

Short Communications

Barriers to Rotation of the Acetyl Groups in Acetyl ruthenocene and 1,1'-Diacetyl ruthenocene. A ^1H and ^{13}C NMR Study

J. SANDSTRÖM* and J. SEITA

Division of Organic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

In a previous study¹ we measured the barriers to acyl group rotation in a number of acylferrocenes, including acetylferrocene and 1,1'-diacetylferrocene. It was observed that, due to the strong donor properties of the ferrocenyl group, the barrier to rotation of the formyl group is higher in ferrocenylaldehyde than in benzaldehyde. The barrier raising effect of the ferrocenyl group was, however, lower than expected on basis of its Hammett σ^+ constant evaluated from protonation of acetylferrocene.² The barriers in acetylferrocene (35.6 kJ/mol) and in 1,1'-diacetylferrocene (32.6 kJ/mol) show a difference significantly larger than the experimental error. The lower barrier in 1,1'-diacetylferrocene was interpreted as due to a transannular effect.

The donor capacity of metallocenyl groups is manifested in ease of solvolysis of α -metallocenylcarbinyl acetates, which increases in the order ferrocenyl < ruthenocenyl < osmocenyl³ and is related to the stabilities of the intermediate metallocenyl carbonium ions. Turbitt and Watts⁴ have measured the optical stability of methylferrocenyl carbonium ion and its ruthenium analog and found barriers to racemization (rotation around the exocyclic bond) of 86.2 and >130 kJ/mol. These large stabilizations, however, are not to be ascribed exclusively to the donor capacity of the substituted cyclopentadienyl ring. It is fairly generally agreed that part of the stabilization stems from a direct interaction between metal orbitals and the carbonium ion center.⁴⁻⁶ The better stabilization of the ruthenocenyl carbonium ion is ascribed to better overlap between the carbonium ion center and the more extended ruthenium 4d orbitals.⁴

* Author to whom correspondence should be addressed.

Other evidence points to a reversed order of donor effect, *i.e.* osmocenyl < ruthenocenyl < ferrocenyl. Such evidence is found in the carbonyl stretching frequency of metallocenylketones,⁷ in the acidity of metallocenylcarboxylic acids,⁷ in the rate of Friedel-Crafts acylation,⁷ and possibly also in the basicity of metallocenyl ketones.²

This study was undertaken with two aims, to decide if the effect of the metal atom on the rotational barriers in acylmetallocenes followed the first or the second of the above sequences, and to decide if the transannular effect observed in the ferrocenes was present also in the ruthenocenes.

Experimental. Acetyl ruthenocene and 1,1'-diacetyl ruthenocene were prepared according to Ref. 7. The ^1H and ^{13}C NMR spectra were recorded as described in Ref. 1. The free energy

Table 1. ^1H NMR chemical shifts for acetyl-ruthenocenes in CHCl_2F at 30 °C.

Compound	δ (2,5) ^{a,b}	δ (3,4)	δ (C_5H_5)	δ (CH_3)
Acetyl-ruthenocene	5.079	4.756	4.575	2.251
1,1'-Diacetyl-ruthenocene	5.089	4.782		2.164

^a In ppm downfield from TMS. ^b Center of multiplet.

Table 2. Free energy barriers from coalescence data.

Compound	$\Delta\nu_0/\text{Hz}^a$	T_c/K	$\Delta G^\ddagger (T_c)/\text{kJ mol}^{-1b}$
^1H Acetyl-ruthenocene	6.2 ^c	152	33.1 ± 0.8 (7.9 ± 0.2)
^{13}C Acetyl-ruthenocene	64	173	34.4 ± 1.2 (8.2 ± 0.3)
^1H 1,1'-Diacetyl-ruthenocene	5.3 ^c	148	32.3 ± 0.8 (7.7 ± 0.2)
^{13}C 1,1'-Diacetyl-ruthenocene	62	171	34.1 ± 1.2 (8.1 ± 0.3)

^a $|\nu_2 - \nu_1|$. ^b In kcal mol⁻¹ in parentheses. ^c Measured between centers of multiplets.

Table 3. ^{13}C NMR chemical shifts for acetylruthenocenes in CHCl_2F with 20 % (v/v) of $(\text{CD}_3)_2\text{CO}$ at 30°C .

Compound	δ (1) ^a	δ (2,5)	δ (3,4)	δ (C ₆)	δ (CO)	δ (CH ₃)
Acetylruthenocene	84.9	71.4	74.0	72.5	200.5	26.8
1,1'-Diacetylruthenocene	86.5	73.1	75.6	—	199.1	26.9

^a In ppm downfield from TMS.

barriers were obtained at the coalescence temperature only, using the expression (1), which is derived from the expression for the rate of exchange at the temperature of coalescence of a symmetrical doublet⁸ in conjunction with the $\Delta G^\ddagger_{1c} = 0.01913 T_c(9.972 + \log T_c - \log \Delta\nu_0)$ (1) Eyring equation.⁹ It was shown in Ref. 1, by comparison with data from complete bandshape analyses, that this approximation gives sufficiently precise free energy barriers, the temperature measurement still being the main source of error.

Results and discussion. The barriers obtained from ^1H spectra and those from ^{13}C spectra are found in Table 2. The deviations between these sets are somewhat larger than normally found but still within the experimental error. The main source of uncertainty is the temperature measurement, which is much more accurate for ^1H than for ^{13}C spectra, and consequently the data from the ^1H spectra are more reliable.

The barrier in acetylruthenocene is thus somewhat lower than that in acetylferrocene, though the region of uncertainty for the ^{13}C barrier of acetylruthenocene shows some overlap with the region for acetylferrocene. The donor effect on the barrier to acyl rotation follows the order ruthenocenyl < ferrocenyl. Furthermore, the barrier difference between acetylruthenocene and 1,1'-diacetylruthenocene is of the same order as the experimental error, *i.e.* no interannular effect has been demonstrated in ruthenocene as opposed to ferrocene.

It has been pointed out² that the donor order osmocenyl < ruthenocenyl < ferrocenyl follows the order of Pauling electronegativity of the metal atoms, Os (2.2), Ru (2.2), Fe (1.8),¹⁰ *i.e.* an order of decreasing electron withdrawal from the cyclopentadienyl rings. This rationalization is in good agreement with the ^1H (Table 1) and ^{13}C chemical shifts (Table 3). In both cases the ruthenocene resonances appear downfield with respect to the analogous signals in the acetylferrocene and 1,1'-diacetylferrocene spectra. The ^1H resonances of the ring protons in acetylruthenocene appear 0.3–0.4 ppm downfield from those in acetylferrocene, and for the ring carbons the corresponding differences vary from 4.8 ppm for C-1 to 1.2 ppm for C-3, C-4. On the other hand, the ^1H and ^{13}C resonances

of the methyl group and the ^{13}C resonance of the carbonyl carbon appear at higher field in acetylruthenocene. This points to a weaker interaction between the acetyl group and the metallocene ring in this molecule than in the ferrocene analogue, in agreement with the observed barriers.

The weaker transannular interaction in 1,1'-diacetylruthenocene is probably related to the inter-ring distances, 3.25 Å in ferrocene¹¹ and 3.68 Å in ruthenocene¹² or to different electronic transmission properties of the iron and ruthenium atoms.

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