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Ligand Exchange in Ruthenocene

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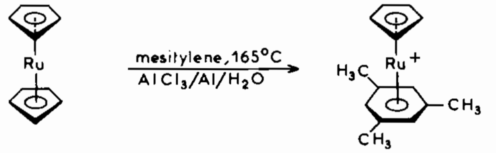
Ruthenocene chemistry [1] is scarce compared to that of ferrocene [1a] and no ligand exchange has been examined. We report here that one cyclopentadienyl ring of ruthenocene can be exchanged with a polymethylarene (*scheme*) – an extension of the analogous reactions found for ferrocene by Nesmeyanov *et al.* [2].



More drastic conditions are needed than for ligand exchange in ferrocene: the reaction is induced by $AlCl_3/H_2O$ at 160–200 °C. In contrast to ferrocene [2], ruthenocene does not give ring exchange at 80 °C with benzene. At 190–200 °C in decalin, or neat at 250 °C, the ligand exchange reaction with hexamethylbenzene proceeds only with a 10% yield, whereas the yield of the ferrocene reaction reaches 60% [3]. This yield can be raised to 50% in the presence of water (Table I), a trend already examined with ferrocene [4–6]. The stoichiometry is now $Cp_2Ru/AlCl_3/Al/H_2O$/arene: 1/3/1/1/excess (decalin 190–200 °C, 8 hours). However, the ^1H and ^{13}C NMR spectra of the salts resulting from this reaction show a mixture of several salts η^5-C_5H_5Ru η^6-C_6H_{6-n}-$(CH_3)_n^+$ resulting from extensive demethylation and disproportionation of hexamethylbenzene under the influence of $AlCl_3/H_2O$ prior to complexation. With a ratio $C_6(CH_3)_6/H_2O$: 4/1, the signals of the arene ligand close to $\delta = 5$ ppm/TMS in the ^1H NMR spectrum show that on average 1/4 of the methyl groups have been replaced by hydrogens on the benzene ligand. No product is predominant, but a statistical distribution is observed showing that a thermodynamic equilibrium is attained more quickly than complexation – an illustration of the difficulty of cleaving a ruthenocene ring. Precedents for this problem are known [7, 8] and are part of the reason why the metal vapor technique is often a necessary tool to synthesize clean homoleptic complexes such as bis(arene)chromium [8]. In the absence of water, the reaction (*vide supra*) provides the desired salts in a purity of ≃ 80%, the medium is still able to give protons from the hydrocarbon solvent [5] under these conditions but of course to a much lesser extent. After metathesis, η^5-C_5H_5Ru η^6-$C_6(CH_3)_6^+$-PF_6^- can be obtained in a pure form after two recrystallisations from acetone. Calcd for $C_{17}H_{23}RuPF_6$: C, 43.10; H, 4.86. Found: C, 43.48; H, 4.88. M.Pt. (dec) 250 °C. I.R., cm^{-1} (hexachlorobutadiene) 3140 (m), 2945 (w), 1550 (s), 1475 (m), 1430 (m), 1400 (s), 1320 (w), 1120 (w), 1060 (m).

TABLE I. Reaction Conditions.

Ligand Exchange	$Cp_2M/AlCl_3/H_2O$	Reaction Time and Temp.	Yield %	Reference
Ferrocene/benzene	1/2/0	80 °C	80	2
Ruthenocene/benzene	1/2/0	80 °C	0	This work
Ferrocene/benzene	1/3/1	80 °C	90	4
Ruthenocene/benzene	1/3/1	80 °C	0	This work
Ferrocene/mesitylene	1/2/0	165 °C	40 (resp. 65)	2 (resp. 5)
Ruthenocene/mesitylene	1/2/0	165 °C	5	This work
Ferrocene/mesitylene	1/3/1	165 °C	90	This work
Ruthenocene/mesitylene	1/3/1	165 °C	30	This work
Ferrocene/HMB[a]	1/2/0	190 °C	60	3
Ruthenocene/HMB	1/2/0	190 °C	10	This work
Ferrocene/HMB	1/3/1	190 °C	95	This work
Ruthenocene/HMB	1/3/1	190 °C	50 (mixture[b])	This work

[a] HMB: hexamethylbenzene (reactions in decaline).

[b] Statistical mixture. Starting from H_2O/Cp_2Ru:1/4, the same ratio of replacement of methyl groups by hydrogens was found by ^1H NMR. In all other reactions quoted in the table, a pure compound was obtained.

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TABLE II. NMR Data $(CD_3COCD_3)^a$ δ (ppm)/TMS

	δ (^1H)			δ (^{13}C)		
	arene H	CH_3	C_5H_5	arene C	CH_3	C_5H_5
$[\eta^5\text{-}C_6H_5Fe\ \eta^6\text{-}C_6H_3(CH_3)_3]^+BF_4^-$	6.20	2.50	5.00	88.48	20.25	78.43
$[\eta^5\text{-}C_5H_5Ru\ \eta^6\text{-}C_6H_3(CH_3)_3]^+BF_4^-$	6.18	2.36	5.31	88.15	20.15	81.79
$[\eta^5\text{-}C_5H_5Fe\ \eta^6\text{-}C_6(CH_3)_6]^+BF_4^-$	–	2.54	4.69	91.0	18.65	80.17
$[\eta^5\text{-}C_5H_5Ru\ \eta^6\text{-}C_6(CH_3)_6]^+BF_4^-$	–	2.50	5.30	90.3	19.3	82.4

[a] For ^1H NMR data of Fe sandwiches, see also ref. 3.

With mesitylene, the ligand exchange proceeds only with 5% yield under anhydrous conditions (165 °C, 8 hours), but the yield reaches 30% upon addition of water. Interestingly, the salt is now obtained pure even when water is added to the reaction mixture. Calcd for $C_{14}H_{17}RuPF_6$: C, 39.00; H, 3.94. Found: C, 39.44; H, 4.43. I.R., cm^{-1} (hexachlorobutadiene) 3140 (m), 2950 (w), 1550 (s), 1475 (m), 1430 (m), 1400 (s), 1315 (w), 1115 (w), 1055 (m). M.Pt.: 195 °C.

The sandwich structures and the purities of these complexes are deduced from the singlet nature of the Cp, arene and CH_3 signals in the ^1H and ^{13}C NMR spectra (Table II). The arene H and C have identical δ values for the Fe and Ru sandwiches. It is noteworthy that the Cp signals for the Ru complexes exhibit larger downfield shifts (by 0.3 to 0.6 ppm, ^1H and 2.2 to 3.4 ppm, ^{13}C) than their iron analogues; these parallel the data reported for the d^6 Cp_2M series [1a].

Other routes to $(\eta^5\text{-}C_5H_5Ru\eta^6\text{-arene})^+X^-$ complexes are known [9], but this ligand exchange reaction from ruthenocene is a valuable alternative whenever the reactions can be carried out at 160–170 °C.

Acknowledgments

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