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Molecular Structure of a Heptadentate Cogwheel: $C_7Me_7^+$ Is Not Planar[†]

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η-Cyclopentadienyl complexes, (η-C_5R_5)M, as well as η-arene complexes, (η-C_6R_6)M, are among the most important classes of compounds in organotransition metal chemistry.[1] In particular, the widespread use of cyclopentadienes as organometallic ligands is due to the large number of ring-substituted derivatives that have been synthesized since the serendipitous synthesis and discovery of ferrocene. Succesive replacement of hydrogen atoms by alkyl or aryl substituents alters the steric and electronic properties of the Cp ring and gives rise to increased steric bulk, solubility and stability of the resulting complexes.[2] Consequently, the introduction of persubstituted derivatives such as the pentamethylcyclopentadienyl ligand Cp* has resulted in the synthesis of a large number of novel complexes and in the discovery of new reactivity patterns.[1,3] This also holds true in the area of ring-substituted arene ligands, and the permethylated analogue hexamethylbenzene has been employed in the synthesis of many transition metal complexes (Figure 1).[1,4]

In contrast, cycloheptatrienyl complexes, (η-C_7R_7)M, with sterically demanding peralkylated or perarylated ligands are unknown despite the fact that the aromatic cycloheptatrienyl cations $C_7Me_7^+$ and $C_7Ph_7^+$ have been known for decades.[5,6] The molecular structure of $C_7Ph_7^+$, however, has been determined only recently and represents the first structurally cycloheptatrienyl cation with seven substituents prior to this work.[7] Attempts to coordinate transition metals to the central seven-membered ring of this perphenylated π-perimeter have not been successful so far.[8]

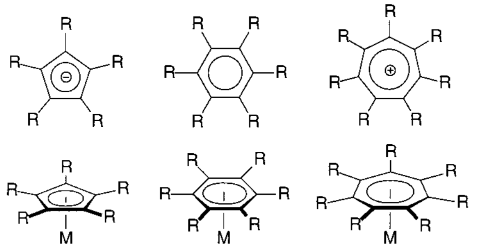
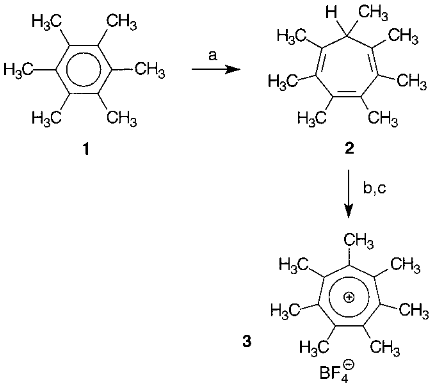


Figure 1. Schematic presentation of C_nR_n complexes ($n = 5$, 6, 7).

Scheme 1[a]



[a] Key: (a) CH_2Cl_2, N_2CHCH_3; (b) CCl_4, PCl_5; (c) AcOH, HBF_4.

In continuation of our work on transition metal complexes with novel cycloheptatrienyl ligands,[9] we became interested in the synthesis of salts containing the heptamethylcycloheptatrienyl cation, $C_7Me_7^+$, and in the use of these compounds as ligands in organotransition metal chemistry. Whereas our attempts to realize the latter are still under investigation, we report herein an improved protocol for the synthesis of heptamethylcycloheptatriene **2** from hexamethylbenzene **1** together with the synthesis and structural characterization of $(C_7Me_7)BF_4$ **3**.

A multistep synthesis of heptamethylcycloheptatriene **2** has been reported by Knoche.[10] The first step involves ring-expansion of C_6Me_6 **1** with ethyl diazoacetate, a reaction which does not only give the desired carbene addition product ethoxycarbonylhexamethylcycloheptatriene and its isomers, but also a significant amount of the C−H insertion product pentamethyldihydrocinnamic ethyl ester. Separation of this mixture followed by reduction of the ethoxycarbonyl group to a methyl group via the sequence $RCOOEt \rightarrow RCH_2OH \rightarrow RCH_2Cl \rightarrow RCH_3$ does only allow the isolation of **2** in very low yield (3.8% based on ethyl diazoacetate).[10]

Therefore, the development of a coordination chemistry based on the C_7Me_7 system required a much better protocol for the synthesis of **2**. According to Scheme 1, **2** can be synthesized in one step from hexamethylbenzene[11] **1** by ring-expansion with diazoethane which is generated

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[†] The title refers to ref 7: "The Structure of a Seven-Bladed Propeller: $C_7Ph_7^+$ is Not Planar".

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from *N*-nitroso-*N*-ethylurea.[12] The conversion of **1** into **2** proceeds in only modest yield (30%). The unreacted starting material, however, can be completely re-isolated and used again without any further purification step giving a nearly 100% yield based on re-isolated **1**.[13]

Hydride abstraction from **2** to form the $C_7Me_7^+$ cation has proven to be rather difficult. The use of complex salts containing the triphenylmethyl cation, Ph_3C^+, were completely unsuccessful, although triphenylmethane was obtained as the result of the hydride abstraction.[10] However, **3** can be synthesized from **2** according to the procedure published by Takeuchi et al.[5] Hence, treatment of **2** with PCl_5 followed by dissolution of the intermediate precipitates, presumably a mixture of chloride and hexachlorophosphate salts, in acetic acid/acetic anhydride and addition of aqueous HBF_4 gives **3** in moderate yield.[14]

The ^{1}H NMR spectrum of **3** in CD_3CN exhibits one resonance for the methyl groups at 2.62 ppm. The ^{13}C NMR resonances for the methyl and ring carbon atoms are observed at 24.4 and 160.2 ppm, respectively. The latter is observed at only sligthly lower field compared to the ^{13}C NMR resonance of the unsubstituted tropylium cation and adopts an intermediate position between $C_7H_7^+$ and $C_7Ph_7^+$.[15]

After the addition of diethyl ether **3** crystallized directly from the reaction mixture affording single crystals of $\mathbf{3}\cdot{}^1/_3CH_3COOH$ suitable for X-ray structure determination.[16] The asymmetric unit contains three independent molecules, and the molecular structure of one cation (molecule B) is shown in Figure 2.

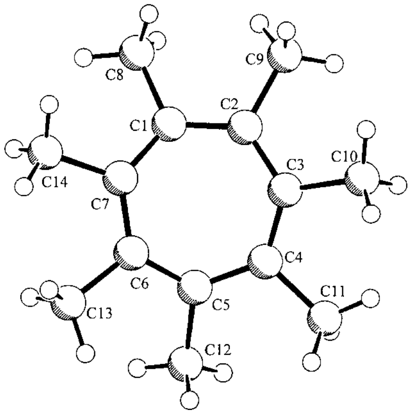

Figure 2. Molecular structure of $C_7Me_7^+$.

Table 1. Selected Bond Lengths (Å) and Angles (Deg) in $\mathbf{3}\cdot{}^1/_3CH_3COOH$[a]

	molecule A	molecule B	molecule C
C1−C2	1.315(10)	1.399(7)	1.410(7)
C1−C7	1.321(10)	1.397(7)	1.420(7)
C2−C3	1.332(10)	1.409(8)	1.390(8)
C3−C4	1.392(11)	1.408(8)	1.395(7)
C4−C5	1.527(13)	1.392(8)	1.389(6)
C5−C6	1.429(12)	1.404(7)	1.423(6)
C6−C7	1.356(10)	1.401(7)	1.375(7)
∅ C−C	1.38	1.40	1.40
C1−C2−C3	127.5(7)	125.5(4)	128.1(4)
C2−C3−C4	126.5(6)	126.2(5)	124.7(4)
C3−C4−C5	122.3(5)	126.6(5)	127.2(4)
C4−C5−C6	122.6(6)	124.9(4)	124.3(4)
C5−C6−C7	123.3(5)	125.6(4)	125.7(4)
C6−C7−C1	129.6(5)	127.2(4)	126.1(4)
C7−C1−C2	127.0(6)	125.2(4)	122.9(4)
ϕ	30.6	28.8	31.8
γ	21.7	21.4	19.1

[a] Standard deviations are given in parentheses.

Due to disorder of the incorporated acetic acid the structure could only be refined with reduced accuracy. Molecule A is most strongly affected by this disorder as indicated by larger standard deviations of the respective bond lengths and angles (Table 1). Therefore, a meaningful discussion of the bonding parameters must be confined to molecules B and C. The intra-ring bond distances in these cations do not alter significantly, and a mean value of 1.40 Å is observed which is similar to the average C−C distance found for the $C_7Ph_7^+$ cation ($\varnothing = 1.41$ Å).[7]

Figure 2 shows an alternative presentation of the cation and reveals that the seven-membered ring is not planar but rather adopts a boat conformation. Similar boat forms have been observed for the $C_7Ph_7^+$ cation as well as for the seven-membered rings in [7]circulene[17] and in the bis[tris(bicyclo[2.2.2]octeno)tropylium]acetylene dication.[18] The bend angles ϕ and γ for molecules A, B and C have been determined and are summarized in Table 1. These results are in agreement with semiempirical MO calculations which predict a ground-state C_s-optimized structure with interplanar angles of 22° (ϕ) and 18° (γ) to be almost 15 kcal mol^{-1} more stable than its planar C_{7h} conformer.[7] Comparison with the molecular strucuture of the perphenylated cation $C_7Ph_7^+$ ($\phi = 10.7°$, $\gamma = 12.8°$)[7] confirms the prediction that nonplanar substituents unlike the phenyl group would increase the distortion of the central C_7 ring (Figure 3).

In contrast to $C_7Me_7^+$, the corresponding, iso-π-electronic perimeters $C_5Me_5^-$ and C_6Me_6 exist as planar

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(13) A solution of diazoethane was prepared by the addition of solid *N*-ethyl-*N*-nitrosourea (25 g, 210 mmol) to a mixture of KOH (23 g, 410 mmol), water (60 mL) and CH_2Cl_2 (180 mL) at −15 °C over 45 min. The organic phase was separated using a cooled separatory funnel and was dried over KOH pellets for 1 h at −78 °C. The diazoethane solution was added via a cooled (−78 °C) dropping funnel to a refluxing mixture of **1** (4.94 g, 30 mmol), CuBr (10 g, 74 mmol) and CH_2Cl_2 (30 mL) over 75 min. CuBr was removed by filtration over Celite, and all volatiles were removed in vacuo. **2** was extracted from the residue with petroleum ether (3 × 15 mL). Evaporation afforded 1.6 g of **2** in essentially pure form: ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.98 (q, $J = 7.8$ Hz, 1H, 7-C*H*), 1.94 (s, 6H, C*H*$_3$), 1.76 (m, 6H, C*H*$_3$), 1, 74 (s br, 6H, C*H*$_3$), 1.20 (d, 3H, 7-C*H*$_3$); ^{13}C NMR (151 MHz, $CDCl_3$): δ 134.9, 131.5, 126.3 (C=C), 39.4 (7-CH), 17.7, 16.1, 14.2, 14.1 (*C*H$_3$).

(14) Anal. Calcd for $C_{14}H_{21}BF_4$ ($M_r = 276.12$): C, 60.89; H, 7.66. Found: C, 59.20; H, 7.85.

(15) The ^{13}C NMR spectra (in CD_3CN) of $(C_7H_7)BF_4$ and $(C_7Ph_7)BF_4$ exhibit resonances for the ring carbon atoms at 156.3 and 167.2 ppm, respectively.

(16) X-ray crystal structure analysis of $\mathbf{3}\cdot{}^1/_3CH_3COOH$: formula $C_{14}H_{21}BF_4\cdot{}^1/_3CH_3COOH$, $M = 296.14$, yellow crystal, 0.30 × 0.30 × 0.25 mm, $a = 14.982(2)$, $b = 9.063(1)$, $c = 17.975(4)$ Å, $\beta = 106.70(1)°$, $V = 2337.7(7)$ Å^3, $\rho_{calcd} = 1.262$ g cm^{-3}, $F(000) = 940$ e, $\mu = 1.07$ cm^{-1}, absorption correction ($0.969 \leq T \leq 0.974$), $Z = 6$, monoclinic, space group P2$_1$ (No. 4), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 9838 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 9838 independent ($R_{int} = 0.000$) and 5953 observed reflections [$I \geq 2\,\sigma(I)$], 552 refined parameters, $R = 0.096$, w$R^2 = 0.254$, max. residual electron density 0.52 (−0.40) e Å^{-3}, hydrogens calculated and refined as riding atoms, three chemically identical molecules with different conformation in the asymmetric unit. The anisotropic displacement parameters of molecule A indicate some unrefined positional disorder. Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data acquisition COLLECT, data reduction DENZO-SMN, absorption correction SORTAV, structure solution SHELXS-86, structure refinement SHELXL-97, graphics DIAMOND.

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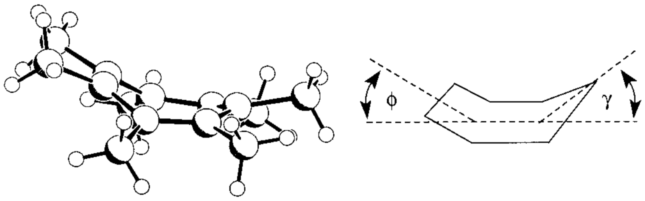

Figure 3. Presentation of the boat-conformation of $C_7Me_7^+$.

aromatic species[1] despite the fact that increasing the ringsize lengthens the radial distance of the external methyl groups from the center of the molecule. This, however, is more than compensated by substantially decreasing the angle beween adjacent methyl groups and the center of the internal ring from 72° and 60° to 51.4° ($360°/n$, $n = 5,6,7$).

The strong distortion together with the electrophilicity of the heptamethylcycloheptatrienyl cation might impede applications of the $C_7Me_7^+$ ligand to the synthesis of organometallic derivatives. Nevertheless, we are currently focusing on the preparation of complexes (η-C_7Me_7)M incorporating early-transition metals in (formally) low-oxidation states where strong back-bonding from the metal centers can be expected which will increase the intra-ring C−C-bond distances significantly. In addition, *Umpolung* and generation of the anti-aromatic $C_7Me_7^-$ anion seems to be a feasible goal in view of the related chemistry of the C_7Ph_7 system.[19]

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Supporting Information Available: X-ray crystal structure determination of **3**·$^1/_3CH_3COOH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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