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Preliminary communication

A novel ring substitution reaction in a cyclopentadienylruthenium phosphine complex

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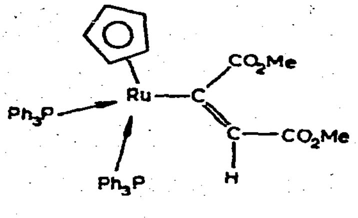
SUMMARY

The reaction between hexafluoroacetone and $Ru(PPh_3)_2(\pi\text{-}C_5H_5)[\sigma\text{-}C_2(CO_2Me)_2H]$ affords a 1/1 adduct, containing a coordinated ester group and an intramolecular hydrogen bond; formal insertion of $(CF_3)_2CO$ into a C–H bond of the cyclopentadienyl group has also occurred.

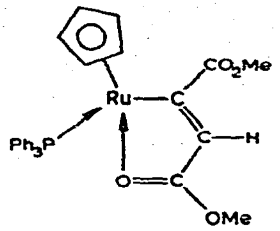
Hexafluoroacetone reacts with the complex $Ru(PPh_3)_2(\pi\text{-}C_5H_5)[\sigma\text{-}C_2(CO_2Me)_2H]$ (I)[1], affording a pale yellow, air-stable, crystalline solid (II), with a stoichiometry corresponding to a 1/1 adduct, less one PPh_3 molecule. The mass spectrum indicates that (II) is monomeric. Notable ions include *m/e* 595 ($[P - C_2(CO_2Me)_2]^+$), 450 ($[Ru(PPh_3)C_2(CO_2Me)H]^+$), and 333 ($[C_5H_4C(CF_3)_2OH]Ru^+$), suggesting that $C_2(CO_2Me)_2H$ remains as an intact unit, and that the C_5-ring has been substituted. The infrared spectrum shows no new ketonic ν(CO) bands, but a broad band at 3146 cm^{-1} suggested the presence of an OH group. Strong bands at 1664 and 1571 cm^{-1} can be assigned to ν(ester-CO) and ν(C=C) of the dicarboxylic ester fragment, respectively.

The proton NMR spectrum exhibits a broad resonance at τ2.72 (15H), assigned to PPh_3, but no sharp singlet which could be due to a $\pi\text{-}C_5H_5$ group. Other signals occurred at τ2.85s (1H), 3.29d (1H), 4.64m (1H), 5.54m (1H), 6.28m (2H), 6.63s (3H) and 6.83s (3H).

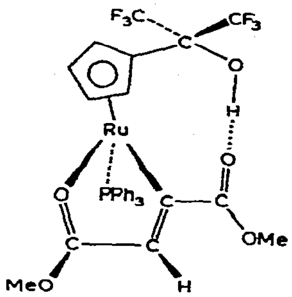
The last two signals were assigned to the two methoxy groups. On shaking with D_2O, the resonance at τ2.85 disappeared, again suggesting the presence of an OH group. Double and triple resonance experiments on the four peaks between τ3.9–6.3 indicated that the lowest resonance was independent of the remaining four protons, and that the latter were coupled together. The ^{19}F NMR spectrum showed two resonances of equal intensity at 75.6qd and 77.95q ppm ($CFCl_3$, 0.0 ppm). The two CF_3 groups are coupled



(I)



(III)



(II)

together (J(FF), 10Hz), and the CF_3 group at lower field is also coupled to a proton (J(HF), 1.5Hz).

The proton resonance spectrum suggests that the π-C_5H_5 group is no longer present as such, but that a π-C_5H_4R ligand has been formed, where R = $C(CF_3)_2OH$. The four protons remaining are all inequivalent, in marked contrast with the usual A_2B_2 system found for monosubstituted cyclopentadienyl groups. This feature suggests that the C_5 ring is no longer freely rotating.

The loss of a PPh_3 ligand also occurs simply on heating complex (I). In this case, the resulting complex (III) is formed by coordination of one of the ester carbonyl groups to ruthenium. A similar structure may be proposed for complex (II). Studies of models of the resulting complex show that rotation of the C_5 ring could be prevented by formation of a hydrogen bond from the alcohol substituent and the free carbonyl group, as suggested by the infrared spectrum.

Electrophilic substitution of aromatic systems by hexafluoroacetone has been reported[2], but no examples of similar reactions with organometallic systems *e.g.* ferrocene, have hitherto been described. Acetylation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ has been reported[3], and we suggest that in (I), the possibility of substitution would be enhanced by the presence of the phosphine ligands, leading to an excess of electron density on the metal, and by backbonding, on the C_5-ring carbon atoms. Complex (II) may also be considered to be the product of a formal insertion of hexafluoroacetone into a C–H bond of the π-cyclopentadienyl group.

The unusual structure suggested by the spectroscopic data reported above has been fully confirmed by a single crystal X-ray structure determination.

Crystals of (II), obtained from light petroleum ether, are triclinic, $P\bar{1}$, with a = 10.131, b = 15.107, c = 10.798 Å, α = 102.14, β = 107.04, γ = 89.64°, Z = 2. The intensities of 4958 reflections were measured with Cu–Kα radiation (maximum sin θ/λ = 0.514). Using the 4457 observed reflections, the structure was solved by the heavy-atom method after the Ru and P atoms had been located using a sharpened Patterson map. The structure has been refined by least-squares methods to a conventional R value of 0.040 and a weighted R value of 0.041. A stereoscopic view of the molecular geometry is given in Fig. 1.

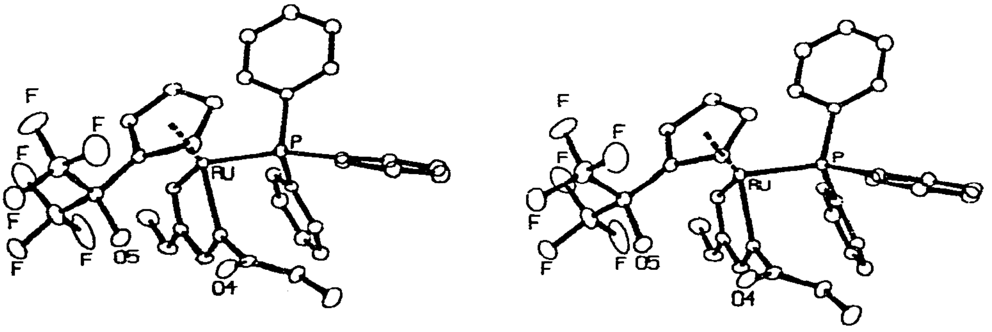


Fig. 1. Stereoscopic view of the molecular geometry of [π-$C_5H_4C(CF_3)_2OH$]Ru(PPh_3)[$C_2(CO_2Me)_2H$].

One ester group is directly bonded through the carbonyl oxygen to the metal at a Ru–O distance of 2.14 Å. This ester group is nearly coplanar with the carbon–carbon double bond, while the other ester group is twisted out of this plane by about 69°. The carbonyl oxygen (O4) of this free ester group is hydrogen bonded with the alcohol substituent of the $C(CF_3)_2OH$ group (O5). Dimensions of the hydrogen bond are: distance O4–O5 = 2.64 Å, distance H5–O5 = 1.67 Å, angle O4·····H5–O5 = 160°. The Ru–C σ-bonded distance is 2.04 Å, which compares with 2.05 Å observed in (π-C_5H_5) Ru(PPh_3)[$C_4(CF_3)_4H$][1].

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