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Preliminary communication

Metallation and related reactions with π-cyclopentadienylruthenium complexes

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The reaction between $(\pi\text{-}C_5H_5)Ru(PPh_3)_2CH_2Ph$ and hexafluoro-2-butyne affords the lemon-yellow $(\pi\text{-}C_5H_5)Ru(PPh_3)[C_2(CF_3)_2]CH_2Ph$ (I), m.p. 200° (dec.)★. The mass spectrum contains a parent ion cluster centred on *m/e* 682. In the IR spectrum, strong bands in the 1400–900 cm^{-1} region confirm the presence of a fluorinated ligand, while a band at 1643 cm^{-1} suggests the presence of a coordinated double bond bearing electronegative substituents.

The ^{19}F NMR spectrum contains two resonances at 47.1 and 59.9 ppm, the fine structure of which can be analysed in terms of a *cis*-$(CF_3)CH{=}C(CF_3)$ group [$J(FF_{cis})$, 11; $J(FH_{gem})$, 11; $J(FH_{trans})$, ~0 Hz]. The proton NMR spectrum exhibits an extended multiplet (resembling those found for *ortho*-metallated systems) centred on τ 2.68, a singlet at τ 4.89 (C_5H_5), a doublet of quartets at τ 7.81 (J(HF), 11; J(HP), 16 Hz), and an AB quartet centred on τ 7.82 (J_{AB}, 17.5 Hz; separation, 208 Hz).

The above data can be interpreted in terms of either of the two structures (Ia) or (Ib). We suggest that (Ia) is the more probable on the following grounds: (i) the presence of a highly asymmetric AB system, assigned to the benzylic methylene group [*cf.* that in $(\pi\text{-}C_5H_5)Ru(PPh_3)[C_2(CO_2Me)_2]CH_2Ph$ (II), where J_{AB} is 16 Hz, but the separation is only 43 Hz; in $(\pi\text{-}C_5H_5)Ru(PPh_3)_2CH_2Ph$, the two protons of the methylene group are equivalent]; (ii) the mass spectrum which exhibits a strong peak at *m/e* 262, with associated ions at *m/e* 183, 152, and 108, suggesting the presence of an unsubstituted PPh_3 group, and a base peak at *m/e* 419, corresponding to the ion $[(C_5H_5)Ru(C_4F_6)(C_7H_6)]^+$. There is no ion at *m/e* 91, as expected for a compound containing a simple benzyl group as depicted in (Ib), and indeed found in high abundance in the spectrum of the parent benzyl complex, and of (II).

On chemical grounds, structure (Ib) is unlikely, since as noted below, loss of the benzyl group as toluene occurs in many reactions of the parent benzyl complex, with concomitant metallation of the phosphine ligand. Complex (I) is probably formed by

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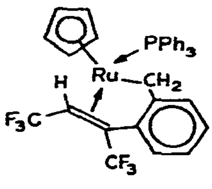
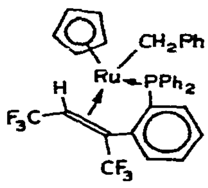
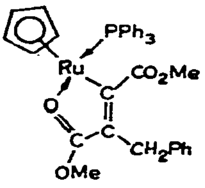
★All new compounds gave satisfactory analytical data.



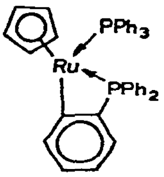
(Ia)



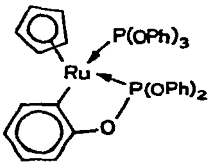
(Ib)



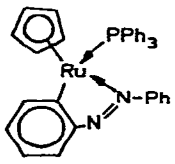
(II)



(III)



(IV)



(V)

insertion of the acetylene into the *ortho*-CH bond of the benzyl group in a metal-activated process. Alternatively, reaction of a π-benzyl complex with the acetylene may be considered, although attempts to prepare the π-benzylic precursor resulted in formation of the *ortho*-metallated complex (III), described below.

In apparently related reactions, several different types of *ortho*-metallated complexes containing the π-cyclopentadienylruthenium group have been prepared. These reactions are facilitated by the presence of a σ-bonded alkyl or aralkyl group attached to the metal. Thus, heating $(\pi\text{-}C_5H_5)Ru(PPh_3)_2R$ (R = Me[1] or CH_2Ph) in decalin results in conversion to the *ortho*-metallated phosphine complex (III), m.p. 223–225°. The mass spectrum of this pale-yellow compound contains a parent ion cluster centred on m/e 690. In addition, the proton NMR spectrum showed the broad multiplet at τ 3.04–3.55 associated with complexes of this type. Formation of complex (III) occurs readily so that it is often the major product isolated from reactions of the methyl compound. Such behaviour is reminiscent of that of $RhMe(PPh_3)_3$, which also readily forms the metallated complex $Rh(C_6H_4PPh_2)(PPh_3)_2$[2].

Intramolecular metallation reactions have also been reported for several triphenyl phosphite complexes[3]. Similarly, with $(\pi\text{-}C_5H_5)Ru[P(OPh)_3]_2Cl$, dehydrochlorination occurred readily in reluxing decalin, with the formation of white $(\pi\text{-}C_5H_5)Ru[(C_6H_4O)P(OPh)_2]P(OPh)_3$ (IV), m.p. 116–118°. The mass spectrum contained a parent ion cluster centred on *m/e* 786, and the IR spectrum exhibited bands at 1290, 1075, and 830 cm^{-1}, not present in the chloride precursor, and reported[3] as being indicative of metallation of one of the phenyl rings.

The reaction between $(\pi\text{-}C_5H_5)Ru(PPh_3)_2Me$ and azobenzene (AzbH) proceeds readily at 100° in light petroleum, with loss of methane, and formation of the known[4] $(\pi\text{-}C_5H_5)Ru(PPh_3)$ (Azb) (V), together with some (III).

The ready formation of the complexes described above illustrates the pronounced tendency of π-cyclopentadienylruthenium complexes containing phosphorus ligands to undergo a wide variety of intramolecular metallation reactions, further examples of which are now being studied in detail.

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