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Protonation of Cp*Fe(η^5-C_6H_7) as a convenient procedure for the preparation of the valuable synthon [Cp*Fe(MeCN)$_3$]$^+$

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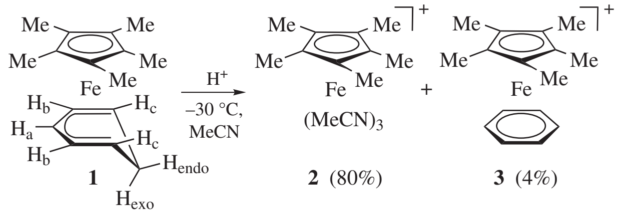
The (cyclohexadienyl)iron complex Cp*Fe(η^5-C_6H_7) obtained by a reaction of the cation [Cp*Fe(η^6-C_6H_6)]$^+$ with $LiAlH_4$ reacts with $HBF_4{\cdot}Et_2O$ or TfOH in MeCN to afford the acetonitrile cation [Cp*Fe(MeCN)$_3$]$^+$ in a high yield. The structure of complex Cp*Fe(η^5-C_6H_7) was determined by X-ray diffraction analysis.

The acetonitrile complex [Cp*Fe(MeCN)$_3$]$^+$ is a milestone in the organometallic chemistry of pentamethylcyclopentadienyl iron compounds. Its reactivity was thoroughly investigated for obtaining various novel complexes[1] and catalysis (*e.g.*, for the cycloaromatization of acyclic and alicyclic enediynes or alkyne [2+2+2] cycloaddition reactions).[2] The cation [Cp*Fe(MeCN)$_3$]$^+$ was previously obtained by the exhaustive photochemical decarbonylation of [Cp*Fe(CO)$_2$(MeCN)]$^+$ or [Cp*Fe(CO)$_3$]$^+$ using an immersion UV lamp.[1(*a*),3] On the other hand, Kuhn *et al.* found that the cyclohexadienyl complex $CpFeC_6H_7$ is protonated by $HBF_4{\cdot}OEt_2$ giving the very reactive diene tetrafluoroborate complex CpFe(η^4-C_6H_8)(FBF_3), which opens an access to a variety of half-sandwich complexes [$CpFeL_3$]$^+$ (L = SMe_2, $SeMe_2$, *etc.*).[4] However, examples of the reactivity of related Cp* derivatives are unknown. Here, we report a straightforward procedure for the preparation of the acetonitrile cation [Cp*Fe(MeCN)$_3$]$^+$ by protonation of the cyclohexadienyl complex Cp*Fe(η^5-C_6H_7) with different acids.

For the synthesis of the neutral cyclohexadienyl complex Cp*Fe(η^5-C_6H_7) **1**, we used a reaction of the cation [Cp*Fe(η^6-C_6H_6)]$^+$ **3** with $NaBH_4$, similar to the preparation of the parent compound CpFe(η^5-C_6H_7).[5] We found that the treatment of complex **1** with either TfOH or $HBF_4{\cdot}Et_2O$ in MeCN leads to the tris(acetonitrile) derivative [Cp*Fe(MeCN)$_3$]$^+$ **2** in a high yield (Scheme 1).[†] In both cases, the complex is formed reproducibly in a yield of 80–85%. Unfortunately, the product is contaminated with benzene cation **3** owing to competitive oxidation.[6] Carrying out the reaction at a low temperature (–30 °C) minimizes the formation of **3** to 4% (according to ^{1}H NMR data). Note that a further decrease in the temperature (using solvent mixtures) also slows down the formation of the target product. Fortunately, the undesirable admixture is easily removed by reprecipitation.



Scheme 1

The reaction of $HCl{\cdot}Et_2O$ with Cp*Fe(η^5-C_6H_7) led only to the benzene complex [Cp*Fe(η^6-C_6H_6)]Cl. Recently, we described a similar reaction for (cyclohexadienyl)ferracarborane analogues (η-9-L-7,8-$C_2B_9H_{10}$)Fe(η-C_6H_7) (L = SMe_2, NMe_3).[7]

The structure of complex **1** was determined by X-ray diffraction analysis (Figure 1).[‡] In spite of the accurate reflection data, the disorder of the cyclohexadienyl ligand in **1** precludes a detailed comparison of the molecular geometry with that of relative compounds. Nevertheless, the bond lengths and angles are comparable with those of the previously reported structures. For example, the mean bond lengths Fe–C(Cp*) of 2.057(2) Å and Fe–C(C_6H_7) 2.060(7) Å are identical to those of the known sandwich cyclohexadienyl complexes, *e.g.*, 2.059(3) and 2.06(3) Å for CpFe(η^5-$C_6H_3Me_3C_6H_5$).[8] Two η^5-coordinated ligands are almost parallel with a dihedral angle of only 1.43(9)°. The methylene carbon atom C(11A) lies out of the C_5 plane of the cyclohexadienyl ligand by 0.649(7) Å, and the tilt angle between the C_5 and C_3 planes [C(12A)–C(11A)–C(16A)] is 43.7(3)°.

We conclude that the protonation of Cp*Fe(η^5-C_6H_7) by strong acids can be used as a simple procedure to prepare the valuable synthon [Cp*Fe(MeCN)$_3$]$^+$, which does not require the use of expensive immersion equipment for UV irradiation.

[†] All reactions were carried out in an argon atmosphere.

*Synthesis of Cp*Fe(η^5-C_6H_7)* **1**. THF (15 ml) was added to the mixture of benzene complex **3** (0.66 g, 1.6 mmol)[9] and $NaBH_4$ (0.3 g, 8.0 mmol). The yellowish-orange mixture was stirred overnight. Water (1.5 ml) was added and the mixture was stirred for 20 min. Hexane (30 ml) was added to the mixture; the precipitated solid was filtered off, and the filtrate was evaporated under a reduced pressure. The residue was dissolved in 10 ml of Et_2O; the solution was filtered and evaporated to dryness giving an orange solid. Yield 0.318 g (74%). The product should be stored in an argon atmosphere. ^{1}H NMR ($CDCl_3$) δ: 5.39 (br. t, 1H, H_a, $J_{H_aH_b}$ 4.8 Hz), 3.73 (br. t, 2H, H_b, $J_{H_bH_c}$ 5.4 Hz), 2.41 (dt, 1H, H_{exo}, $J_{H_{exo}H_{endo}}$ 12.3 Hz, $J_{H_{exo}H_c}$ 6.3 Hz), 1.86 (s, 15H, C_5Me_5), 1.53 (br. d, 1H, H_{endo}, $J_{H_{endo}H_{exo}}$ 12.3 Hz) overlapping with 1.48 (br. t, 2H, H_c, $J_{H_cH_b}$ 5.4 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ: 83.97, 83.75, 81.46, 25.87, 25.27, 10.20. Found (%): C, 70.98; H, 8.16. Calc. for $C_{16}H_{22}Fe$ (%): C, 71.12; H, 8.21.

*Synthesis of [Cp*Fe(MeCN)$_3$](OTf)* **2**·OTf. Complex **1** (270 mg, 1.0 mmol) was suspended in 5 ml of MeCN and chilled to –30 °C. Triflic acid solution in Et_2O (1.4 ml, 1.13 M) was added through the septum cap. The mixture quickly turns into a clear purple solution. The stirring was continued for 30 min at –30 °C, and the product was precipitated with 40 ml of Et_2O chilled to –30 °C to give a purple precipitate. The crude product was repeatedly reprecipitated with Et_2O from MeCN to remove impurity compound **3**.The precipitate was filtered off, washed with 10 ml of Et_2O and dried *in vacuo*. Yield, 80–85%. ^{1}H NMR (CD_3CN) δ: 1.93 (s, 9H, MeCN), 1.48 (s, 15H, C_5Me_5). ^{1}H NMR (acetone-d_6) δ: 2.40 (s, 9H, MeCN), 1.65 (s, 15H, C_5Me_5). *Cf.* ref. 1.

Complex **2**·BF_4 was prepared similarly to **2**·OTf from compound **1** (270 mg, 1.0 mmol) and $HBF_4{\cdot}Et_2O$ (0.22 ml, 1.5 mmol). Purple powder. Yield, 80–85%.

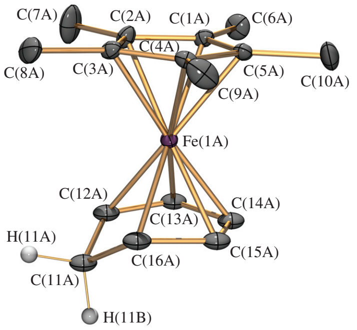


Figure 1 Molecular structure of compound **1** (independent molecule A). Ellipsoids are shown at a 50% probability level. Hydrogen atoms [except for the methylene carbon C(11A)] and a second part of the disordered cyclohexadienyl ligand are omitted for clarity. Selected bond lengths (Å) and angles (°): Fe(1A)–C(1A) 2.077(3), Fe(1A)–C(2A) 2.059(3), Fe(1A)–C(3A) 2.048(3), Fe(1A)–C(4A) 2.044(2), Fe(1A)–C(5A) 2.058(2), Fe(1A)–C(12A) 2.095(5), Fe(1A)–C(13A) 2.032(7), Fe(1A)–C(14A) 2.015(6), Fe(1A)–C(15A) 2.034(7), Fe(1A)–C(16A) 2.127(4), Fe(1A)···centroid(Cp) 1.661(1), Fe(1A)···centroid[C(12A) to C(16A)] 1.543(2); ∠(Cp/η^5-C_6H_7) 1.43(9).

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[‡] Crystals were grown by the slow evaporation of a hexane solution of **1**.

Crystal data for **1**: $C_{16}H_{22}Fe$, triclinic, space group $P\bar{1}$, $a = 8.5507(4)$, $b = 11.9706(6)$ and $c = 13.9200(7)$ Å, $\alpha = 105.492(1)°$, $\beta = 94.310(1)°$, $\gamma = 93.586(1)°$, $V = 1364.09(12)$ Å^3, $Z = 4$, $d_{calc} = 1.316$ g cm^{-3}, $\mu = 1.081$ mm^{-1}, orange/plate, crystal size 0.31 × 0.26 × 0.14 mm, $F(000) = 576$, T_{min}/T_{max} 0.7304/0.8633, $R_1 = 0.0385$ [from 4779 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.1056$ (from all 5363 unique reflections), GOF = 0.991, $\Delta\rho_{min}/\Delta\rho_{max} = 1.239/–0.609$. X-ray diffraction analysis was carried out on a Bruker SMART APEX2 diffractometer equipped with a CCD area detector at 100 K, using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). An absorption correction was applied semiempirically using the APEX2 program. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in an anisotropic approximation for non-hydrogen atoms. The cyclohexadienyl ligand in complex **1** was disordered over two positions with equal occupancies for both independent molecules. All hydrogen atom positions were refined in an isotropic approximation in a 'riding' model with the U_{iso}(H) parameters of $1.2\,U_{eq}(C_i)$, for methyl groups equal to $1.5\,U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. All calculations were performed using the SHELXTL software.

CCDC 985004 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2014.