Protonated 'Open' and 'Half-open' Ruthenocenes exhibiting Agostic Interactions with C–H Bond Rupture involved in the Most Facile Dynamic Process

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The cations $[Ru(\eta^5\text{-}C_7H_{11})_2H]^+$ (**1**), $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_7H_{11})H]^+$ (**2**), and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_7H_{11})H]^+$ (**3**) have provided quantitative evidence for the existence of a class of complexes in which rupture of the C–H component of a C–H–M agostic interaction is involved in the lowest energy fluxional processes.

Mononuclear organometallic complexes containing a C–H–M agostic interaction commonly exhibit fluxional behaviour.[1] For many complexes, two separate fluxional processes give rise to distinct degenerate equilibria, and these processes have previously been described as involving rupture of either the M–H or the C–H component of the agostic interaction.[2] When first-row transition elements are involved,[2—7] available data indicate that the lowest energy fluxional processes almost always involve M–H bond rupture.† When second- or third-row transition elements are involved, however, there are not yet sufficient data available to generalise.[8,9]

The results of a variable temperature (145—300 K) ^1H and ^{13}C n.m.r. study of three protonated 'open' or 'half-open' ruthenocenes are now outlined. We have shown that these cations all contain an agostic interaction, and that C–H bond rupture is consistently involved in the lowest energy fluxional processes. Hence, we use an [M–H · · C] notation in Figure 1. The new salts $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_7H_{11})H][BF_4]$ (**2**) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_7H_{11})H][BF_4]$ (**3**) were synthesised from the previously reported $[Ru(\eta^5\text{-}C_7H_{11})_2H][BF_4]$ (**1**) by treatment with 1 mol. equiv. of cyclopentadiene or pentamethylcyclopentadiene, respectively.[10]

For (**1**), all fluxional processes are stopped at 145 K on the 360 MHz ^1H and 90 MHz ^{13}C n.m.r. time-scales. An agostic Ru–H–C interaction involving a terminal carbon atom of one of the ligands can now unequivocally be assigned [^1J(CH agostic) 80 Hz].‡ Three fluxional processes were subsequently distinguished and are shown in Figure 1. The 1,1′-interligand H transfer (**A**) and the 1,5-intraligand H transfer (**B**) were distinguished since only the former renders the central CH

$$[Ru(\eta^5\text{-}C_7H_{11})_2H]^+$$
(**1**)

$$[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_7H_{11})H]^+$$
(**2**)

$$[Ru(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_7H_{11})H]^+$$
(**3**)

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† Some quantitative examples [complex, $\Delta G^\ddagger$ (kJ mol^{-1}) for M–H bond rupture process, $\Delta G^\ddagger$(kJ mol^{-1}) for C–H bond rupture process]: $Mn(\eta^3\text{-}C_6H_9)(CO)_3$, 34.7, 64.4;[2] $Cr(\eta^4\text{-}C_7H_{12})(CO)_2[P(OMe)_3]$, 28.6, 68.1;[3] $\{Mn(\eta^4\text{-}C_5H_8)[(Me_2PCH_2)_3CMe]\}^+$, 39.7, 69.0;[4] $[Co(\eta^5\text{-}C_5Me_5)(Et)L]^+$ for L = $P(OMe)_3$, 38.5, 56.0 and for L = PMe_2Ph, 40, >60;[5] $[Fe(\eta^3\text{-alkenyl})L_3]^+$ (numerous examples), <46, unobserved.[6] The facile 1,1′-H transfers observed in $[Co(\eta^5\text{-}C_5Me_4R)(C_2H_4)_2H]^+$ (R = Me or Et) constitute the only reported exceptions to date.[7]

‡ *Spectroscopic data* for (**1**): ^1H n.m.r. ($CHFCl_2/CD_2Cl_2$, 145 K), δ 6.06 (1H, CH), 5.02 (1H, CH), 4.39 (1H, *exo*-CH_2), 3.10 (1H, *exo*-CH_2), 3.02 (1H, *exo*-CH_2), 2.37 (1H, *endo*-CH_2), 2.23 (1H, *exo*-CH_2), 2.15—1.90 (12H, 4Me), 1.36 (1H, *endo*-CH_2), 1.07 (1H, *endo*-CH_2), −0.13 (1H, *endo*-CH_2), −5.80 (1H, RuH); ^{13}C n.m.r. ($CHFCl_2/CD_2Cl_2$, 145 K), δ 113.6 (s), 113.1 (s), 111.8 (s), *ca.* 103 (d), 95.6 (s), 90.5 (d, *J* 170 Hz), 61.9, 60.4, and 53.4 (3t, *J* 160 Hz), 25.6, 25.3, 24.2, and 23.9 (4q, *J* 130 Hz), 8.2 (td, *J* 145 and 80 Hz).

For (**2**): ^1H n.m.r. (CD_2Cl_2, 200 K), δ 6.52 (s, 1H, CH), 5.26 (s, 5H, C_5H_5), 3.02 (dd, 2H, ^2J 3.5 and 7.0 Hz, *exo*-CH_2), 2.16 (s, 6H, Me), −0.31 (dd, 2H, ^2J 3.5 and 8.0 Hz, *endo*-CH_2), −10.13 (tt, 1H, RuH); ^{13}C n.m.r. (CD_2Cl_2, 200 K), δ 100.7 (s), 97.8 (d, *J* 166 Hz), 82.4 (d, *J* 183 Hz), 30.3 (td, *J* 156 and 36 Hz), 26.3 (q, *J* 129 Hz).

For (**3**): ^1H n.m.r. (CD_2Cl_2, 200 K), δ 5.99 (s, 1H, CH), 2.51 (dd, 2H, ^2J 5.0 and 7.0 Hz, *exo*-CH_2), 2.06 (s, 6H, Me), 1.82 (s, 15H, C_5Me_5), −0.18 (dd, 2H, ^2J 5.0 and 8.0 Hz, *endo*-CH_2), −9.82 (tt, 1H, RuH); ^{13}C n.m.r. (CD_2Cl_2, 200 K) δ 99.4 (s), 98.0 (d, *J* 163 Hz), 95.4 (s), 31.8 (td, *J* 154 and 39 Hz), 24.2 (q, *J* 129 Hz), 9.1 (q, *J* 129 Hz).

For (**2**) and (**3**), the 1,5-H transfer process is in the fast exchange domain at 200 K. The observed *J* (^{13}C–H) values of 36 and 39 Hz, respectively, are therefore time-averaged values of zero coupling and the static agostic coupling constant.

Table 1. Calculated activation energies, $\Delta G^{\ddagger}$ in kJ mol^{-1}, for the fluxional processes observed in (**1**), (**2**), and (**3**).[a]

Fluxional process	(1)	(2)	(3)
1,1′-Interligand H transfer	30.4[b]	—	—
1,5-Intraligand H transfer	38.8[c]	<30	<30
endo-Methyl rotation	46.6[d]	52.7[d]	47.2[d]

[a] Estimated errors are $< \pm 1$ kJ mol^{-1} for the H transfers and $< \pm 0.4$ kJ mol^{-1} for the *endo*-methyl rotations. [b] At 165 K. [c] At 187 K. [d] At 298 K.

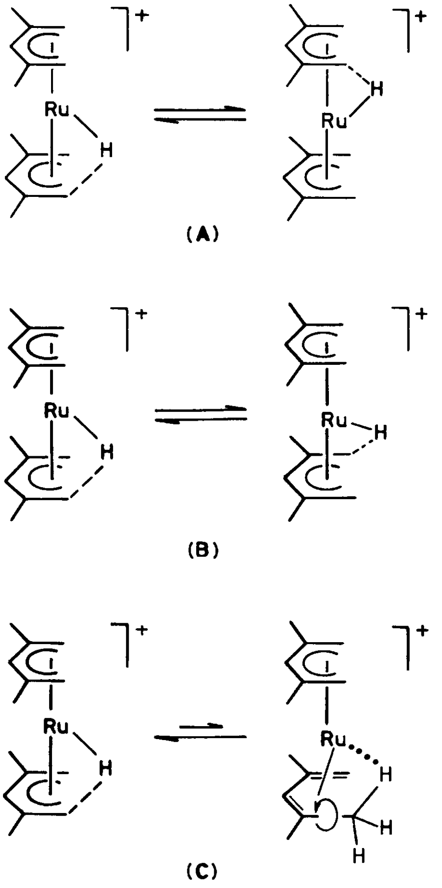

Figure 1. The three distinct fluxional processes observed for (**1**): (**A**) 1,1′-interligand H transfer; (**B**) 1,5-intraligand H transfer; (**C**) *endo*-methyl rotation.

groups equivalent. *endo*-Methyl rotation (**C**), contrary to our earlier report,[10] has no effect on the δ value of the resonance(s) due to the carbon atoms at the termini of the organic ligands. The δ value of this resonance at 300 K (46.8 p.p.m.) corresponds well with the mean δ of the resonances observed at 145 K. An apparent upfield shift was originally noted only because the four signals coalesce pairwise owing to the two H transfer processes and, after the first coalescence, the high field component remains too broad to detect.

For (**2**) and (**3**), agostic structures similar to (**1**) are clearly indicated by the ^1J(CH agostic) coupling constants of 72 Hz for (**2**) and 78 Hz for (**3**), as derived from the ^{13}C n.m.r. spectra at 200 K.‡ Both 1,5-intraligand H transfer and *endo*-methyl rotation were observed as fluxional processes in (**2**) and (**3**), although for the former process completely limiting spectra were not obtained even at 145 K.

The $\Delta G^{\ddagger}$ values for all the fluxional processes in (**1**), (**2**), and (**3**) have been determined, either from a range of concording coalescence temperature measurements (H transfer processes), or from line-shape simulations (*endo*-methyl rotations).[11] The results are listed in Table 1 and are now discussed. First, the 1,5-intraligand H transfer in (**2**) and (**3**) is considerably more facile than in (**1**). A change in orientation of the methylene group that binds the agostic hydride is proposed so that the H jump between methylene groups is shorter in (**2**) and (**3**) than in (**1**).[12] It is presumably also responsible for the variation in δ(RuH): −10.1 (**2**); −9.8 (**3**); −5.8 (**1**). Second, cation (**2**) exhibits the largest $\Delta G^{\ddagger}$ for *endo*-methyl rotation and this correlates nicely with the lowest ^1J(CH agostic) coupling constant. A rationalisation is that the C_5H_5 ligand in (**2**) is less electron releasing than either the C_5Me_5 ligand in (**3**) or the (η^5-C_7H_{11}) ligand in (**1**). Consequently, electron deficiency is less tolerated by the Ru centre in (**2**) and the agostic hydride is kept under closer metal control. Third, the H transfer processes in (**1**), (**2**), and (**3**) all require C–H bond rupture and consistently occur with lower activation energies than the *endo*-methyl rotations which require M–H bond rupture. The ^1J(CH agostic) coupling constants of 72—80 Hz, however, are in the range typical for normal M–H–C agostic interactions.

The marked change in dynamic behaviour relative to many first-row transition element complexes is in broad agreement with the general hypothesis that terminal hydride structures become relatively more stable in the sequence 3d < 4d < 5d.[1] Hence, we believe that many other examples may be found and have already identified similar dynamic behaviour in some related agostic complexes, *e.g.* $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)H]^+$.

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12 See scheme 9 of ref. 6 for a related proposal.