Deprotonation of the complexes $[Ru(arene)Cp]^+PF_6^-$ (arene = C_6Me_6 and fluorene): X-ray crystal structure of $[Ru(\eta^5\text{-}C_6Me_5CH_2)Cp]$ and determination of the pK_a values using the iron analogues ☆

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Abstract

The ruthenium complexes $[RuCp(C_6Me_6)]^+$ (**2**) and $[RuCp(fluorene)]^+$ (**6**) (PF_6^- salts throughout this communication) have been deprotonated to **4** and **7** respectively. The X-ray crystal structure of **4** shows an angle of 34.4 (9)° between the cyclohexadienyl plane and the plane defined by C(11), C(12) and C(16). The pK_a values of **2** and **6** were determined by the direct method using the analogous iron complexes and indicate promising proton-reservoir properties.

Keywords: Iron; Ruthenium; X-ray structure; Deprotonation

Although iron and ruthenium organometallic complexes often have closely related chemical properties [1], their electrochemical and electron-transfer properties are very different owing to the higher energy level of the metal orbitals in the second row [2]. Recently, we have determined the pK_a of the yellow complex $[FeCp(C_6Me_6)]^+PF_6^-$ (**1**) and the benzylic C–H bond energy using reversible redox potential values [3]. In the analogous ruthenium complex, however, the redox processes occur at very different potentials and are irreversible owing to localization of the lowest unoccupied molecular orbital (LUMO) on the arene ligand [4]. Thus, the search for benzylic C–H bond dissociation energies using thermodynamic diagrams is hazardous for the $[RuCp(arene)]^+$ complexes. We have studied the deprotonation of $[RuCpCC_6Me_6)]^+PF_6^-$ (**2**) [5] in order to determine the acidity of this complex and to compare it with that of **1**. Given the outstanding proton reservoir

properties of $[FeCp(arene)]^+$ complexes [6], we are interested in the investigation of the possibilities of the ruthenium analogues given the reduced steric problem in the second-row complexes compared with first-row complexes [7]. pK_a values have been determined for arene complexes, in particular by Terrier and coworkers [8–11]. However, the direct method [11b], in which a known quantity of base of a strength similar to that of the compound under investigation is added to the solution containing this compound for spectroscopic observation of the resulting equilibrium, has not been used in this area before our studies [3].

The white complex **2**, synthesized by the Mann's [5] method [4a] was deprotonated by reaction with KH in tetrahydrofuran (THF) at 20°C overnight. Work-up and recrystallization at −40°C from pentane yielded 60% of canary-yellow crystals of $[RuCp(C_6Me_5CH_2)]$, (**4**) which was identified by ^1H and ^{13}C NMR [12a] and by its X-ray crystal structure [12b]. The X-ray crystal structures of **3** [14a] and **4** (Fig. 1 and Table 1) are quite similar on the molecular level, although their packing shows pronounced differences which will be discussed in a forthcoming paper. The dihedral angle between the

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☆ Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.
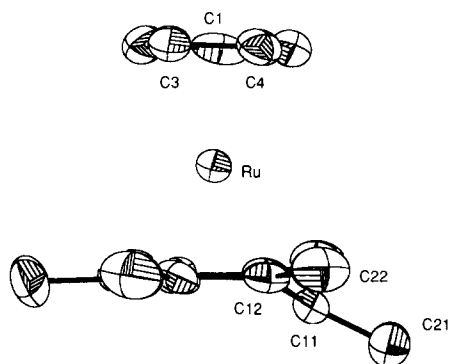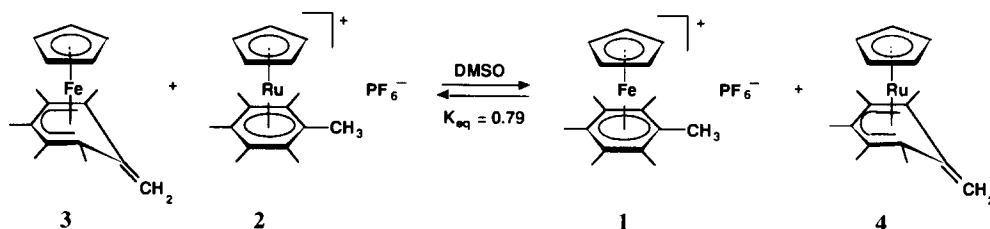* Corresponding author.

Fig. 1. ORTEP diagram of $[RuCp(C_6Me_5CH_2)]$ (4) (30% probability). Selected distances: C(11)–C(21), 1.36 (1) Å; Ru–Cp (centroid); 1.8328 (7) Å; Ru plane defined by C(12)–C(16); 1.6960 (7) Å.

cyclohexadienyl plane and the plane defined by C(11), C(12) and C(16) is 34.4 (9)° for the Ru complex 4 and 32.6° for the Fe analogue 3 [14a]; the difference is thus not significant. These values are lower than in cyclohexadienyl complexes which do not bear an exocyclic double bond (39–50°) [15a] but larger than in 8 (11°) [15b].

The ^1H NMR signals of 4 were sufficiently separated from those of the deep-red complex 3, however, to allow titration. Thus the pK_a value of 2 was determined by ^1H NMR spectroscopy in dimethylsulphoxide (DMSO)-d_6 at 250 MHz by mixing either equimolar amounts of 1 and 4 or of 2 and 3. The results were the same in both cases ($K_{eq} = 0.79$):
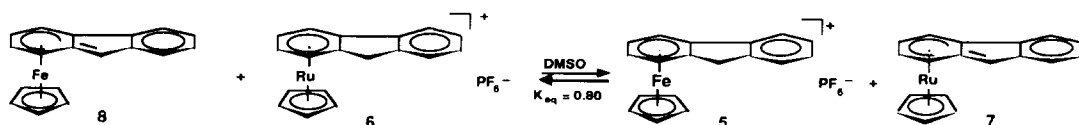
Table 1

Crystallographic data, data collection parameters and refinement parameters

Formula	$C_{17}H_{22}Ru$
Formula weight	327.43
Space group	$P2_1/c$ (No. 14)
a (Å)	8.327(1)
b (Å)	23.481(3)
c (Å)	8.284(1)
β (°)	117.588(9)
V (Å^3)	1436(1)
Z	4
d(calc) (g cm^{-3})	1.515
μ (cm^{-1})	10.52
Temperature (°C)	−15
Radiation; λ (Å)	Mo Kα; 0.7107
Crystal dimensions (mm^3)	0.15×0.30×0.45
Measured reflections	3753
Scan range	$3° \leqslant \theta \leqslant 28°$
Scan type	ω
Absorption correction	Numerical
Maximum transmission; minimum transmission	0.8601; 0.7161
Secondary extinction coefficient E	Not refined
Number of observed independent reflections	2048 $(I > 1\sigma(I))$
Number of parameters refined	163
R ^{a}; R_w ^{b}	0.069; 0.065
Goodness of fit	1.401
Residual electron density (electrons Å^{-3})	1.23 (1.02 Å from Ru)

^{a} $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$.
^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w^{-1} = \sigma^2(F_o)$.

(1)

The pK_a value is given by

$$pK_a(2) = pK_a(1) + pK_{eq} = 29.2 + 0.1 = 29.3 \qquad (2)$$

Thus the ruthenium complex 2 is very slightly less acidic than its iron homologue 1, owing to the larger electron density on the ruthenium atom than on iron.

The pK_a of the fluorene complex [FeCp(fluorene)]$^+$-PF$_6^-$ (5) was known [11] as that of 1 [3]. Thus we have

synthesized the white analogue [(RuCp(fluorene)]$^+$PF$_6^-$ (6) and the deprotonated complexes of iron and ruthenium (the deep-red complex 7 and the deep-blue complex 8 respectively) by reactions of ^{t}BuOK with the cations in THF according to the method of Johnson and Treichel [15b]. The determination of the pK_a of the ruthenium complex 6 was effected similarly by ^1H NMR in DMSO-d_6 by mixing equimolar amounts of 6 and 8 or of 5 and 7 which gave the same results:

(3)

Table 2

pK_a values of [MCp(arene)]$^+$ complexes and of the free arene ligands in DMSO at 20°C

pK_a	C_6Me_6	Fluorene
FeCp(arene)$^+$	29.2 [3]	14.6 [11]
RuCp(arene)$^+$	29.3	14.7
Free arene ligand	43 ($C_6H_5CH_3$ [16,17])	22.6 [18]

with

$$pK_a(6) = pK_a(5) + pK_{eq} = 14.6 + 0.1 = 14.7 \qquad (4)$$

One can see that the pK_a of the C_6Me_6 complexes **1** and **2** are 14 units lower than that of C_6Me_6 and that the pK_a of **5** and **6** are (only) 8 units lower than that of fluorene, owing to extensive electronic delocalization in these complexes (Table 2).

In conclusion, the [RuCp(arene)]$^+$ complexes are about as acidic as their iron analogues. This property is promising in terms of the starburst proton-reservoir chemistry given the larger space available around the arene ligands bound to Ru compared with Fe. Indeed, preliminary synthetic results indicate that **2** reacts with a mixture of base and of halide ($CH_3I, CH_2 = CHCH_2Br$) to give cleanly hexasubstituted complexes in one-pot reactions.

Acknowledgment

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[12] (a) 4: ^{1}H NMR (250 MHz): δ 4.17 (s, 5H, Cp); 3.73 (s, 2H, CH_2); 2.13 (s, 3H, p. CH_3); 1.91 and 1.89 (2s, 2×3H, o- and m-CH$_3$) ppm. ^{13}C NMR (62.38 MHz): δ 151 (C=CH$_2$); 92.5 (m-C-CH$_3$); 88.0 (p-C-CH$_3$); 78.7 (CH$_2$); 78.3 (Cp); 59.3 (o-C-CH$_3$); 21.2 and 18.5 (o- and m-CH$_3$); 17.6 (p-CH$_3$) ppm. (b) Structure determination of [RuCp($C_6Me_5CH_2$)]: geometry and intensity data were collected on an ENRAF–Nonius CAD4 diffractometer equipped with graphite monochromators. The structure was solved by conventional heavy-atom methods and subsequent Fourier difference synthesis. All non-hydrogen atoms were refined [13] anisotropically. All hydrogen atoms were treated as riding atoms with idealized geometry (d(C–H) = 0.98 Å; B(H) = 1.3B_{iso}(C)). A statistical weighting scheme $w^{-1} = \sigma^2(F_0)$ was used for all reflections. Crystal data, data collection parameters and convergence results are compiled in Table 1. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen.

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