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Direct Synthesis of a Cesium Azaallyl Compound

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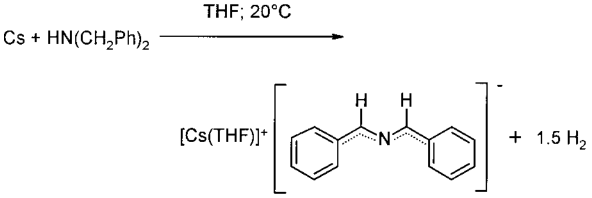
Summary: The purple-red cesium 2-aza-allyl compound $[\{Cs(THF)\}\{N(CHPh)_2\}]$ *(**1**) was obtained by the reaction of Cs in THF with* $HN(CH_2Ph)_2$ *with evolution of* H_2*. **1** was characterized by NMR, IR, and Raman spectra as well as by X-ray crystallography. In the solid state **1** forms infinite layers of* $[Cs(THF)]^+$ *and* $[N(CHPh)_2]^-$ *ions connected mainly by* $Cs^+{-}\pi$*-electron interactions in the solid state. The layers are stacked along [001].*

Introduction

2-Aza-allyl anions can be prepared by deprotonation of *N*-benzyl-substituted imines[1,2] or by a decomposition of $MN(CH_2Ph)_2$ (Li, Na, K) in the presence of donor ligands such as THF, DME, crown ethers, TMEDA, or PMDETA $[(Me_2NCH_2CH_2)_2NMe]$.[3−7] Therefore, 2-aza-allyl anions were observed often as byproducts in reactions with amides of the type $MN(CH_2Ph)_2$, as indicated by red-colored solutions.[3−8] Closer investigations of the formed salts $MN(CHPh)_2$ in solution and in the solid state showed a more or less planar $[\mathrm{PhHC}\overset{\cdot\cdot}{-}\mathrm{N}\overset{\cdot\cdot}{-}\mathrm{CHPh}]^-$ anion, which is responsible for the intense purple-red color. Theoretical studies verified the results.[7] A possible mechanism for the decomposition of the amide $MN(CH_2Ph)_2$ to $MN(CHPh)_2$ is a β-MH elimination in the first step followed by the attack on the second benzyl group by MH, resulting in H_2 generation.[6,7] However, there is no convenient synthesis for a salt of the 2-aza-allyl anion directly from the amine, e.g., $HN(CH_2Ph)_2$ (the use of ^nBuNa or ^nBuK was described earlier, but the two reagents have to be prepared first[7]). Therefore, we developed a one-step synthesis in THF, starting from elemental cesium and dibenzylamine.

Results and Discussion

When $HN(CH_2Ph)_2$ was added to Cs in THF at room temperature, vigorous gas evolution was observed. The colorless solution instantly turned bright purple-red (eq 1).



(1)

The extremely air-sensitive compound **1** displayed satisfactory spectra and analytical data. The $\mathrm{HC}\overset{\cdot\cdot}{-}\mathrm{N}\overset{\cdot\cdot}{-}\mathrm{CH}$ fragment shows one characteristic signal for the all-*trans* conformation[7] (see Figure 1) at 6.71 ppm in the ^1H NMR spectrum and at 114.4 pm in the ^{13}C NMR spectrum at room temperature. A partial multiple bond character in this anion leads to bands at 1539 cm^{-1} (IR) and 1504 cm^{-1} (Raman effect, RE) in the vibrational spectra, which can be assigned to the N−C stretching vibrations.

Figure 1 shows an ensemble of four units of $[\{Cs(THF)\}\{N(CHPh)_2\}]$ (**1**). The two crystallographical independent anions in **1** exhibit an almost planar $\mathrm{PhCH}\overset{\cdot\cdot}{-}\mathrm{N}\overset{\cdot\cdot}{-}\mathrm{HCPh}$ arrangement. The angle between the

Table 1. Crystallographic Data for 1

instrument	IPDS I (Stoe)
radiation	Mo Kα
formula	$C_{18}H_{20}CsNO$
fw	399.27
cryst size (mm)	0.49 × 0.47 × 0.20
a (Å)	11.003(1)
b (Å)	11.015(1)
c (Å)	14.578(2)
α (deg)	93.54(1)
β (deg)	102.91(1)
γ (deg)	102.81(1)
V (Å^3)	1667.7(3)
cryst syst	triclinic
space group	$P\bar{1}$
Z	4
ρ_{calcd} (g/cm^3)	1.590
temp (K)	193
μ (cm^{-1})	22.2
$2\theta_{max}$ (deg)	51.86
h, *k*, *l* values	$-13 \le h \le 13$ $-13 \le k \le 13$ $-17 \le l \le 17$
no. of reflns	16 555
no. of unique reflns (R_{int})	6082 (0.0569)
no. of reflns with $F_o > 4\sigma(F_o)$	4355
no. of params	396
R_1[a]	0.053
wR_2 (all data)[b]	0.138
max/min resid electron density (e/Å^3)	1.24/−2.9

[a] $\sum||F_o| - |F_c||/\sum|F_c|$. [b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0946P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

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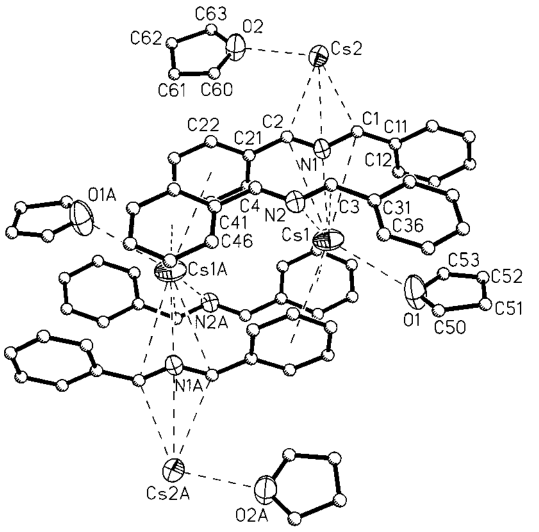

Figure 1. Ensemble of four units of **1** (H atoms omitted for clarity; thermal ellipsoids 50%). Selected bond lengths (Å) and bond angles (deg): Cs1−O1 3.303(6), Cs1−N1 3.112(5), Cs1−C3 3.301(6), Cs2−O2 3.054(4), Cs2−C1 3.401(6), Cs2−N2a 3.212(4), N1−C1 1.337(7), N1−C2 1.321(7), N2−C3 1.336(7), N2−C4 1.345(7), C1−C11 1.438(8), C2−C21 1.439(7), C3−C31 1.441(7), C4−C41 1.429(8); O1−Cs1−N1 122.6(1), O2−Cs2−N2a 120.8(1), C1−N1−C2 121.6(5), C3−N2−C4 120.6(5).

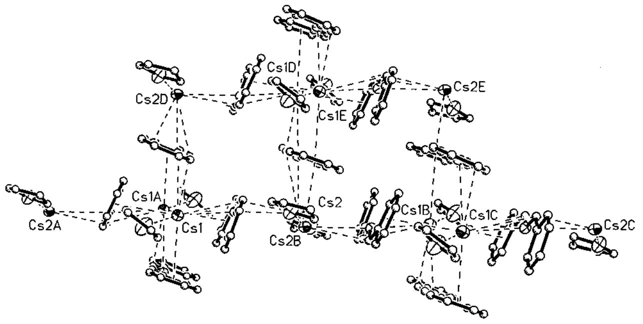

Figure 2. Part of the infinite layers of cations and anions in **1**.

two planar CHPh fragments is 4°, indicating the presence of a delocalized π-electron system which is responsible for the ruby-red color of solid **1**. The two anions are perpendicluar to each other (angle 88°). The Cs^+ ions are coordinated by a THF ligand and by the two π-electron systems of the CNC triad as well as by two phenyl rings. The soft−soft interaction of the heavy alkali metal cations with π-electron systems is a typical behavior of such cations and can be used to stabilize unusual anions or coordination spheres in complexes and metalates.[9−11] In **1**, this leads to a two-dimensional infinite arrangement of squares built up from four cations and four anions (Figure 2). Stacking of the layers takes place along [001] (crystallographic *c*-axis). The Cs−O bonds average 3.04 Å, a typical value for the coordination of THF ligands to Cs^+ ions. A good comparison are the values of 3.06 Å [coordination number (CN) 5 of the Cs^+ ion] and 3.14 Å (CN 6) in the polymeric $[\{Cs(THF)_2\}\{Cs(THF)\}\{Al(O^cHex)_4\}_2]_n$ (cyclohexyl = ^{c}Hex).[12] The $C\overset{...}{-}N\overset{...}{-}C$ sequences are bound rather closely in a η^3-fashion to the Cs centers, as indicated by the distances 3.112(5) Å (Cs1−N1) and 3.212(4) Å (Cs2−N2a). The corresponding Cs−C contacts have a mean value of 3.50 Å. Cations and anions have a bridging function. The distance from one Cs^+ ion to the nitrogen atom of the second η^3-C−N−C unit amounts to 3.726(5) (Cs1···N2) and 3.471(4) Å (Cs2···N1). In addition to the $Cs^+{-}C\overset{...}{-}N\overset{...}{-}C$ contacts there are two Cs^+−aryl interactions for every cesium center. The average distance of the ring C41a→C46a, which is bridging two metal cations, is 3.87 Å to Cs1 and 3.76 Å to Cs2, respectively. This type of "inverse sandwich" function is quite common for Cs^+−aryl compounds.[11b,d] The rings C21a→C26a (average value 4.19 Å, Cs1) and C31a→C36a (4.43 Å, Cs2) are only weakly bound to the Cs centers in a η^2-fashion.

C11→C16 does not belong to the coordination sphere of a Cs^+ ion. In $[\{Na(PMDETA)\}\{N(CHPh)_2\}]$ a short N−Na bond of 2.384(2) Å and close (*ortho*-Ph)-C−H···Na contacts were observed.[5] This is in good agreement with the Pearson principle and verifies again the soft−soft interactions in **1**.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of argon using Schlenk techniques. Purification and drying of the solvent THF and of $HN(CH_2Ph)_2$ were performed by standard methods.[13] $HN(CH_2Ph)_2$ was purchased from Aldrich. Cs was donated by Prof. Dr. F. Hensel (University of Marburg, Germany) in sealed ampules.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX-200 spectrometer (^1H, 200.135 MHz; ^{13}C, 50.324 MHz). The standard is TMS (external) with $\delta = 0.0$ ppm. The IR spectra were obtained using a Bruker IFS-88 intrument (Nujol mulls, CsI disks for the range 4000−500 cm^{-1}; polyethylene disks for the range 500−100 cm^{-1}). The Raman spectrum was recorded on a Jobin Yvon spectrometer (LABRAM HR800; He-Ne laser; 633 nm). The melting point was measured with a Dr. Tottoli (Büchi) melting point apparatus in a sealed capillary under argon (value not corrected).

X-ray Structure Determination. The structure was solved by the Patterson method (SHEXLTL-Plus)[14] and refined against F_o^2 (SHELXL-97).[15] A numerical absorption correction was performed, and all non-hydrogen atoms were refined anisotropically by full-matrix least squares. The hydrogen atoms except H1−H4 were calculated for ideal positions and refined with a common displacement parameter. Free refinement was used for H1−H4.

Synthesis of $[\{Cs(THF)\}\{N(CHPh)_2\}]$ (1). To 6.5 g (48.9 mmol) of Cs in 100 mL of THF was added dropwise 9.4 mL (9.65 g; 48.9 mmol) of $HN(CH_2Ph)_2$ in 50 mL of THF under stirring (reaction was performed in a 250 mL Schlenk flask equipped with an alkali metal inert stirring bar; the Cs was poured from the ampule in a flow of argon. (*Safety advice*: Cs

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reacts vigorously by contact with O_2 or H_2O!) The color of the solution immediately turned purple-red, and gas evolution was observed (H_2). The solution was concentrated in vacuum and covered with 30 mL of toluene. **1** crystallized as ruby-red columns at room temperature (yield: 12.9 g; 66%). THF was removed from **1** in a vacuum to give a purple-brown powder (mp 260° (dec)). Data for **1**: ^{1}H NMR (THF-d_8): 1.87 (m, 4 H, CH_2, THF), 3.72 (m, 4 H, OCH_2, THF), 6.29 (m, 2 H, H-C^4, phenyl), 6.71 (s, 2 H, PhCH), 6.89 (m, 4 H, H-C$^{3/5}$, phenyl), 7.17 (s, br, 4 H, H-C$^{2/6}$, phenyl). ^{13}C NMR (THF-d_8): 24.7 (CH$_2$, THF), 66.8 (OCH$_2$, THF), 110.0 (C^4), 114.4 (PhCH), 118.6 ($C^{2/6}$), 128.3 ($C^{3/5}$), 144.7 (C^1). IR (Nujol): 2725 (w), 1578 (m, νCC, aryl), 1554 (m, νCC), 1539 (m, νNC), 1403 (vs), 1313 (s), 1271 (m), 1211 (s), 1157 (vs), 1064 (m), 1026 (m), 979 (vs), 873 (w), 813 (w), 744 (s), 694 (s), 637 (w), 613 (w), 505 (m), 483 (m), 464 (m), 428 (w), 390 (w), 308 (m, br), 118 (s, br) cm^{-1}. RE (crystalline): 1587 (vs, νCC, aryl), 1504 (s, br, νNC), 1445 (m), 1428 (m), 1408 (w), 1302 (w), 1260 (m), 1249 (m, br), 1185 (s), 1168 (vs), 1115 (w), 1062 (vw), 1020 (w), 988 (vs), 973 (m), 879 (s), 806 (vw), 721 (vw), 629 (w), 618 (m), 606 (w), 507 (m, br), 449 (vw), 420 (vw), 373 (vs), 308 (w, br), 254 (s−m) cm^{-1}. Anal. Calcd for $C_{18}H_{20}CsNO$: C, 54.15; H, 5.05; N, 3.51; Cs, 33.29. Found: C, 54.00; H, 4.87; N 3.38; Cs, 33.50.

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Supporting Information Available: Full details and tables of the crystal structure analysis for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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