters were obtained by a full-matrix least-squares refinement of 1331 reflections. Data collection was performed at 173 K within a θ-range of 3.33° < θ < 25.34°. Nine data sets were measured in rotation scan mode with $\Delta\varphi/\Delta\Omega$ = 1.0°. A total number of 16425 intensities were integrated. Raw data were corrected for Lorentz, polarisation and latent decay and absorption effects (arising from the scaling procedure). After merging (R_{int} = 0.042), a sum of 1266 (all data) and 1173 [$I > 2\sigma(I)$] reflections remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 90 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97weighting scheme and the refinements were stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography.* All calculations were performed with an Intel Pentium II PC with the STRUX-V system including the programs PLATON, SIR92 and SHELXL-97.[24]

CpCNCs: Crystal data and details of the structure determination are presented in Table 1. Suitable single-crystals for the X-ray diffraction study were grown from acetonitrile. A clear light brown fragment was stored under perfluorinated ether, transferred to a Lindemann capillary, fixed and sealed. Preliminary examinations and data collection were carried out with an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The unit-cell parameters were obtained by a full-matrix least-squares refinement of 759 reflections. Data collection was performed at 173 K within a θ-range of 3.08° < θ < 25.36°. Eight data sets were measured in rotation scan mode with $\Delta\varphi/\Delta\Omega$ = 2.0°. A total number of 13279 intensities were integrated. Raw data were corrected for Lorentz, polarisation and latent decay and absorption effects (arising from the scaling procedure). After merging (R_{int} = 0.046), a sum of 1238 (all data) and 1215 [$I > 2\sigma(I)$] reflections remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were calculated in ideal positions (riding model). Full-matrix least-squares refinements with 75 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97weighting scheme and were stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. As shown by Flack's parameter ε = 0.15(3), the crystal is slightly twinned. A correction for extinction was applied using the SHELXL-97 procedure with a final ε value of 0.0125(4). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography.* All calculations were performed with an Intel Pentium II PC with the STRUX-V system including the programs PLATON, SIR92, and SHELXL-97.[24]

Table 1. Summary of the crystal data, details of data collections and refinements for the compounds CpCNK and CpCNCs.

	CpCNK	CpCNCs
Empirical formula	C_6H_4KN	C_6H_4CsN
Formula mass	129.20	223.01
Crystal system	monoclinic	orthorhombic
Space group	*C*2/*c* (no. 15)	$P2_12_12_1$ (no. 19)
a [Å]	10.4879(1)	7.5274(1)
b [Å]	12.2297(2)	8.6227(2)
c [Å]	11.6318(1)	10.3183(2)
β [°]	111.4875(6)	90
V [Å^3]	1388.25(3)	669.72(2)
Z	8	4
$\rho_{calcd.}$ [g cm^{-3}]	1.236	2.212
μ [mm^{-1}]	0.658	5.418
T [K]	173	173
F(000)	528	408
Crystal size [mm]	0.61×0.19×0.08	0.56×0.28×0.18
θ-range [°]	3.33/25.34	3.08/25.36
Index ranges	$h = \pm12$, $k = \pm14$, $l = \pm13$	$h = \pm9$, $k = \pm10$, $l = \pm12$
Reflections collected	16425	13279
Independent reflections [$I_o>2\sigma(I_o)$/all data/R_{int}]	1173/1266/0.042	1215/1238/0.046
Data/restraints/parameters	1266/0/90	1238/0/75
R_1 [$I_o>2\sigma(I_o)$/all data]	0.0235/0.0259	0.0128/0.0133
wR_2 [$I_o>2\sigma(I_o)$/all data]	0.0613/0.0628	0.0308/0.0309
GoF	1.085	1.146
Weights *a*/*b*	0.0305/0.5258	0.0095/0.7628
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.13/–0.20	0.49/–0.38

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