

Molecular Structure and Reactivity of Tri(1-cyclohepta-2,4,6-trienyl)amine, $N(C_7H_7)_3$

Max Herberhold, Jinnan Liu, and Wolfgang Milius

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51,
D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. M. Herberhold. Fax: +49 (0)-921-55 2157.

E-mail: Max.Herberhold@uni-bayreuth.de

Z. Naturforsch. **59b**, 27–32 (2004); received November 6, 2003

Compared with the tertiary phosphane $P(C_7H_7)_3$ (**1**), the amine $N(C_7H_7)_3$ (**2**) possesses the structure of a flattened trigonal pyramid with a sum of CNC angles of 350.0° (cf. 300.2° (av.) in **1**). The heteroatom (with the lone pair) is situated 27.0 pm above the C_3 basal plane in **2**, but 86.4 pm in **1**. The amines $N(C_7H_7)_3$ (**2**), $NH(C_7H_7)_2$ (**2a**) and $N(Ph)(C_7H_7)_2$ (**2b**) react with tropylium tetrafluoroborate, $[C_7H_7]BF_4$, to give N-tropylidene-(1-cyclohepta-2,4,6-trienyl)-immonium tetrafluoroborates, $[(C_7H_6)N(R)(C_7H_7)]BF_4$ **3** (R = H, from **2** and **2a**), **4** (R = Ph, from **2b**), which have been characterized by their IR and NMR (1H , ^{13}C) spectra.

Key words: Cyclohepta-2,4,6-trienyl Amines, Tropylium Tetrafluoroborates, X-Ray

Introduction

Numerous transition metal complexes of the olefinic ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ (**1**), have been synthesized recently (for typical examples see, e.g., [1–6]). In nearly all cases the phosphorus atom with its lone pair of electrons acts as the primary contact to the metal, although additional support may come from the olefinic cycloheptatrienyl substituents [5].

Attempts to use the amine $N(C_7H_7)_3$ (**2**) in a similar manner as a ligand in transition metal complexes were essentially unsuccessful. Although interactions of **2** with the metal complex were occasionally indicated by colour effects, no defined products could be isolated.

The missing tendency of $N(C_7H_7)_3$ (**2**) towards coordination was tentatively ascribed to its molecular structure which is described below.

Results and Discussion

*X-ray crystal structure of $N(C_7H_7)_3$ (**2**)*

The molecular structure and the numbering scheme are shown in Fig. 1; relevant bond distances and angles are given in Table 1.

The tertiary amine **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with 4 molecules in the unit

cell. In the crystal all cyclohepta-2,4,6-trienyl substituents have the boat conformation and are all connected to nitrogen in an equatorial position. Compared with the analogous tertiary phosphane, $P(C_7H_7)_3$ (**1**), which contains the C_7H_7 substituents both in equatorial and in axial connection (ratio 2:1) [7], the amine **2** has a relatively flat pyramid NC_3 with C-N-C angles of $116.7 \pm 2^\circ$ (av.) and N-C bond lengths of 145.9 pm (av.); the corresponding parameters for **1** are C-P-C angles of $100.05 \pm 3^\circ$ (av.) and P-C bond lengths of 187.2 pm (av.) [7]. The sum of the angles around N and P, respectively, is 350.0° in **2** and 300.2° (av.) in **1**, the height of the pyramid (*i.e.* the distance of the heteroatom from the $C(1)C(8)C(15)$ plane) is 27.0 pm in **2** but 86.4 pm in **1**. The lone pair at N in **2** which is necessary for complexation is therefore less exposed than the lone pair at P in the versatile ligand **1**.

The bond distances and bond angles of the three cyclohepta-2,4,6-trienyl substituents in $N(C_7H_7)_3$ (**2**) are comparable (Fig. 1), both among each other and with the corresponding values of the phosphane, $P(C_7H_7)_3$ (**1**). The bending of the boat-shaped rings can be characterized by the dihedral angles α and β , as defined in Fig. 2.

The parameters $\alpha = 54.2^\circ$ (av.) and $\beta = 26.5^\circ$ (av.) in $N(C_7H_7)_3$ (**2**) have the typical values of equatorial C_7H_7 substituents (cf. $\alpha = 55.7^\circ$ (av.) and $\beta = 27.0^\circ$ (av.) in $P(C_7H_7)_3$ (**1**), $\alpha = 58.3^\circ$ (av.) and $\beta = 28.7^\circ$

Bond lengths					
N-C(1)	145.3(5)	N-C(8)	147.2(5)	N-C(15)	145.3(4)
C(1)-C(2)	148.9(5)	C(8)-C(9)	149.5(5)	C(15)-C(16)	149.6(5)
C(1)-C(7)	147.9(5)	C(8)-C(14)	147.0(5)	C(15)-C(21)	150.4(5)
C(2)-C(3)	133.6(6)	C(9)-C(10)	134.7(6)	C(16)-C(17)	133.8(6)
C(3)-C(4)	143.5(7)	C(10)-C(11)	143.2(6)	C(17)-C(18)	142.2(7)
C(4)-C(5)	132.7(7)	C(11)-C(12)	133.0(7)	C(18)-C(19)	134.8(6)
C(5)-C(6)	143.0(7)	C(12)-C(13)	140.5(6)	C(19)-C(20)	142.5(6)
C(6)-C(7)	132.8(6)	C(13)-C(14)	133.0(6)	C(20)-C(21)	133.7(5)
Bond angles					
C(1)-N-C(8)	116.1(3)	C(8)-N-C(15)	115.1(4)	C(1)-N-C(15)	118.8(4)
N-C(1)-C(2)	110.9(4)	N-C(8)-C(9)	116.6(4)	N-C(15)-C(16)	112.1(4)
N-C(1)-C(7)	117.5(4)	N-C(8)-C(14)	111.5(4)	N-C(15)-C(21)	118.0(4)
C(2)-C(1)-C(7)	106.2(4)	C(9)-C(8)-C(14)	106.9(4)	C(16)-C(15)-C(21)	105.3(3)
C(1)-C(2)-C(3)	122.6(5)	C(8)-C(9)-C(10)	120.6(5)	C(15)-C(16)-C(17)	120.6(5)
C(2)-C(3)-C(4)	125.0(6)	C(9)-C(10)-C(11)	125.7(5)	C(16)-C(17)-C(18)	124.8(5)
C(3)-C(4)-C(5)	124.6(7)	C(10)-C(11)-C(12)	125.0(5)	C(17)-C(18)-C(19)	125.8(5)
C(4)-C(5)-C(6)	126.6(7)	C(11)-C(12)-C(13)	126.6(6)	C(18)-C(19)-C(20)	125.0(5)
C(5)-C(6)-C(7)	124.7(5)	C(12)-C(13)-C(14)	124.8(5)	C(19)-C(20)-C(21)	125.2(5)
C(6)-C(7)-C(1)	123.1(5)	C(13)-C(14)-C(8)	122.4(5)	C(20)-C(21)-C(15)	121.2(4)
Dihedral angles (Fig. 2) ^a					
α_1 52.5	α_8 54.2	α_{15} 55.8			
β_1 26.6	β_8 25.8	β_{15} 27.2			

Table 1. Atomic distances (pm) and angles ($^\circ$) for tri(1-cyclohepta-2,4,6-trienyl)amine, $N(C_7H_7)_3$ (**2**).

^a The numbering of the dihedral angles α and β (Fig. 2) for the 3 cyclohepta-2,4,6-trienyl substituents refer to the N-bonded carbon atom.

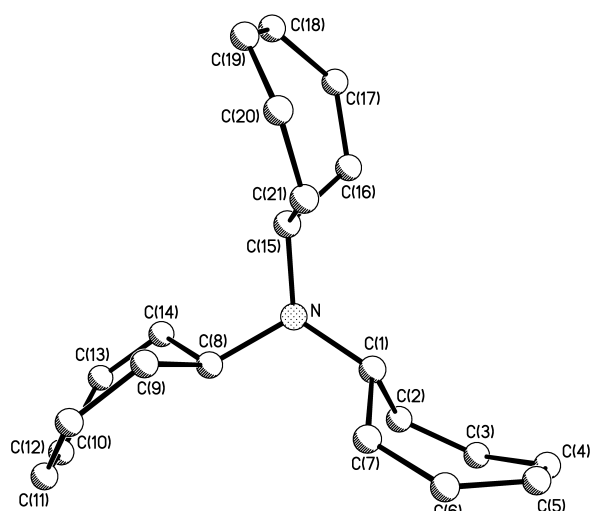


Fig. 1. Molecular structure of tri(1-cyclohepta-2,4,6-trienyl)amine, $N(C_7H_7)_3$ (**2**).

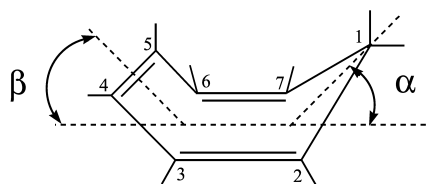


Fig. 2. Conformation of the 1-cyclohepta-2,4,6-trienyl substituent ([7]).

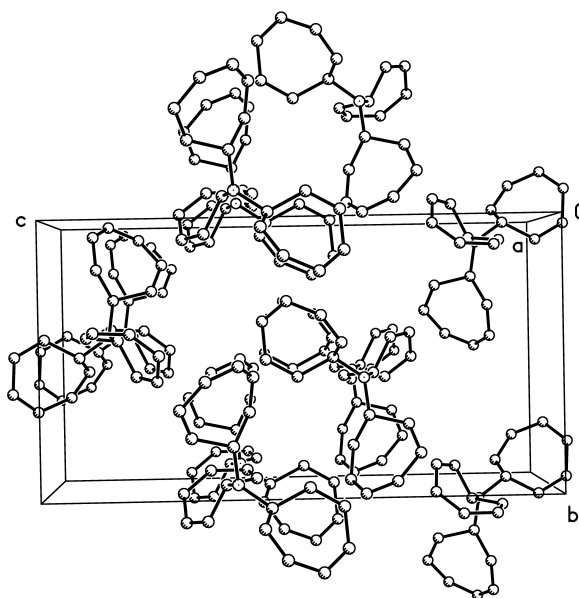


Fig. 3. Packing diagram of tri(1-cyclohepta-2,4,6-trienyl)amine, $N(C_7H_7)_3$ (**2**).

(av.) in $[P(C_7H_7)_4]BF_4$ [7]). Axial C_7H_7 substituents which are necessary for π -complexation have significantly smaller α and β parameters [7].

The packing diagram (Fig. 3) shows the arrangement of the $N(C_7H_7)_3$ molecules in the crystal, which leads to the formation of channels along axis a .

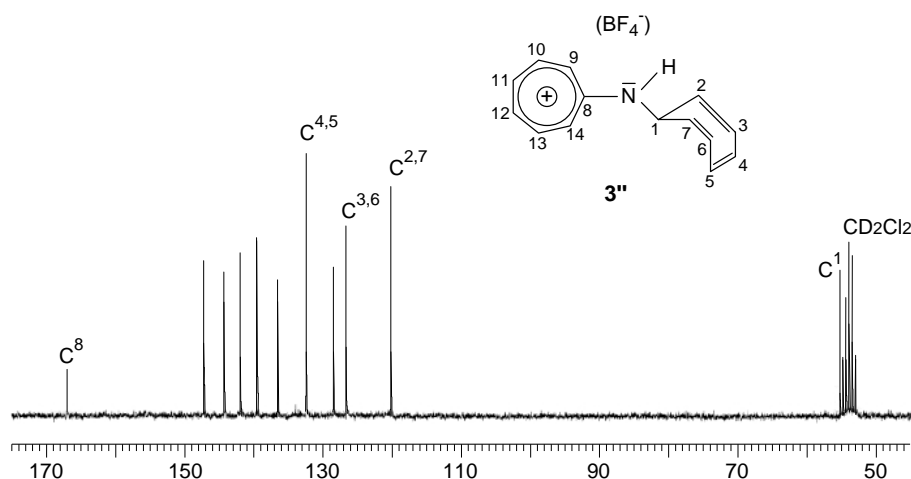
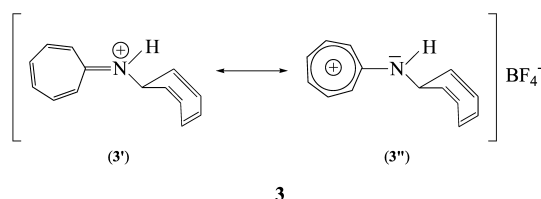


Fig. 4. ^{13}C NMR Spectrum of $[(\text{C}_7\text{H}_6^+)\text{NH}(\text{C}_7\text{H}_7)]\text{BF}_4^-$ (**3**).

Reaction of $N(\text{C}_7\text{H}_7)_3$ (**2**) with $[\text{C}_7\text{H}_7]\text{BF}_4$

Whereas $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) reacts with tropylium tetrafluoroborate, $[\text{C}_7\text{H}_7]\text{BF}_4$, in tetrahydrofuran or dichloromethane solution to give the phosphonium salt $[\text{P}(\text{C}_7\text{H}_7)_4]\text{BF}_4$ in quantitative yield [7], the corresponding reaction of $N(\text{C}_7\text{H}_7)_3$ (**2**) with $[\text{C}_7\text{H}_7]\text{BF}_4$ (1:1) leads to the N-tropylidene-N-(1-cyclohepta-2,4,6-trienyl)-immonium salt, $[(\text{C}_7\text{H}_6)\text{-N}(\text{H})(\text{C}_7\text{H}_7)]\text{BF}_4$ (**3**), for which two canonical structures (**3'** and **3''**) can be formulated [8]:

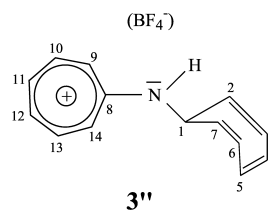


The use of $[\text{C}_7\text{H}_7]\text{BF}_4$ for the abstraction of a hydride ion from (1-cyclohepta-2,4,6-trienyl)amines, $(\text{C}_7\text{H}_7)\text{-N}(\text{R})(\text{R}')$ ($\text{R} = \text{R}' = \text{Me}$ [8], Et [9]; $\text{R} = \text{H}$, $\text{R}' = \text{Me}$ [8], Pr [9], C_7H_7 [8]) had been described earlier [8, 9], and **3** had been obtained [8] with $\text{NH}(\text{C}_7\text{H}_7)_2$ (**2a**) as the educt. The formation of the secondary amine derivative **3** from the reaction of $N(\text{C}_7\text{H}_7)_3$ (**2**) with $[\text{C}_7\text{H}_7]\text{BF}_4$ can be ascribed to the facile hydrolytic splitting of N- C_7H_7 bonds. Thus, $N(\text{C}_7\text{H}_7)_3$ (**2**) dissolves easily in diluted acids such as HCl and HBF_4 to give tropylium salts, as shown by the characteristic singlet of the tropylium ion, $[\text{C}_7\text{H}_7]^+$, in the ^1H and ^{13}C NMR spectra, *e.g.* $\delta(^1\text{H}) = 9.2$ and $\delta(^{13}\text{C}) = 155.4$ (in D_2O), after treatment of **2** with diluted HBF_4 acid.

The ^1H and ^{13}C NMR spectra (Table 2) clearly demonstrate that the products **3** obtained from the reactions of either $N(\text{C}_7\text{H}_7)_3$ (**2**) or $\text{NH}(\text{C}_7\text{H}_7)_2$ (**2a**) with $[\text{C}_7\text{H}_7]\text{BF}_4$ are essentially identical. In both cases the NMR spectra indicate the presence of a normal (bent) 1-cyclohepta-2,4,6-trienyl substituent (as in $N(\text{C}_7\text{H}_7)_3$ (**2**) and $\text{NH}(\text{C}_7\text{H}_7)_2$ (**2a**)) and a “more aromatic” seven-membered ring system. The observation of 7 different ^{13}C NMR signals for the “aromatic” ring (Fig. 4) can be rationalized on the assumption that the rotation around the N-C(8) bond is restricted due to partial double bond character.

The N-H group in **3** is indicated by a broad ^1H NMR signal ($\delta(^1\text{H}) = 9.44$ in CD_2Cl_2 solution) and a broadened absorption ($\nu(\text{N-H}) = 3277 \text{ cm}^{-1}$) in the IR solution spectra (CH_2Cl_2), although the corresponding band was not observed using CsI pellets.

A preliminary X-ray structure analysis of **3** (which suffers from severe disorder, in particular of the BF_4^- anions) leads to the conclusion that the cation is best described by the amino-substituted tropylium structure **3''** (*cf.* [8]). It is known that alkylamino substituents increase the stability of tropylium ions [10, 11].



The (1-cyclohepta-2,4,6-trienyl)amino substituent in the cation of **3** corresponds to the geometry found

Table 2. NMR spectra^a.

	N(C ₇ H ₇) ₃ 2	NH(C ₇ H ₇) ₂ 2a	N(Ph)(C ₇ H ₇) ₂ 2b	[(C ₇ H ₆ ⁺)N(H)(C ₇ H ₇)]BF ₄ (3) A ^b	[(C ₇ H ₆ ⁺)N(Ph)(C ₇ H ₇)]BF ₄ B ^b	[(C ₇ H ₆ ⁺)N(Ph)(C ₇ H ₇)]BF ₄ 4
¹ H NMR ^c	(CDCl ₃)	(CDCl ₃)	(CDCl ₃)	(CD ₂ Cl ₂)	(CD ₂ Cl ₂)	(CD ₂ Cl ₂)
δ(H ¹)	3.07t (3H)	3.03t (2H)	2.79t (2H)	3.72t (1H)	3.74br (1H)	2.85t (1H)
δ(H ² , H ⁷)	5.52dd (6H)	5.38dd (4H)	5.37dd (4H)	5.57m (2H)	5.57m (2H)	5.42m (2H)
δ(H ³ , H ⁶)	6.10m (6H)	6.16m (4H)	6.27m (4H)	6.42m (2H)	6.43m (2H)	6.28m (2H)
δ(H ⁴ , H ⁵)	6.61m (6H)	6.66t (4H)	6.72t (4H)	6.89t (2H)	6.88m (2H)	6.76m (2H)
δ(NH)		1.84s (1H)		9.45br (1H)	9.34br (1H)	
δ(Ph)			7.41–7.60m (5H)			7.40–7.74m (11H)
δ(C ₇ H ₆ ⁺)				7.32m, 7.63–7.95m (6H)	7.28/7.32m, 7.63–7.89m (6H)	
¹³ C NMR ^c	(CDCl ₃)	(CDCl ₃)	(CDCl ₃)	(CD ₂ Cl ₂)	(CD ₂ Cl ₂)	(CD ₂ Cl ₂)
δ(C ¹)	58.2	54.6	44.7	55.1	54.9	45.2
δ(C ² , C ⁷)	122.4	123.8	125.2	120.1	120.0	125.2
δ(C ³ , C ⁶)	127.0	126.2	125.0	126.5	126.5	125.3
δ(C ⁴ , C ⁵)	130.8	130.9	131.1	132.2	132.2	131.4
δ(Ph) ^c			123.7 (o) 129.2 (m); 122.7 (p) 145.4 (i)			124.9 (o) 130.0 (m); 133.6 (p) 146.3 (i)
δ(C ₇ H ₆ ⁺)				128.3, 136.3, 139.4, 141.8, 144.2, 147.1, 166.8	128.3, 136.1, 139.6, 141.8, 144.2, 147.2, 166.8	129.3, 136.4, 140.6, 141.8, 145.1, 146.7, 166.6
¹¹ B NMR				2.14	2.14q [J(B,F) 1.0 Hz]	

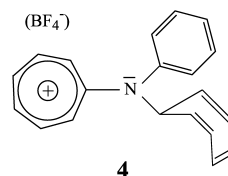
^a The amines **2**, **2a** and **2b** were measured in CDCl₃, the tetrafluoroborates **3** and **4** in CD₂Cl₂; ^b **A** was obtained by the reaction of **2** with [C₇H₇]BF₄ in CH₂Cl₂, **B** by the reaction of **2a** with [C₇H₇]BF₄ in CH₂Cl₂; ^c for comparison: [C₇H₇]Br: δ(¹H) 9.20 s; δ(¹³C) 155.4 (in D₂O); [C₇H₇]BF₄: δ(¹H) 9.17s; δ(¹³C) 155.3, δ(¹¹B) 1.59 (in D₂O); NPh₃: δ(¹H) 6.97 (1H), 7.13 (2H), 7.23 (2H); δ(¹³C) 122.6(p), 124.1(o), 129.1(m), 147.8(i) (in CDCl₃) [16].

in N(C₇H₇)₃ (**2**) with an equatorial attachment of the boat-shaped seven-membered ring to nitrogen ($\alpha = 56.9^\circ$, $\beta = 25.9^\circ$, N-C(1) 146.9(7) pm; *cf.* Table 1). The angle C(1)-N-C(8) (126.8(4)°) is also in the range expected for a flat pyramid; however, the hydrogen atom attached to the central nitrogen could not be located. The N-C(8) bond (130.9(6) pm) indicates some multiple bond character, the calculated bond lengths are 147 pm for the C-N single and 122 pm for the C=N double bond [12].

At first sight, the tropylium ring (C(8)-C(14)) appears to be nearly planar (with an average deviation of the carbon atoms of $\Delta = 3.5$ pm), and the C(8)=N bond protrudes by an angle of 6.1° from this plane. However, the cationic ring is actually present in a very shallow boat conformation (with $\alpha = 7.4^\circ$ and $\beta = 3.6^\circ$). This form had been observed earlier for the salt [O(C₇H₆)₂](CF₃SO₃)₂ [13] containing an ether dication in which two substituted tropylium rings (C₇H₆⁺) are connected through an oxo bridge. Comparable with the situation in **3**, the dication [O(C₇H₆)₂]²⁺ contains a bent C-O-C system (125.3(4)°) and shortened C-O bond lengths (135.6(3) pm), the calculated values are 143 pm for the C-O single bond and 119 pm for the C=O double bond [12]). The very shallow boat confor-

mation appears to be also characteristic of tropone and simple tropone derivatives [13].

As expected, the (so far unreported) tertiary amine N(Ph)(C₇H₇)₂ (**2b**) reacted with [C₇H₇]BF₄ to give the dark-red salt **4**.



The spectroscopic data of the amines **2**, **2a** and **2b** and of the tetrafluoroborate salts **3** and **4** are compared in Table 2.

Experimental Section

An atmosphere of dry argon was routinely used for the synthetic work and for the handling of the samples; the solvents were dry and saturated with argon.

The tropylium compounds, C₇H₇Br [14] and [C₇H₇]BF₄ [15], were prepared on the basis of the established literature methods. Aniline, PhNH₂, is commercially available.

Instrumentation: NMR spectra: Bruker ARX 250; IR spectra: Perkin Elmer 983G.

Tri(1-cyclohepta-2,4,6-trienyl)amine, N(C₇H₇)₃ (**2**) [15]

The suspension of 1.026 g (6 mmol) of tropylium bromide, C₇H₇Br, in 100 ml of dry ether was cooled to 0 °C in an ice bath, then saturated with NH₃ gas and stirred for 40 min while NH₃ was slowly passed through the reaction mixture. Ammonium bromide was filtered off and the solution was concentrated and cooled to give light-yellow crystals. The product **2** was twice recrystallized from diethylether. White prisms, yield 370 mg (64.4%), m.p. 122 °C (*cf.* 124–125 °C [15]).

Di(1-cyclohepta-2,4,6-trienyl)amine, NH(C₇H₇)₂ (**2a**) [15]

A solution of 1.026 g (6 mmol) of tropylium bromide, C₇H₇Br, in 5 ml of water was added dropwise under vigorous stirring to 60 ml of ice-cooled, concentrated aqueous ammonia. The oily product **2a** was isolated by extraction with pentane. From the concentrated pentane solution light-yellow crystals were obtained which were recrystallized twice from pentane to give **2a** as colorless crystals. Yield 300 mg (76%), m.p. 30 °C (*cf.* 28–30 °C [15]).

Di(1-cyclohepta-2,4,6-trienyl)phenylamine, N(Ph)(C₇H₇)₂ (**2b**)

PhNH₂ (93 mg, 1 mmol) was added to a solution of 342 mg (2 mmol) of tropylium bromide, C₇H₇Br, in 20 ml of ethanol. The solution was stirred for 2 h at r. t. Evaporation of ethanol left a yellow-brown solid, PhN(C₇H₇)₂ (**2b**), which was crystallized from ethanol/pentane and dried under high-vacuum. Yield 210 mg (77%), dec. 150 °C. EI-MS; *m/e* (%): 273 (16%) [M⁺], 183 (100%) [N(H)(Ph)(C₇H₇)], 182 (33%) [(C₇H₇)₂].

(N-1-Cyclohepta-2,4,6-trienyl)amino-tropylium tetrafluoroborate, [(C₇H₆⁺)NH(C₇H₇)]BF₄[−] (**3**)

A solution of 287 mg (1 mmol) of N(C₇H₇)₃ (**2**) was added dropwise to a suspension of 178 mg (1 mmol) of tropylium tetrafluoroborate, [C₇H₇]⁺BF₄[−], in 10 ml of CH₂Cl₂. The mixture was stirred at room temperature and became a homogeneous solution after *ca.* 30 min. Evaporation of the solvent left an orange solid which was washed repeatedly with diethylether. Recrystallization from CH₂Cl₂ afforded orange-yellow crystals of **3**, dec. above 95 °C, yield 123 mg (43.5%). The salt **3** is soluble in water, ethanol and CH₂Cl₂.

The analogous (1:1) reaction of 197 mg (1 mmol) of NH(C₇H₇)₂ (**2a**) with [C₇H₇]⁺BF₄[−] gave **3** as yellow crystals in slightly better yield (155 mg, 54.8%). C₁₄H₁₄BF₄N

(283.07): calcd. C 59.40, H 4.98, N 4.95, B 3.82, F 26.85; found C 58.42, H 4.90, N 4.98, B 3.96, F 26.10.

(N-1-Cyclohepta-2,4,6-trienyl)(N-phenyl)amino-tropylium tetrafluoroborate, [(C₇H₆⁺)N(Ph)(C₇H₇)]BF₄[−] (**4**)

A solution of 273 mg (1 mmol) of N(Ph)(C₇H₇)₂ (**2b**) in 5 ml of CH₂Cl₂ was added dropwise to a stirred suspension of 178 mg (1 mmol) of [C₇H₇]⁺BF₄[−] in 10 ml of CH₂Cl₂. After 30 min the homogeneous solution was brought to dryness in a vacuum. The dark-red residue was washed several times with small portions of diethylether and then crystallized from CH₂Cl₂. Dark-red crystals, m.p. 113 °C, yield 210 mg (58.5%).

*Crystal structure analysis of N(C₇H₇)₃ (**2**)*

The reflection intensities were collected on a STOE Image Plate Diffraction System (Mo-K_α-radiation, λ = 71.073 pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. The measuring temperature was 293 K.

All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms are in calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

C₂₁H₂₁N, colorless plate with dimensions 0.16 × 0.14 × 0.06 mm, crystallizes in the orthorhombic space group *P*2₁2₁2₁ with the lattice parameters *a* = 899.11(18), *b* = 1010.3(2), *c* = 1873.5(4) pm, *V* = 1701.8(6) 10⁶ pm³, *Z* = 4, μ = 0.064 mm^{−1}; 13400 reflections collected in the range 2.17° ≤ 2θ ≤ 26.18°; 3351 reflections independent, 906 assigned to be observed [*I* > 2σ(*I*)], full-matrix least squares refinement on *F*² with 199 parameters converged at *R*₁/*wR*₂-values of 0.0412/0.0676; the max./min. residual electron density was 0.188/−0.082 10^{−6} e pm^{−3}.

Supplementary material

Crystallographic data (excluding structure factors) for N(C₇H₇)₃ (**2**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, no CCDC-225012. Copies of the data may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged.

[1] M. Herberhold, N. Akkus, W. Milius, Z. Naturforsch. **58b**, 528 (2003); Z. Anorg. Allg. Chem. **629**, 2458 (2003).

[2] M. Herberhold, A. Pfeifer, W. Milius, Z. Anorg. Allg. Chem. **628**, 2919 (2002).

- [3] M. Herberhold, W. Milius, A. Pfeifer, Z. Naturforsch. **58b**, 1 and 11 (2003); J. Organomet. Chem. **684**, 300 (2003).
- [4] M. Herberhold, Th. Schmalz, W. Milius, B. Wrackmeyer, Inorg. Chim. Acta. **334**, 10 (2002) and **352**, 51 (2003); J. Organomet. Chem. **641**, 173 (2002); Z. Anorg. Allg. Chem. **628**, 437 and 979 (2002); Z. Naturforsch. **57b**, 53 and 255 (2002).
- [5] M. Herberhold, W. Milius, St. Eibl, Z. Anorg. Allg. Chem. **625**, 341 (1999).
- [6] M. Herberhold, St. Eibl, W. Milius, B. Wrackmeyer, Z. Anorg. Allg. Chem. **626**, 552 (2000).
- [7] M. Herberhold, K. Bauer, W. Milius, Z. Anorg. Allg. Chem. **620**, 2108 (1994).
- [8] H. J. Dauben, Jr., D. F. Rhoades, J. Am. Chem. Soc. **89**, 6764 (1967).
- [9] N. L. Bauld, Y. S. Rim, J. Am. Chem. Soc. **89**, 6763 (1967).
- [10] B. Foehlich, R. Braun, Tetrahedron Letters 2735 (1978) (No. 30).
- [11] E. Haug, B. Foehlich, Chem. Ber. **104**, 2338 (1971).
- [12] A. F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, 101. Edition, p. 1842, W. de Gruyter, Berlin-New York (1995).
- [13] R. F. Childs, R. Faggiani, C. J. L. Lock, C. V. Rogerson, J. Org. Chem. **48**, 3043 (1983).
- [14] W. von E. Doering, L. H. Knox, J. Am. Chem. Soc. **76**, 3202 (1954).
- [15] W. von E. Doering, H. Krauch, Angew. Chem. **68**, 661 (1956); W. von E. Doering, L. H. Knox, J. Am. Chem. Soc. **79**, 352 (1957).
- [16] cf. <http://www.aist.go.jp/RIODB/SDBS/menu-e.html> (SDBS No 3093 [Chem. Abstr. 603-34-9]).