1,1'-Di(tert-butyl)metallocenium Cations. The X-Ray Crystal Structures of [M(C₅H₄'Bu)₂]PF₆ (M = Fe, Co) and [Co(C₅H₄'Bu)₂]CoCl₄

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

The hexafluorophosphate salts [Fe(C₅H₄'Bu)₂]PF₆ (1) and [Co(C₅H₄'Bu)₂]PF₆ (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 tetra-chlorocobaltate salt, [Co(C₅H₄'Bu)₂]₂CoCl₄ (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°, 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 \( \eta^2 \)-(tert-butyl-cyclopentadienyl) metal complexes, we have isolated crystals of the salt [Co(C₅H₄'Bu)₂]₂CoCl₄ (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(C₅H₄'Bu)₂]PF₆ (M = Fe (1), Co (2)). The structures of 1 and 2 are isotypic and contain strictly centrosymmetric (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 \( C^1 - Z-Z' - C^1' \), 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 (C^1 or C^1', respectively).

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

It is not easy to predict the conformation of 1,1'-disubstituted ferrocenes. Whereas unsubstituted ferrocene is eclipsed (\( \Delta_{R} \), \( \tau = 0^\circ \)) [1, 2], the peremethylated analogue, Fe(C₅Me₅)₂, is staggered (\( \Delta_{sd} \), \( \tau = 36^\circ \)) both in the crystal [3, 4] and in the gas phase [5]. This can be ascribed to steric reasons because the decamethylferrocenium cation, \( [\text{Fe(C}_5\text{Me}_5)_2]^{+} \), again prefers [6 - 8] the elliptic (\( \Delta_{sh} \), \( \tau = 0^\circ \)) or almost elliptic (e. g. \( \tau = 4^\circ \) [8]) arrangement, as it is also found in ferrocenium salts such as \( \text{[Fe(C}_5\text{H}_5)_2]BiCl}_4 \) (\( \tau \sim 1^\circ \) [9]) or \( \text{[Fe(C}_5\text{H}_5)_2]FeCl}_4 \) (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 \( [\text{CoCp}_2][\text{SbPh}_2\text{Cl}_3] \) [11], \( [\text{CoCp}_2][\text{Sb(R)}\text{Cl}_3] \)

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Complex Conformation Angle $\tau$ Other angles Ref.  
Fe(C$_5$H$_4$-R)$_2$:  
R = COOH eclipsed 1.6° H-bonded dimers, $\alpha = 1.3^\circ$ [16]  
SnCl$_3$ staggered 85.3° $\alpha = 3.8^\circ$; $\beta = 3.5^\circ$ [17]  
C(O)Ph nearly eclipsed 108° $\alpha = 1.3^\circ$ [17]  
C(O)CH$_3$ eclipsed 137.4° $\alpha = 4.8^\circ$; $\beta = 1.8^\circ$, 2.8° [19]  
B(NPr$_2$)$_2$ almost eclipsed 149° $\alpha = 1.02^\circ$ [20]  
Ti(NEt$_2$)$_3$ 153.4° $\alpha = 1^\circ$ [21]  
SnPh$_3$ 163.4(4)° [22]  
BBr$_2$ staggered 180° $\beta = 10.2^\circ$ (inwards) [19]  
C(O)-C(O)Ph staggered 180° $\alpha = 0^\circ$ [23]  
PPh$_2$ staggered 180° $\alpha = 0^\circ$ [24]  
P(O)Ph$_2$ staggered 180° $\alpha = 0^\circ$ [25 - 27]  
P(S)Ph$_2$ staggered 180° $\alpha = 0^\circ$ [27]  
SO$_2$Cl almost staggered $\sim 180^\circ$ $\beta = 5.5^\circ$ (inwards) [28]  
TePh $\sim 180^\circ$ $\alpha = 0.95^\circ$ [29]  
Ru(C$_5$H$_4$-PPh$_2$)$_2$ staggered 180° $\alpha = 0^\circ$ [30]  
[Fe(C$_5$H$_4$-CH$_3$)$_2$]I$_3$ eclipsed 2.2° $\alpha = 6.6^\circ$ [32]  
[Fe(C$_5$H$_4$'-Bu)$_2$]PF$_6$ staggered 180° $\alpha = 0^\circ$; $\beta = 8.0^\circ$ this work

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

Fig. 1. Perspective view of cation and anion in [Co(C$_5$H$_4$-Bu)$_2$]PF$_6$ (2) and numbering scheme.

(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$_2$]$_2$[TCNQ(I)$_2$] [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° 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.
The hexafluorophosphates \([\text{M}(\text{C}_5\text{H}_4\text{Bu})_2]\text{PF}_6\) (\(\text{M} = \text{Fe}\) (1), \(\text{Co}\) (2)) both crystallize isotypically in the monoclinic space group \(\text{C}2/m\) 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 \((\alpha = 0)\); 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 \(\text{C}(1)\) bearing the tert-butyl substituent is involved in the longest distances and is situated opposite to the shortest carbon-carbon ring bond \((\text{C}(3)-\text{C}(3'))\).

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

- \(\alpha\) is defined as the tilt angle of the cyclopentadienyl ring planes; it is zero in centrosymmetric structures;
- \(\beta\) describes the deviation of the bond between the respective ring carbon and the substituent \((\text{R}, \text{R'})\) from the cyclopentadienyl ring plane;
- \(\delta\) is the angle at the metal atom between the two ring centers \((Z, Z')\); it is 180° in the centrosymmetric case;
- \(\tau\) 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 (\(\text{Fe}^{2+} 78\text{ pm} / \text{Co}^{2+} 75\text{ pm}\) and \(\text{Fe}^{3+} 65\text{ pm} / \text{Co}^{3+} 61\text{ pm}\) 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>Complex</th>
<th>Fe-C(1)</th>
<th>Co-C(1)</th>
<th>Co-C(3)</th>
<th>Co(1)-C(3)</th>
<th>Co(2)-C(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(C₅H₄['Bu])₂]PF₆ (1)</td>
<td>209.2(3)</td>
<td>206.6(3)</td>
<td>207.5(3)</td>
<td>202.8(2)</td>
<td></td>
</tr>
<tr>
<td>[Co(C₅H₄['Bu])₂]PF₆ (2)</td>
<td>208.3(2)</td>
<td>203.6(2)</td>
<td>207.5(3)</td>
<td>202.8(2)</td>
<td></td>
</tr>
<tr>
<td>[Co(C₅H₄['Bu])₂]CoCl₄ (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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)</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>
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<td></td>
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<td></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)₂]PF₆ (A)</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></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at Co(2) (eclipsed)</td>
<td>164.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>{[Co(C₅H₄-COOH)(C₅H₄-COO)]}² (K)(PF₆)</td>
<td>162.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>[Co(C₅H₄-CHPh₂)₂]PF₆ (B)</td>
<td>163.7</td>
<td>3.3</td>
<td>6.5</td>
<td>178.22</td>
<td>2.5</td>
<td>[36]</td>
</tr>
</tbody>
</table>

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 δ(Me)</th>
<th>¹³C NMR spectra δ(C₅H₄)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(C₅H₄['Bu])₂</td>
<td>1.21</td>
<td>31.6</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>3.99vt</td>
<td>31.8</td>
<td>C₆D₆</td>
</tr>
<tr>
<td>[Co(C₅H₄['Bu])₂]PF₆ (2)</td>
<td>1.29</td>
<td>31.0</td>
<td>CDCl₃</td>
</tr>
<tr>
<td></td>
<td>5.61vt</td>
<td>30.7</td>
<td>C(O)(CD₃)₂ [42]</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; the substituent is bent outwards (away from the central metal), unless noted otherwise; the substituent is bent inwards (towards the central metal).

The assignment of the α and β ring carbon atoms has been discussed by F. H. Köhler [38, 42].
The crystal structure of [Co(C₅H₅'Bu)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(C₅H₅'Bu)₂ [38 - 40] and Co(C₅H₅'Bu)₂ [41, 42] have been included in systematic ¹H and ¹³C NMR spectroscopic investigations. Both complexes are easily oxidized to the corresponding cations [Fe(C₅H₅'Bu)₂]⁺ [43] and [Co(C₅H₅'Bu)₂]⁺ [40] which were also studied by NMR spectroscopy. The ¹H and ¹³C NMR data for the diamagnetic complexes Fe(C₅H₅'Bu)₂ and [Co(C₅H₅'Bu)₂]⁺ are summarized in Table 4.

Na[C₅H₅'Bu] was freshly prepared from tert-butyl cyclopentadiene, C₅H₅'Bu [44], and a threefold excess of NaH in boiling THF.

Preparation of the salts 1 - 3

Synthesis of [Fe(C₅H₅'Bu)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[C₅H₅'Bu] was kept under reflux (65°) for 24 h. The solvent was removed under reduced pressure and the residue extracted in a Soxhlet apparatus using 100 ml of hexane. Evaporation of the solvent hexane left an orange oil of Fe(C₅H₅'Bu)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(C₅H₅'Bu)₂ in 20 ml of THF was stirred overnight in the presence of 5 ml of conc. HNO₃. 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(C₅H₅'Bu)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[C₅H₅'Bu] 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(C₅H₅'Bu)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[C₅H₅'Bu] was heated 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]. The 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 V.5.1. 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(C₅H₅'Bu)₂]PF₆ (1): C₁₈H₁₈FePF₆, dark blue prism with dimensions 0.35 x 0.18 x 0.12 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 (= 2σ(I)), full-matrix least squares refinement against F² with 70 parameters converging at Rω/R2-values of 0.053/0.138, max./min. residual electron density 0.533/-0.916·10⁻⁶ e pm⁻³.
Crystal structure of [Co(C_5H_4Bu)_2]PF_6 (2): C_{18}H_{26}CoPF_6, orange prism of dimensions 0.25 × 0.20 × 0.16 mm; monoclinic space group C2/m with the lattice parameters \(a = 1175.1(7)\), \(b = 1017.07(7)\), \(c = 880.45(5)\) pm, \(\beta = 106.537(4)\)°, \(V = 1008.76(11) \times 10^6\) pm\(^3\), \(Z = 2\), \(\mu = 0.982\) mm\(^{-1}\); 2538 reflections collected in the range \(3° < 2\theta < 55°\), 1224 reflections independent, 1057 assigned to be observed \([I > 2\sigma(I)]\), full-matrix least squares refinement against \(F^2\) with 70 parameters converging at \(R1/wR2\)-values of 0.038/0.106; empirical absorption correction \((\psi\)-scans) yielding min./max. transmission factors of 0.4960/0.5431, max./min. residual electron density 0.4266/0.280 × 10\(^{-6}\) e pm\(^{-3}\).

Crystal structure of [Co(C_5H_4Bu)_2]CoCl_4 (3): [C_{18}H_{26}Co]_2CoCl_4, green plate with dimensions 0.35 × 0.18 × 0.08 mm; monoclinic space group P2_1/c with the lattice parameters \(a = 1528.5(4)\), \(b = 1565.0(7)\), \(c = 1725.3(4)\) pm, \(\beta = 110.568(7)\)°, \(V = 3864.2 \times 10^6\) pm\(^3\), \(Z = 4\), \(\mu = 1.572\) mm\(^{-1}\); 7813 reflections collected in the range \(3° < 2\theta < 50°\), 6438 reflections independent, 4444 assigned to be observed \([I > 2\sigma(I)]\), full-matrix least squares refinement against \(F^2\) with 388 parameters converging at \(R1/wR2\)-values of 0.051/0.134; empirical absorption correction \((\psi\)-scans) resulting in min./max. transmission factors of 0.5531/0.9143, max./min. residual electron density 0.46/0.02 × 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

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[36] D. Braga, L. Maini, M. Polito, F. Greppioni, Organometallics 18, 2577-2579 (1999); cf. D. Braga, F. Greppioni, Chem. Soc. Rev. 29, 229-238 (2000). (The data given in Table II were calculated (W. Milius) from the deposited X-ray crystallographic files which were obtained via the Internet at http://pubs.acs.org/OM990131D.)