1,1'-Di(tert-butyl)metallocenium Cations. The X-Ray Crystal Structures of \([M(C_5H_4'Bu)_2]PF_6\) (M = Fe, Co) and \([Co(C_5H_4'Bu)_2]_2CoCl_4\)

Max Herberhold\(^a\), Yan-Xiang Cheng\(^a,b\), Guo-Xin Jin\(^b\), and Wolfgang Milius\(^a\)

\(^a\) Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany
\(^b\) Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.O. Box 1022, P. R. China

Reprint requests to Prof. Dr. M. Herberhold. Fax: +49 (0) 921 55 2157.
E-mail: Max.Herberhold@uni-bayreuth.de

Z. Naturforsch. 55 b, 814-820 (2000); received May 26, 2000

1,1'-Disubstituted Ferrocenes, Ferrocenium Cations, Cobaltocenium Salts

The hexafluorophosphate salts \([Fe(C_5H_4'Bu)_2]PF_6\) (1) and \([Co(C_5H_4'Bu)_2]PF_6\) (2) crystallize in isotypic structures with centrosymmetric cations which have a staggered (transoid) conformation of the exactly parallel ring ligands (conformational angle \(\tau = 180^\circ\)). The tetrachlorocobaltate salt, \([Co(C_5H_4'Bu)_2]_2CoCl_4\) (3), contains one almost eclipsed (\(\tau = 140.4^\circ\)) and one almost staggered (\(\tau = 101.4^\circ\)) cobaltocenium cation; in both cases, the cyclopentadienyl ring planes are slightly inclined (by \(\alpha = 5.4^\circ\) and \(4.1^\circ\), respectively) to give more room to the tert-butyl substituents which are bent away from the metal in all three complexes 1 - 3.

Introduction

In the course of studies on \(\eta^5\)-(tert-butyl-cyclopentadienyl) metal complexes, we have isolated crystals of the salt \([Co(C_5H_4'Bu)_2]_2CoCl_4\) (3) which contains two cobaltocenium sandwiches with different conformational arrangement of the ring ligands. For the purpose of comparison we then have determined the structures of the 1,1'-di(tert-butyl)metallocenium hexafluorophosphates, \([M(C_5H_4'Bu)_2]PF_6\) (M = Fe (1), Co 2). The structures of 1 and 2 are isotypic and contain strictly centrosymmetrical (transoid) cations.

Results and Discussion

General remarks on the structure of 1,1'-disubstituted metallocenes

The conformational angle (\(\tau\)) in 1,1'-disubstituted metallocenes is defined as the torsional angle C1-Z'-Z1, i.e. the dihedral angle between the planes which include the two cyclopentadienyl ring centers (Z, Z') and the ring carbon atom bearing the substituent R (C1 or C1', respectively).

A 1,1'-disubstituted metallocene with two equal substituents (R) may then assume angles of \(\tau = 72\) and \(144^\circ\) in the ideal eclipsed forms, and angles of \(\tau = 36, 108\) and \(180^\circ\) in the ideal staggered conformations.

It is not easy to predict the conformation of 1,1'-disubstituted ferrocenes. Whereas unsubstituted ferrocene is eclipsed (\(D_{sh}, \tau = 0^\circ\)) [1, 2], the perethylated analogue, Fe(C5Me3)2, is staggered (\(D_{sd}, \tau = 36^\circ\)) both in the crystal [3, 4] and in the gas phase [5]. This can be ascribed to steric reasons because the decamethylferrocenium cation, \([Fe(C_5Me_5)]^+\), again prefers \(D_{sh}, \tau = 0^\circ\) [6-8]; the eclipsed \(D_{sh}, \tau = 0^\circ\) or almost eclipsed (e.g. \(\tau = 4^\circ\) [8]) arrangement, as it is also found in ferrocenium salts such as \([Fe(C_5H_5)Cl]BiCl_4\) (\(\tau \sim 1^\circ\) [9]) or \([Fe(C_5H_5)Cl_2]FeCl_4\) (nearly eclipsed [10]).

A similar situation is observed in the salts of the cobaltocenium cation which is isoelectronic with the 18e molecule ferrocene: The unsubstituted cobaltocenium cation is eclipsed in salts such as \([CoC_2][SbPh_2Cl_2]\) [11], \([CoC_2][Sb(R)Cl_3]\) [12].
Complex | Conformation | Angle $\tau$ | Other angles | Ref.
--- | --- | --- | --- | ---
Fe(C$_5$H$_4$-R)$_2$:  
R = COOH | eclipsed | 1.6$^\circ$ | H-bonded dimers, $\alpha = 1.3^\circ$ | [16]
SnCl$_3$ | staggered | 85.3$^\circ$ | $\alpha = 3.8^\circ$; $\beta = 3.5^\circ$ | [17]
C(O)Ph | nearly eclipsed | 108$^\circ$ | $\alpha = 4.8^\circ$; $\beta = 1.8^\circ$, 2.8$^\circ$ | [18]
B(N'Pr$_2$)$_2$ | eclipsed | 139.4$^\circ$ (av.) | $\alpha = 1.15^\circ$ | [19]
SiMe$_2$SiMe$_3$ | almost eclipsed | 149$^\circ$ | $\alpha = 1.02^\circ$ | [20]
SnPh$_3$ | 153.4$^\circ$ | $\alpha = 1^\circ$ | [21]
BBr$_2$ | staggered | 163.4(4)$^\circ$ | $\beta = 10.2^\circ$ (inwards) | [19]
C(0)-C(0)Ph | staggered | 180$^\circ$ | $\alpha = 0^\circ$ | [22]
PPh$_2$ | staggered | 180$^\circ$ | $\beta = 0.95^\circ$ | [23]
SO$_2$Cl | almost staggered | $\sim 180^\circ$ | $\alpha = 5.5^\circ$ (inwards) | [24]
TePh | $\sim 180^\circ$ | $\alpha = 6.6^\circ$ | [25 - 27]
Ru(C$_5$H$_4$-PPh$_2$)$_2$ | staggered | 180$^\circ$ | $\alpha = 0.95^\circ$ | [28]
[Fe(C$_5$H$_4$-CH$_3$)$_2$]$_3$ | eclipsed | 2.2$^\circ$ | $\alpha = 0^\circ$ | [29]
[Fe(C$_5$H$_4$-Bu)$_2$]PF$_6$ | staggered | 180$^\circ$ | $\alpha = 0^\circ$; $\beta = 8.0^\circ$ | this work

Table 1. Conformation of the cyclopentadienyl rings in 1,1'-disubstituted ferrocenes.

(\(R = p\)-tolyl [12] or Me$_3$SiCH$_2$ [13]) and [CoCp$_2$][CpMo(NO)$_2$Et] [14], whereas the decamethyl-cobaltocenium cation prefers the staggered arrangement of the rings (approximately $D_{5h}$ symmetry) in the salts [CoCp$_2$][HfCl$_5$(thf)] [15] and [CoCp$_3$]$_2$[TCNQ(II)] [8].

A considerable amount of structural data has been reported for 1,1'-disubstituted ferrocene derivatives (Table 1), and conformational angles $\tau$ between 0 and 180$^\circ$ have been noted. The centrosymmetric, "transoid" structure ($\tau = 180^\circ$) appears to be favoured.

**Structural studies**

The structures of the cobaltocenium salts [Co(C$_5$H$_4$-Bu)$_2$]PF$_6$ (2) and [Co(C$_5$H$_4$-Bu)$_2$]$_2$CoCl$_4$ (3) are shown in Figures 1 - 3. Relevant distances and angles for 1 - 3 are summarized in Tables 2 and 3.
Fig. 2. Perspective view of cations and anion in [Co(C₅H₄Buv)₂]₂CoCl₄ (3).

The hexafluorophosphates [M(C₅H₄'Buv)₂]PF₆ (M = Fe (1), Co (2)) both crystallize isotypically in the monoclinic space group C2/m with 2 formula entities in the unit cell. The centrosymmetric cations contain the metal atom at an inversion center. The cyclopentadienyl rings are therefore strictly parallel (α = 0); however, they are shifted from the ideal position with the metal atom above or below the ring centers (Z, Z'). Both the metal-carbon and the intra-annular carbon-carbon distances differ slightly: The carbon atom C(1) bearing the tert-butyl substituent is involved in the longest distances and is situated opposite to the shortest carbon-carbon ring bond (C(3)-C(3')).

In general, the molecular structure of substituted sandwich complexes can be discussed on the basis of four angles (Fig. 4), cf. [33 - 35]:

α is defined as the tilt angle of the cyclopentadienyl ring planes; it is zero in centrosymmetric structures; β describes the deviation of the bond between the respective ring carbon and the substituent (R, R') from the cyclopentadienyl ring plane; δ is the angle at the metal atom between the two ring centers (Z, Z'); it is 180° in the centrosymmetric case; τ characterizes the conformational arrangement of the two ring ligands relative to each other; it is 180° in centrosymmetric molecules.

In agreement with the difference of the ionic radii (Fe²⁺ 78 pm / Co²⁺ 75 pm and Fe³⁺ 65 pm / Co³⁺ 61 pm according to Pauling), the distance between the metal and the ring centers (Z, Z') is larger in the
Table 2. Bond distances [pm] in the metallocenium cations of 1 - 3.

<table>
<thead>
<tr>
<th></th>
<th>[Fe(C₅H₄'Bu)₂]PF₆ (1)</th>
<th>[Co(C₅H₄'Bu)₂]PF₆ (2)</th>
<th>at Co(1) (ecl.)</th>
<th>[Co(C₅H₄'Bu)₂][CoCl₄] (3) at Co(2) (stagg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C(1)</td>
<td>209.2(3)</td>
<td>206.6(3)</td>
<td>206.1(5)</td>
<td>206.0(5)</td>
</tr>
<tr>
<td>Fe-C(2)</td>
<td>208.2(3)</td>
<td>203.6(2)</td>
<td>204.8(5)</td>
<td>203.4(5)</td>
</tr>
<tr>
<td>Fe-C(3)</td>
<td>207.5(3)</td>
<td>202.8(2)</td>
<td>202.9(6)</td>
<td>203.6(6)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>142.3(4)</td>
<td>142.0(3)</td>
<td>142.8(2)</td>
<td>142.2(3)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>139.9(9)</td>
<td>138.4(8)</td>
<td>138.6(6)</td>
<td>138.8(6)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>150.1(5)</td>
<td>150.9(5)</td>
<td>150.8(5)</td>
<td>150.9(5)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>142.3(4)</td>
<td>142.0(3)</td>
<td>142.2(3)</td>
<td>142.2(3)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>150.1(5)</td>
<td>150.9(5)</td>
<td>150.8(5)</td>
<td>150.9(5)</td>
</tr>
</tbody>
</table>

Table 3. Structural parameters of the metallocenium salts 1 - 3 and related cobaltocenium salts.

<table>
<thead>
<tr>
<th>Complex</th>
<th>M-Z [pm]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>δ [°]</th>
<th>τ [°]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(C₅H₄'Bu)₂]PF₆ (1)</td>
<td>169.8</td>
<td>0</td>
<td>7.3</td>
<td>180</td>
<td>180</td>
<td>this work</td>
</tr>
<tr>
<td>[Co(C₅H₄'Bu)₂]PF₆ (2)</td>
<td>164.9</td>
<td>0</td>
<td>8.0</td>
<td>180</td>
<td>180</td>
<td>this work</td>
</tr>
<tr>
<td>[Co(C₅H₄'Bu)₂]CoCl₄ (3) at Co(1) (nearly eclipsed)</td>
<td>164.3</td>
<td>5.4</td>
<td>6.6</td>
<td>176.35</td>
<td>140.4</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>164.4</td>
<td></td>
<td></td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at Co(2) (nearly staggered)</td>
<td>164.2</td>
<td>4.1</td>
<td>6.2</td>
<td>177.08</td>
<td>101.4</td>
<td>this work</td>
</tr>
<tr>
<td>[Co(C₅H₄-COOH)]PF₆ (A) (staggered, centrosymm.)</td>
<td>159.7</td>
<td>0</td>
<td>8.1</td>
<td>180</td>
<td>180</td>
<td>[36]</td>
</tr>
<tr>
<td>[Co(C₅H₄-COOH)(C₅H₄-COO)]·[A] at Co(1) (eclipsed)</td>
<td>163.7</td>
<td>2.3</td>
<td>6.5</td>
<td>177.68</td>
<td>4.1</td>
<td>[36]</td>
</tr>
<tr>
<td>[Co(C₅H₄-CHP₄₂)]PF₆ (B) (staggered, centrosymm.)</td>
<td>163.7</td>
<td>0</td>
<td>3.2</td>
<td>180</td>
<td>180</td>
<td>[37]</td>
</tr>
</tbody>
</table>

* For the definition of the angles α, β, δ and τ see text and Fig. 4; Z is the center of the cyclopentadienyl ring; b the substituent is bent outwards (away from the central metal), unless noted otherwise; c the substituent is bent inwards (towards the central metal).

Table 4. NMR data of the diamagnetic complexes Fe(C₅H₄'Bu)₂ and [Co(C₅H₄'Bu)₂]PF₆ (2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹H NMR spectra</th>
<th>¹³C NMR spectra</th>
<th>Solvent</th>
<th>¹H NMR spectra</th>
<th>¹³C NMR spectra</th>
<th>¹³C NMR spectra</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(C₅H₄'Bu)₂</td>
<td>1.21</td>
<td>31.6</td>
<td>61.6</td>
<td>CDCl₃</td>
<td>1.21</td>
<td>31.6</td>
<td>61.6</td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>31.6</td>
<td>61.6</td>
<td>3,99 vt</td>
<td>31.8</td>
<td>30.7</td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td>1.21</td>
<td>31.6</td>
<td>61.6</td>
<td>3.92 vt</td>
<td>31.8</td>
<td>30.7</td>
<td>60.6</td>
</tr>
<tr>
<td>[Co(C₅H₄'Bu)₂]PF₆ (2)</td>
<td>1.29</td>
<td>31.0</td>
<td>80.7</td>
<td>CDCl₃</td>
<td>1.29</td>
<td>31.0</td>
<td>80.7</td>
</tr>
<tr>
<td></td>
<td>1.29</td>
<td>31.0</td>
<td>80.7</td>
<td>5.67</td>
<td>31.0</td>
<td>80.7</td>
<td>83.3</td>
</tr>
<tr>
<td></td>
<td>1.28</td>
<td>30.7</td>
<td>81.5</td>
<td>[42]</td>
<td>1.28</td>
<td>30.7</td>
<td>81.5</td>
</tr>
<tr>
<td></td>
<td>1.28</td>
<td>30.7</td>
<td>81.5</td>
<td>5.57 vt</td>
<td>30.7</td>
<td>81.5</td>
<td>83.6</td>
</tr>
</tbody>
</table>

* The assignment of the α and β ring carbon atoms has been discussed by F. H. Köhler [38, 42].
ferrocenium than in the cobaltocenium cations (169.8 pm (1) / 164.9 pm (2) and 164.3 (av.) pm (3), respectively, cf. Table 3).

The crystal structure of [Co(C5H4rBu)2]2CoCl4 (3) is described in the monoclinic space group P21/c with four cobaltocenium cations in the unit cell (Z = 2). There are two crystallographically independent cations with different conformational arrangements of the cyclopentadienyl ring ligands (Table 3). In general, the substituents (R, R') in 1,1'-disubstituted cobaltocenium salts are bent away from the central metal atom, as observed for 2,3, A and B, unless intermolecular interactions such as hydrogen bonds induce other geometries, as in the supramolecular compounds investigated by D. Braga et al. [36].

**Experimental**

The 1,1-di(tert-butyl)-substituted metallocenes Fe(C5H4rBu)2 [38 - 40] and Co(C5H4rBu)2 [41, 42] have been included in systematic 1H and 13C NMR spectroscopic investigations. Both complexes are easily oxidized to the corresponding cations [Fe(C5H4rBu)]+ [43] and [Co(C5H4rBu)]+ [40] which were also studied by NMR spectroscopy. The 1H and 13C NMR data for the diamagnetic complexes Fe(C5H4rBu)2 and [Co(C5H4rBu)]+ are summarized in Table 4.

Na[C5H4rBu] was freshly prepared from tert-butyl cyclopentadiene, C5H5rBu [44], and a threefold excess of NaH in boiling THF.

**Preparation of the salts 1 - 3**

_Synthesis of [Fe(C5H4rBu)2]PF6 (1):_ A THF solution (20 ml) of 0.34 g (2.68 mmol) of FeCl2 and 0.82 g (5.69 mmol) of Na[C5H4rBu] was kept under reflux (65°) for 24 h. The solvent was removed under reduced pressure at 25°C and the residue extracted in a Soxhlet apparatus using 100 ml of hexane. Evaporation of the solventhexane left an orange oil of Fe(C5H4rBu)2 which solidified on cooling. Yield 0.71 g (88.5%), cf. m. p. 29 - 30°C [44], 26 - 28°C [38]. MS (EI, 70 eV): m/z(%) = 298 (100) [M]+, 283 (16) [M+-CH3]. 1H and 13C NMR data see Table 4.

A solution of 0.21 g (0.70 mmol) of Fe(C5H4rBu)2 in 20 ml of THF was stirred over night in the presence of 5 ml of conc. HNO3 cf. [43b]. A solution of 0.15 g (0.92 mmol) of NH4PF6 in 20 ml of acetone was then added. After stirring for 2 h the solvents were completely removed under reduced pressure and the dark residue extracted with 40 ml of CH2Cl2. Upon addition of 100 - 200 ml of hexane, the formation of blue needles of 1 was observed. Yield 0.26 g (83.9%). MS (EI, 70 eV): m/z(%) = 298 (100) [M]+, 283 (50) [M+-CH3].

_Synthesis of [Co(C5H4rBu)2]PF6 (2):_ The solution of 30 g (1.3 mmol) of [Co(NH3)6]Cl2 and 0.45 g (3.1 mmol) of Na[C5H4rBu] in 30 ml of THF was heated under reflux for 12 h cf. [41]. The brown reaction mixture was then filtered and a few drops of 30% H2O2 added, before a stream of air was blown through the brown solution for 40 min. Addition of an aqueous solution of 0.35 g (2.2 mmol) of NH4PF6 resulted in the formation of a brown precipitate. The mixture was stirred over night at room temperature. Then the solid product was filtered off, washed with a small volume of THF and with ice-cold water, and dried under vacuum. Yield 0.46 g (79.3%). MS (EI, 70 eV): m/z(%) = 301 (100) [M]+, 271 (78) [M+-2CH3]. 1H and 13C NMR data (in CD3CN solution) see Table 4.

_Synthesis of [Co(C5H4rBu)2]2CoCl4 (3):_ A THF solution (20 ml) containing 0.58 g (2.5 mmol) of [Co(NH3)6]Cl2 and 0.36 g (2.5 mmol) of Na[C5H4rBu] was kept under reflux for 24 h. The solvent was removed under reduced pressure and the residue extracted three times with 20 ml of CH2Cl2. The combined green extracts were brought to dryness and the green solid residue was recrystallized from CH2Cl2/hexane. Yield 0.44 g (87.6%). MS (EI, 70 eV): m/z(%) = 301 (100) [M]+, 271 (60) [M+-2CH3]. 1H and 13C NMR data (in CDCl3) are given in Table 4.

_Crystal structures of the salts 1 - 3_

The reflection intensities were collected on a Siemens P4 diffractometer (Mo-Kα radiation, λ = 71.073 pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V5.1. The temperature for all structure determinations was 296 K.

All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were included on calculated positions and refined applying the riding model with fixed isotropic temperature factors.

_Crystal structure of [Fe(C5H4rBu)2]PF6 (1):_ C18H12FePF6, dark blue prism with dimensions 0.35x0.18x0.12 mm; monoclinic space group C2/m with the lattice parameters a = 1172.27(7), b = 1008.73(7), c = 892.11(5) pm, β = 105.815(4)°, V = 1014.99(11)·10⁶ pm³, Z = 2, μ = 0.873 mm⁻¹; 2542 reflections collected in the range 3° ≤ 2θ ≤ 55°, 1233 reflections independent, 1101 assigned to be observed [1 > 2σ(I)], full-matrix least squares refinement against F² with 70 parameters converging at R1/wR2-values of 0.053/0.138, max./min. residual electron density 0.533/-0.916 · 10⁻⁶ e pm⁻³.
Crystal structure of [Co(C₅H₄Bu)₂]PF₆ (2): C₁₅H₂₆CoPF₆, orange prism of dimensions 0.25 × 0.20 × 0.16 mm; monoclinic space group C2/m with the lattice parameters a = 1175.11(7), b = 1017.07(7), c = 880.45(5) pm, β = 106.537(4)°, V = 1008.76(11) × 10⁶ pm³, Z = 2, μ = 0.982 mm⁻¹; 2538 reflections collected in the range 3° ≤ 2θ ≤ 55°, 1224 reflections independent, 1057 assigned to be observed [I > 2σ(I)], full-matrix least squares refinement against F² with 70 parameters converging at R1/wR2-values of 0.038/0.106; empirical absorption correction (Ψ-scans) yielding min./max. transmission factors of 0.4960/0.5431, max./min. residual electron density 0.426/-0.280 • 10⁻⁶ e pm⁻³.

Crystal structure of [Co(C₅H₄Bu)₂]₂CoCl₄ (3): [C₁₈H₃₂Co]₂CoCl₄, green plate with dimensions 0.35 × 0.18 × 0.08 mm; monoclinic space group P2₁/c with the lattice parameters a = 1528.5(4), b = 1565.0(7), c = 1725.3(4) pm, β = 110.568(7)°, V = 3864.2 × 10⁶ pm³, Z = 4, μ = 1.572 mm⁻¹; 7813 reflections collected in the range 3° ≤ 2θ ≤ 50°, 6438 reflections independent, 4444 assigned to be observed [I > 2σ(I)], full-matrix least squares refinement against F² with 388 parameters converging at R1/wR2-values of 0.051/0.134; empirical absorption correction (Ψ-scans) resulting in min./max. transmission factors of 0.5531/0.9143, max./min. residual electron density 0.46/-0.52 • 10⁻⁶ e pm⁻³.

Crystallographic data (excluding structure factors) for the structures 1 - 3 reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-145 590 (1), CCDC-145 591 (2) and CCDC-145 589 (3). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax Int. Code +44 (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk].

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged. Y.-X. Cheng is particularly grateful for a fellowship within the framework of the Chinese-German Cooperation Program, administered by the Chinese Academy of Sciences and the Max-Planck-Gesellschaft.