C–C Bond Formation in Organoruthenium Complexes by Friedel–Crafts Reactions

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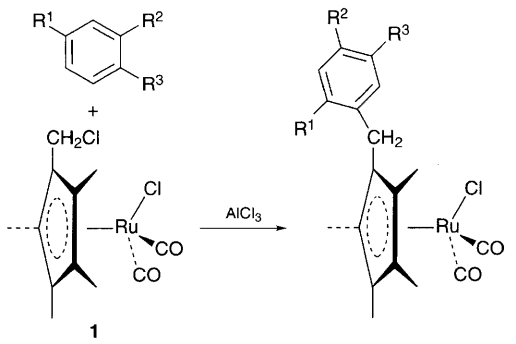
In the presence of $AlCl_3$ the complex $[(\eta^5\text{-}C_5Me_4CH_2Cl)Ru(CO)_2Cl]$ **1** readily acts as an electrophile towards aromatic hydrocarbons (ArH = C_6H_6, C_6H_5Me, $C_6H_4Me_2$) giving $[(\eta^5\text{-}C_5Me_4CH_2Ar)Ru(CO)_2Cl]$; the structure of $[\{\eta^5\text{-}C_5Me_4CH_2(C_6H_3Me_2\text{-}2,4)\}Ru(CO)_2Cl]$ is determined by X-ray methods.

We have recently discussed the functionalisation of pentamethylcyclopentadienyl–ruthenium complexes by an oxygen induced C–H activation of $[\{(\eta^5\text{-}C_5Me_5)RuCl_2\}_2]$;[1] when that reaction is coupled to a carbonylation, the product is the chloromethyl complex $[(\eta^5\text{-}C_5Me_4CH_2Cl)Ru(CO)_2Cl]$, **1**. The carbon bearing the chlorine is very susceptible to nucleophilic substitution and a variety of amino- and oxy-substituted derivatives $[(\eta^5\text{-}C_5Me_4CH_2X)Ru(CO)_2Cl]$ (X = NR_2, OR, *etc.*) have been made, by reaction with amines and alcohols.[2]

We now report that carbon–carbon bonds can be formed by a type of Friedel–Crafts reaction,[3] using the ring CH_2 as an electrophile. Thus reaction of **1** with aluminium chloride (2.5 equiv.) in *m*-xylene as solvent at 10 °C gives the 2,4-dimethylphenyl derivative **5**, in 90% yield (Scheme 1). Elemental analysis showed that the xylyl group had been incorporated, replacing Cl bonded to C. The IR [ν(CO) 1980, 2033 cm^{-1}] and the ^1H NMR [δ 1.81, 1.97 (2 × s, 2 × Me), 3.53 (s, ring CH_2)] spectra showed that the core $[(\eta^5\text{-}C_5Me_4CH_2X)Ru(CO)_2Cl]$ was unchanged; the presence of the xylyl methyls (δ 2.28, 2.31) and the substitution pattern of the aromatic region [δ 6.62 (d, 1 H, *J* 8 Hz), 6.91 (s, 1 H) and 7.01 (d, 1 H, *J* 8 Hz)] in the ^1H NMR spectrum showed the orientation of the attacking CH_2 to be *ortho* and *para* to the methyls.

Complex **1** underwent similar reactions with benzene giving the phenyl complex **2** (25% yield), with toluene to give the *p*-tolyl complex **3** (65%), with *o*-xylene, giving the 3,4-dimethylphenyl complex **4** (45%), and *p*-xylene giving the 2,5-dimethylphenyl complex **6** (85%).† In each case only a single isomer was formed, the orientation of which was consistent with attack on the aromatic by a large electrophile, that is, steric interactions favoured *p*- over *o*-substitution. The approximate relative reactivities, determined by competition experiments using a deficiency of the electrophile **1** at 20 °C in nitromethane solvent were: benzene, 1; toluene, 10; *o*-xylene, 50; *p*-xylene, 100; and *m*-xylene, 500. This agrees well with typical aromatic electrophilic attack, for example, mercuriation.[4]



1

2 $R^1 = R^2 = R^3 = H$
3 $R^1 = R^3 = H$, $R^2 = Me$
4 $R^2 = R^3 = Me$, $R^1 = H$
5 $R^1 = R^2 = Me$, $R^3 = H$
6 $R^1 = R^3 = Me$, $R^2 = H$

Scheme 1

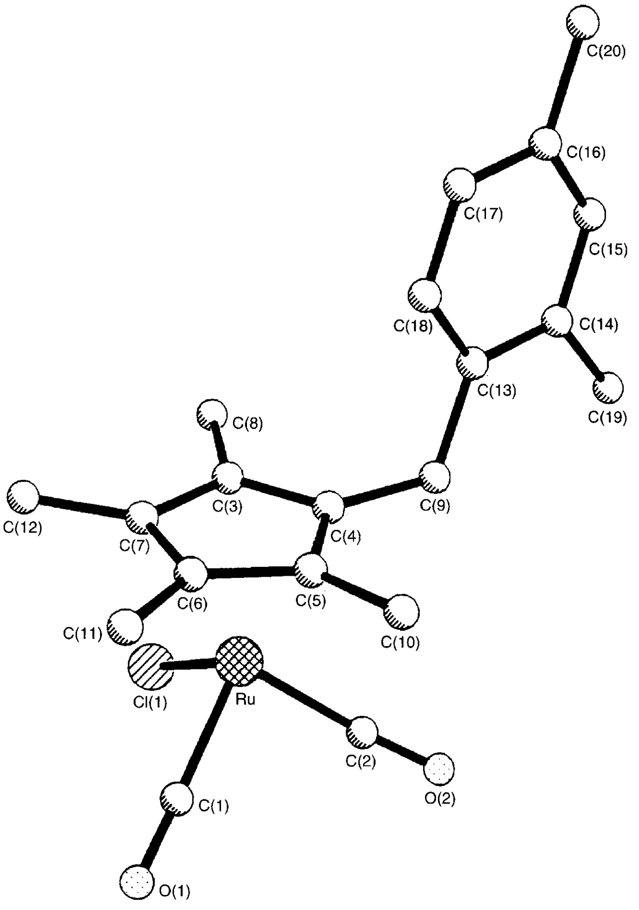


Fig. 1 View of the structure of complex $[\{\eta^5\text{-}C_5Me_4CH_2(C_6H_3Me_2\text{-}2,4)\}Ru(CO)_2Cl]$, **5**, hydrogens omitted; key bond lengths (Å) and angles (°): Ru(1)–Cl(1) 2.418(2), Ru(1)–C(1) 1.884(5), Ru(1)–C(3) 2.263(4), Ru(1)–C(4) 2.241(4), Ru(1)–C(5) 2.188(4), Ru(1)–C(6) 2.220(4), Ru(1)–C(7) 2.239(4), C(4)–C(9) 1.509(6), C(9)–C(13) 1.519(7); C(1)–Ru(1)–C(2) 90.6, Cl(1)–Ru(1)–C(1) 90.9, Cl(1)–Ru(1)–C(2) 96.7°

The structure of complex **5** was confirmed by a single-crystal X-ray determination‡ which showed (Fig. 1) the arrangement deduced from spectroscopic data, namely that the Ru had a 'piano-stool' coordination, with two carbonyls and a chlorine, and an $\eta^5\text{-}C_5$ ring, which was bonded *via* a CH_2 to a 2,4-dimethylphenyl.

While Friedel–Crafts type reactions have been reported before for a few ferrocenylcarbenium ions,[5] they were frequently complicated by redox processes, and are thus rather limited in scope. The reactions on the ruthenium systems described here appear to be much more widely applicable, and thus to foreshadow a range of transformations.

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Footnotes

† *Microanalytical, IR*, and NMR data. **2**, Anal. found (calc.): C 53.5 (53.5), H 4.7 (4.6), Cl 8.8 (8.8%); ν(CO) 1982, 2033 cm^{-1}; ^{1}H NMR δ: 1.86 (6 H), 1.87 (6 H), 3.60 (2 H), 7.04 (m, 2 H), 7.22 (m, 3 H). **3**; C, 54.7 (54.6); H, 4.8 (5.0); Cl, 8.3 (8.2%); ν(CO) 1980, 2034 cm^{-1}; 1H NMR δ: 1.91 (12 H), 3.61 (2 H), 6.99 (d, 2 H, J = 8 Hz), 7.10 (d, 2 H, J = 8 Hz), 2.24. **4**: C, 55.8 (55.6); H, 5.2 (5.4%); ν(CO) 1980, 2033 cm^{-1}; ^{1}H NMR δ: 1.91 (6 H), 1.92 (6 H), 3.58 (2 H), 6.82 (d, 1 H, J = 8 Hz), 6.90 (1 H), 7.05 (d, 1 H, J = 8 Hz), 2.22, 2.23. **5**: C, 55.7 (55.6); H 5.3 (5.4); Cl, 8.4 (8.2%); ν(CO) 1980, 2033 cm^{-1}; ^{1}H NMR δ: 1.81 (6 H), 1.97 (6 H), 3.53 (2 H), 6.62 (d, 1 H, J = 8 Hz), 6.91 (d, 1 H, J = 8 Hz); 7.01 (1 H), 2.28, 2.31. **6**: C, 55.7 (55.6); H, 5.4 (5.4); Cl, 8.2 (8.2%); ν(CO) 1980, 2033 cm^{-1}; ^{1}H NMR δ: 1.74 (6 H), 1.94 (6 H), 3.48 (2 H), 6.55 (1 H), 6.95 (d, 1 H, J = 7 Hz), 7.06 (d, 1 H, J = 7 Hz), 2.25, 2.29.

‡ Crystals of **5** were grown from diethyl ether as yellow needles; crystal dimensions, 0.76 × 0.35 × 0.30 mm. *Crystal data*: $C_{20}H_{23}ClO_2Ru$, M = 431.9; triclinic, a = 7.529(4), b = 11.275(5), c = 12.780(6) Å, α = 92.82(4), β = 101.91(4), γ = 108.60(4)°; U = 998.3(8) Å^3; Z = 2; D_c = 1.437 g cm^{-3}, space group $P\bar{1}$, Mo-Kα radiation (λ = 0.710 739 Å), μ(Mo-Kα) = 0.927 mm^{-1}, $F(000)$ = 440. Three-dimensional room-temperature X-ray data were collected in the range $1.92 < \theta < 22.50°$ on a Siemens P4 diffractometer by the omega scan method. The 2345 independent reflections (of 3187 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares methods on F^2; goodness of fit on F^2 = 1.076; final R indices [$I > 2\sigma(I)$] $R1$ = 0.0339 ($wR2$ = 0.0908); R indices (all 2552 independent data) $R1$ = 0.0378 ($wR2$ = 0.0943) using the program package SHELX93[6] as implemented on the Viglen 486dx computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at The Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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