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Preliminary communication

Ligand exchange in some π-allylic tris(trifluorophosphine)rhodium(I) complexes

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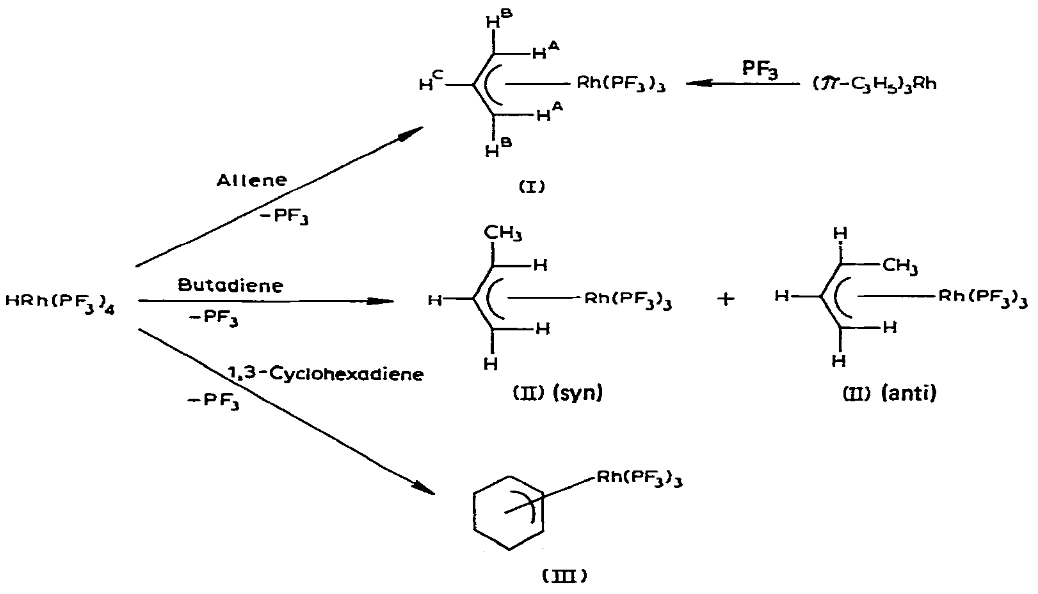
We have recently synthesised[1] several volatile, liquid, π-allylic tris(trifluorophosphine)rhodium(I) complexes (see Scheme 1) by either (i) insertion of allene or conjugated dienes into the metal–hydrogen bond of $HRh(PF_3)_4$, [for (I), (II), and (III)], or (ii) displacement of two π-allyl groups from tris(π-allyl)rhodium(III) with trifluorophosphine [for (I)]. In (i) exactly one PF_3 ligand was displaced from the hydride in each case.



Scheme 1.

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The room temperature ^{19}F NMR spectrum of a toluene solution of (I) consists of a broad 1/1 doublet [φ_F 8.1 ppm (rel. CCl_3F) ^{1}J(PF) 1396 Hz] characteristic of PF_3 coordinated to a transition metal[2]. There was no observable coupling to the ^{103}Rh nucleus (100% abundance; *I* ½).

On cooling the solution to –50° the ^{19}F NMR spectrum of (I) exhibits a complex pattern of lines (Fig. 1), which has been fully analysed[3] as an $[X_3A]_3$ spin system[4] (X = fluorine, A = phosphorus), each line being split further into a 1/1 doublet by the ^{103}Rh nucleus (*J*(RhF) 18.0 Hz).

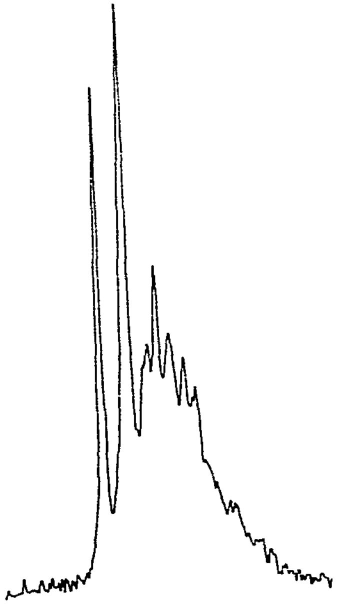

Fig. 1. High field half of the ^{19}F NMR spectrum (at 94.1 MHz) of $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ in toluene at 50°

The ^{1}H NMR spectrum of (I) at room temperature (Fig. 2a) is characteristic of a π-allyl complex showing the expected three resonances for the unique proton H^C, and the *syn*, H^B, and *anti*, H^A pairs of protons. Only H^C is coupled significantly to the ^{103}Rh nucleus and the resonance consists of symmetric 16 line pattern of relative intensity 1/1/2/2/2/3/1/4/4/1/3/2/2/2/1/1 which arises from the overlap of a doublet ($^{2}J(RhH^C)$ 1.8 Hz) of triplets ($^{3}J(H^CH^A)$ 10.2 Hz) of triplets ($^{3}J(H^CH^B)$ 6.1 Hz).

On cooling a solution of (I) to –50° the H^B resonance remains unaffected, but the H^C signal broadens and the H^A resonance changes to a symmetric six line pattern of relative intensities 1/3/4/4/3/1 (Fig. 2b). The latter arises from overlap of two 1/3/3/1 quartets from spin coupling between H^A and H^C and three equivalent phosphorus atoms ($^{3}J(PH^A)$ 4.6 Hz). The changes in both ^{1}H and ^{19}F NMR spectra are reversible, and indicate that there is a ready exchange between free and coordinated PF_3 in $\pi\text{-}C_3H_5Rh(PF_3)_3$. Heck[5] has proposed a dissociative mechanism in substitution reactions of the analogous π-allylCo(CO)$_3$ compound. Compounds (II) and (III) also show similar

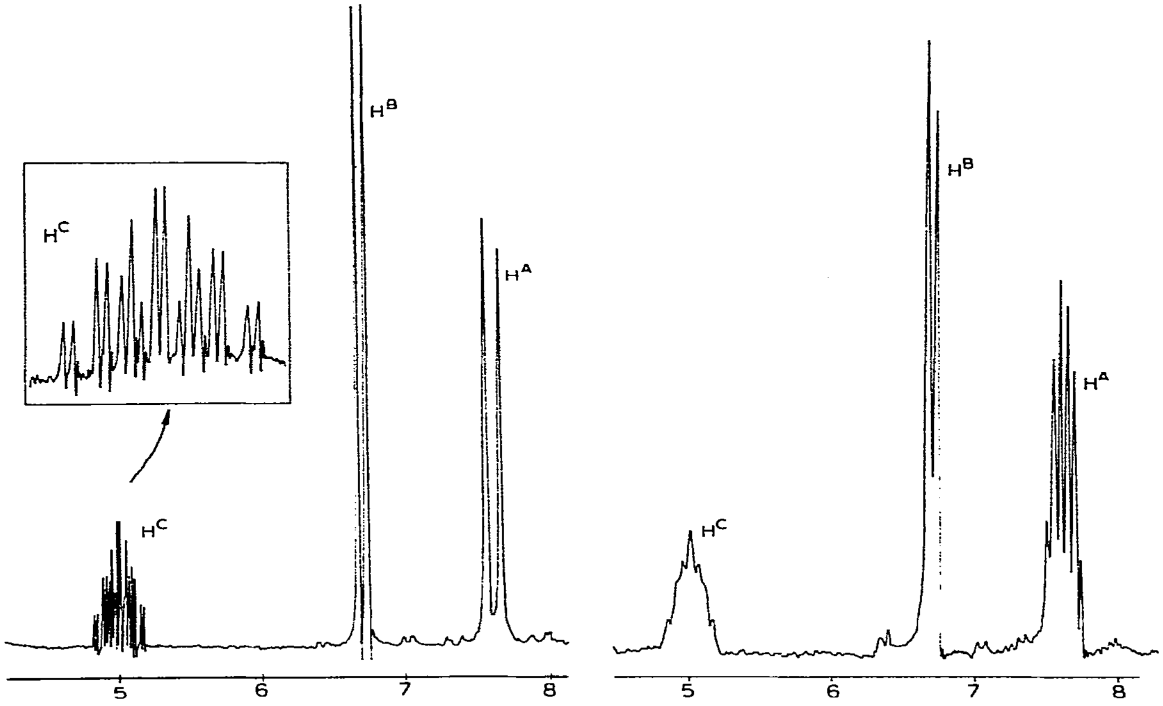

Fig. 2. The ^1H NMR spectrum (at 100 MHz) of $Rh(\pi\text{-}C_3H_5)(PF_3)_3$ in CCl_3F solution (a) at ambient temperature; (b) at −50°

behaviour to (I) and the ^{19}F NMR spectrum of (II) indicates the presence of *syn* and *anti* isomers which both undergo phosphine exchange but are not interconverted at room temperature. The apparent magnetic equivalence of all three PF_3 ligands at −50° in (I), (II) and (III) is probably due to an intramolecular exchange process if the metal is considered 5-coordinate. Fluxional behaviour is known for $CF_3Co(CO)_3(PF_3)$[6], butadiene $Fe(PF_3)_3$[7], and $HRh(PF_3)_4$[8] and Rice and Osborn[9] recently found that inter- and intramolecular exchange processes operate independently in $CH_3Rh(diene)L_2$.

Although analytical data for (I) (Found: C, 9.0; H, 1.3; P, 22.9. $C_3H_5Rh(PF_3)_3$ calcd.: C, 8.8; H, 1.2; P, 22.8%.) confirms the presence of three PF_3 ligands in the complex, the highest mass peak observed in the mass spectrum is at *m/e* 320 corresponding to the $C_3H_5Rh(PF_3)_2^+$ ion.

O'Brien[10] has formulated the monomeric product from the reaction of allylmagnesium chloride and $[RhCl(CO)_2]_2$ as the di-carbonyl complex, $\pi\text{-}C_3H_5Rh(CO)_2$, (IV) partly on the basis of the observation of $Rh(CO)_2C_3H_5^+$ as the highest molecular ion in the mass spectrum. A di-carbonyl complex is unexpected in view of the close similarity in coordinating ability of PF_3 and CO[2], furthermore, (IV) is also readily obtained from the room temperature reaction between $\pi\text{-}(C_3H_5)_3Rh$ and CO[11,12]. Studies are underway to clarify the nature of compound (IV).

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