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ACETYLENE INSERTION AND DOUBLE INSERTION REACTIONS OF RHODIUM HYDRIDO COMPLEXES†

H. ESHTIAGH-HOSSEINI, JOHN F. NIXON* and JOHN S. POLAND‡

School of Molecular Sciences, University of Sussex, Brighton (Great Britain)

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Summary

$RhH(L)(PPh_3)_3$ (L = CO or PF_3) react with $RC{\equiv}CR$ ($R = CF_3$, or CO_2Me) to give vinyl complexes *trans*-$Rh(L)(PPh_3)_2(CR{=}CHR)$. These complexes undergo further acetylene insertion; *e.g.*, *trans*-$Rh(L)(PPh_3)_2(CR^1{=}CHR^1)$ ($R^1 = CF_3$) reacts with $R^2C{\equiv}CR^2$ ($R^2 = CO_2Me$) and *trans*-$Rh(L)(PPh_3)_2(CR^2{=}CHR^2)$ reacts with $R^1C{\equiv}CR^1$ to give unexpectedly the same double inserted product *trans*-$Rh(L)(PPh_3)_2(CR^2{=}CR^2{-}CR^1{=}CHR^1)$ and a possible reaction mechanism is presented. $Rh(PF_3)(PPh_3)_2$-$[C(CF_3){=}CHCF_3]$ and *t*-butyl bromide give $CF_3CH{=}CHCF_3$, isobutene and *trans*-$RhBr(PPh_3)_2(PF_3)$.

Introduction

The formation of σ-vinylic transition-metal complexes and their consequent reactivity are of interest on account of their potential importance in transition-metal catalysed oligomerisation of olefins or acetylenes [1-3].

Synthetic routes include reactions of transition-metal halides with Grignard, alkenyl lithium, or similar reagents [4-6], metal complex anions with activated alkenyl halides [7, 8],

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†No reprints available.
*Author to whom correspondence should be addressed.
‡Present address: Department of Chemistry,
University of the West Indies,
Kingston,
Jamaica.

oxidative-addition of alkenyl halides to co-ordinatively unsaturated transition-metal complexes [9-17], HX attack on co-ordinated acetylenes [10, 18-21], acetylene insertion into M-H or M-C bonds [22-36], and addition to the triple bond of an acetylide [37, 38]. The majority of alkenyl complexes made this way involve electron-withdrawing substituents to activate the acetylene bonds.

Although many alkenyl complexes have been prepared and fully characterised, they are often found to be relatively inert towards further reaction, *e.g.*, with acetylenes to give double inserted products. $IrH(CO)(PPh_3)_3$ and $IrHCl_2(PEt_3)_3$ have been shown to react with activated disubstituted acetylenes to give σ-alkenyl-h^2-acetylene complexes [30], while further studies showed the formation of novel metallocycle-alkenyl complexes [39, 40].

Double insertion reactions have been demonstrated only in very few cases, thus Stone *et al.* [41] have shown that $RuHL_2(h^5-C_5H_5)$ (L = CO, PPh_3) and $CF_3C{\equiv}CCF_3$ afford $Ru(PPh_3)_2(h^5-C_5H_5)[$*cis*$-C(CF_3)=CH(CF_3)]$, $Ru(CO)_2(h^5-C_5H_5)[$*trans*$-C(CF_3)C=CH(CF_3)]$ and $\overline{RuL(h^5-C_5H_5)[C(CF_3)=C(CF_3)C(CF_3)}=CH(CF_3)]$. The doubly inserted complexes $Ru(PPh_3)_2(h^5-C_5H_5)[C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)]$ [42] have been described and $C(CO_2Me){\equiv}C(CO_2Me)$ has been inserted into $PdBr(PBu_3)_2(CH=CPh_2)$ [43] while a few Pt^{II} complexes have been reported very recently [44].

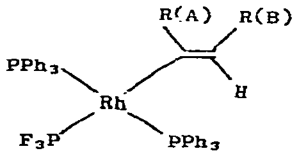
In view of the ready formation of alkenyl complexes of the type $Rh(CO)(PPh_3)_2(CR=CHR)$ [31] (R = CO_2Me, CO_2Et, CO_2H, Ph, CF_3) from $RhH(CO)(PPh_3)_3$ and the similarity in chemical behaviour of CO and PF_3 [45], we decided to study the reactions of $RhH(PF_3)_x(PPh_3)_{4-x}$ (x = 1, 2) [46, 47] with acetylenes containing electron-withdrawing substituents.

Results and discussion

(a) Mono-insertion reactions

Hexafluorobut-2-yne readily inserts into the rhodium-hydrogen bond of $RhH(PF_3)(PPh_3)_3$ to yield yellow crystals of the vinyl complex *trans*-$Rh(PF_3)(PPh_3)_2[$*cis*$-C(CF_3)=CH(CF_3)]$, (I), whose structure can be unambiguously defined by ^1H, ^{19}F and ^{31}P NMR spectroscopy (see Table for data).

In the ^{19}F NMR of (I) the PF_3 resonance occurs as a low field widely spaced doublet $[^1J(PF)]$ of doublets $[^2J(\underline{F}_3P\underline{Rh})]$ of triplets $[^3J(\underline{F}_3PRh\underline{P}Ph_3)]$. A quintet pattern at higher field is assigned to the



[(I) $R = CF_3$; (II) $R = CO_2Me$]

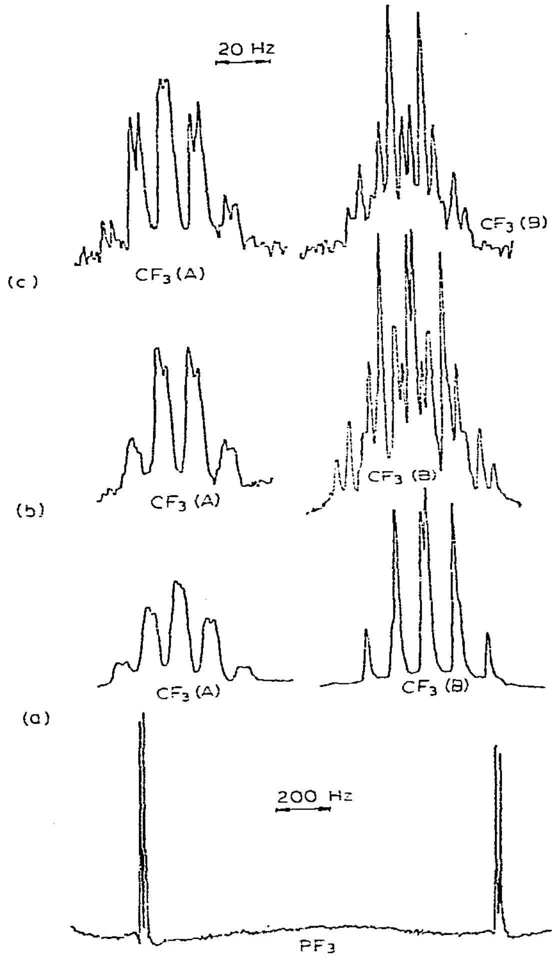


Figure 1 ^{19}F NMR spectrum of (I) on irradiation at the resonant frequency of (a) the PPh_3; (b) the PF_3; and (c) the unique vinyl proton in C_6D_6 solution

TABLE

NMR CHEMICAL SHIFT AND COUPLING CONSTANT DATA

δ in ppm upfield from TMP, Φ in ppm upfield from $CFCl_3$, J in Hz.

COMPLEX	$\delta(PF_3)$	$\delta(PPh_3)$	$\Phi(PF_3)$	$\Phi CF_3(A)$	$\Phi CF_3(B)$	$^1J(PF)$	$^1J(PF_3Rh)$	$^1J(PPh_3Rh)$	$^2J(PRhP')$
$Rh(PF_3)(PPh_3)_2[C(CF_3)=CH(CF_3)](I)^{a-f}$	22.8	111.3	18.3	50.0	57.6	1308	239	144.0	56.1
$Rh(PF_3)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)](II)^{d-e}$	20.7	110.4	19.6	-	-	1307	265	134.2	56.1
$Rh(PF_3)(PPh_3)_2[C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)H](III)^{b,d,e}$	-	-	18.8	58.1	55.1	1310	-	-	-
$Rh(CO)(PPh_3)_2[C(CO_2Me)=C(CO_2Me)C(CF_3)=C(CF_3)H](IV)^{b}$	-	110.4	-	58.8	56.9	-	-	144.0	-

[a] $^1JP\underline{F}_3C\underline{F}_3(A) \approx 11.7$.

[b] $^5J[C\underline{F}_3(A)C\underline{F}_3(B)] = {}^3J[C\underline{F}_3(B)H] \approx 11.7$ (I); 11.5 (III); 12.2 (IV).

[c] $^5J[C\underline{F}_3(B)\underline{P}Ph_3] \approx 1.5$.

[d] $^2J(P\underline{F}_3\underline{Rh}) = 17.8$(I); 18.3(II); 18.0(II).

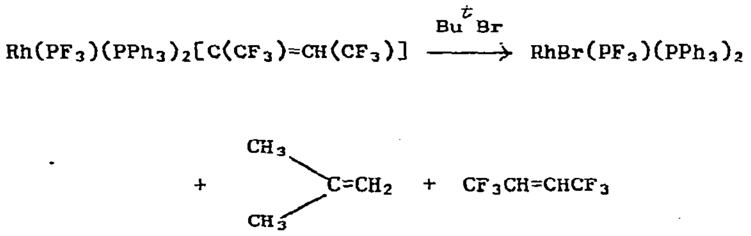
[e] $^3J(P\underline{F}_3Rh\underline{P}Ph_3) \approx 6.1$(I); 6.1(II); 6.0(III).

[f] $^3J[C\underline{F}_3(A)\underline{Rh}] \approx 3.0$.

CF_3(A) group and arises from the overlap of two 1:3:3:1 quartets caused by spin coupling to CF_3(B) and the phosphorus of the PF_3 group. On expansion, further doublet splitting *via* interaction with the rhodium nucleus can be resolved. The highest field resonance assigned to the CF_3(B) group is a multiplet arising from coupling to the vinylic hydrogen, CF_3(A) and the phosphorus nuclei of the two co-ordinated PPh_3 ligands. Assignment of the coupling constants was facilitated by selective phosphorus decoupling studies described below. The ^{19}F resonances of the PF_3 and CF_3 groups obtained by semultaneous irradiation at the resonant frequency of the PPh_3 ligands are shown in Figure 1(a). The PF_3 resonance as expected, collapses to a doublet of doublets while the CF_3(A) resonance is largely unchanged; however, the CF_3(B) resonance simplifies to two overlapping quartets $[^5J\{C\underline{F}_3(A)C\underline{F}_3(B)\}]$ and $[^2J\{C\underline{F}_3(B)\underline{H}\}]$. When the ^{19}F NMR spectrum [Figure 1(b)] is recorded with simultaneous decoupling of the PF_3 phosphorus, the CF_3(A) resonance occurs as a quartet $[^5J\{C\underline{F}_3(A)C\underline{F}_3(B)\}]$, each line being further doubleted by coupling to rhodium; however, the resonance of CF_3(B) remains unchanged. The ^{19}F resonances of CF_3 groups observed while simultaneously irradiating at the resonant frequency of the unique vinyl proton are shown in Figure 1(c). The CF_3(B) resonance as expected gives a quartet $[^5J\{C\underline{F}_3(A)C\underline{F}_3(B)\}]$ of triplets $[^5J\{C\underline{F}_3(B)\underline{P}Ph_3\}]$ and the CF_3(A) resonance remains unchanged. The ^{31}P NMR spectrum exhibits a low field resonance for the PF_3 ligand consiting of a quartet $[^1J(PF)]$ of doublets $[^1J(\underline{P}F_3\underline{Rh})]$ of triplets $[^2J(PRhP')]$ of quartets $[^4J\{\underline{P}F_3C\underline{F}_3(A)\}]$ and a high field resonance assigned to the PPh_3 ligands which appears as a doublet $[^2J(PRhP')]$ of doublets $[^1J(\underline{P}Ph_3\underline{Rh})]$ of quartets $[^5J\{\underline{P}Ph_3C\underline{F}_3(B)\}]$. The NMR spectra are only consistent with PPh_3 groups occupying *trans*- positions (*vide supra*) while the magnitude of the coupling constants, $^5J[C\underline{F}_3(A)C\underline{F}_3(B)]$ and $^3J[C\underline{F}_3(B)\underline{H}]$, show that the CF_3 groups are mutually *cis* [18, 19, 22, 29, 31, 33, 34, 48-50]. The ^1H NMR spectrum as expected shows a quintet pattern from overlapping of two 1:3:3:1 quartets. Coupling constant and chemical shift data are listed in the Table.

The complex, $Rh(PF_3)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)]$, (II), prepared by reaction of $RhH(PF_3)(PPh_3)_3$ with dimethyl acetylenedicarboxylate (DMA) at room temperature is formulated as above on the basis of elemental analysis and ^1H NMR spectroscopy. No definite assignment of the stereochemistry of the CO_2Me groups could be made on the basis of the ^1H NMR spectrum, although a *trans*- configuration has been proposed for the analogous carbonyl complex, on the basis of cleavage of the metal-carbon bond with anhydrous HCl to obtain dimethyl fumarate [31]. Interestingly, in the reaction between $RhH(PF_3)_2(PPh_3)_2$ and DMA, preferential displacement of PF_3 occurs to give a complex of structure similar to (II), which was fully characterised on the basis of ^1H, ^{19}F and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum is very similar to that of $Rh(PF_3)(PPh_3)_2[C(CF_3)=CH(CF_3)]$, as is the ^{19}F NMR spectrum in the PF_3 region, but the ^1H NMR spectrum exhibited two singlets in the CO_2Me region in addition to those expected for (II), suggesting that a mixture of isomers might be present.

Reaction of (I) with *t*-butyl bromide in a sealed NMR tube at 60° C for two days produces $RhBr(PF_3)(PPh_3)_2$, *iso*-butene and a mixture of *cis*- and *trans*-$CF_3CH=CHCF_3$.

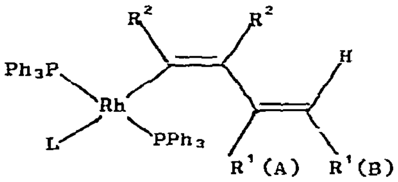


$$\mathrm{Rh(PF_3)(PPh_3)_2[C(CF_3)=CH(CF_3)]} \xrightarrow{\mathrm{Bu^{\mathit{t}}Br}} \mathrm{RhBr(PF_3)(PPh_3)_2} + \mathrm{(CH_3)_2C=CH_2} + \mathrm{CF_3CH=CHCF_3}$$

In this reaction the first step may involve an oxidative-addition reaction followed by β-hydrogen elimination to give *iso*-butene and form a rhodium(III) hydride intermediate. Subsequent hydrogen migration would then give $RhBr(PF_3)(PPh_3)_2$ and $CF_3CH=CHCF_3$. We proposed a similar mechanism for the reaction between Bu^tBr and $Rh(h^3\text{-allyl})(PF_3)(PPh_3)_2$ [51]. All products obtained from this reaction were characterised by their ^{19}F and/or ^1H NMR spectra. The three line pattern of intensity 1:1:1 centred at 61.0 PPM observed in the ^{19}F NMR spectrum is attributable to the known *cis*-$CF_3CH=CHCF_3$ [52] and a very similar pattern centred at 66.2 PPM is tentatively assigned to the *trans*- isomer whose spectrum does not seem to have been reported previously. In the ^1H NMR spectrum the low field resonances centred at $\tau = 4.18$ are attributable to the *cis*- isomer [52] and the slightly higher resonances centred at $\tau = 4.8$ are assigned to the *trans*-isomer. The compound $RhBr(PF_3)(PPh_3)_2$ was identified by a comparison of its IR spectrum with that of *trans*-$RhCl(PF_3)(PPh_3)_2$ [53].

(*b*) *Double insertion reactions*

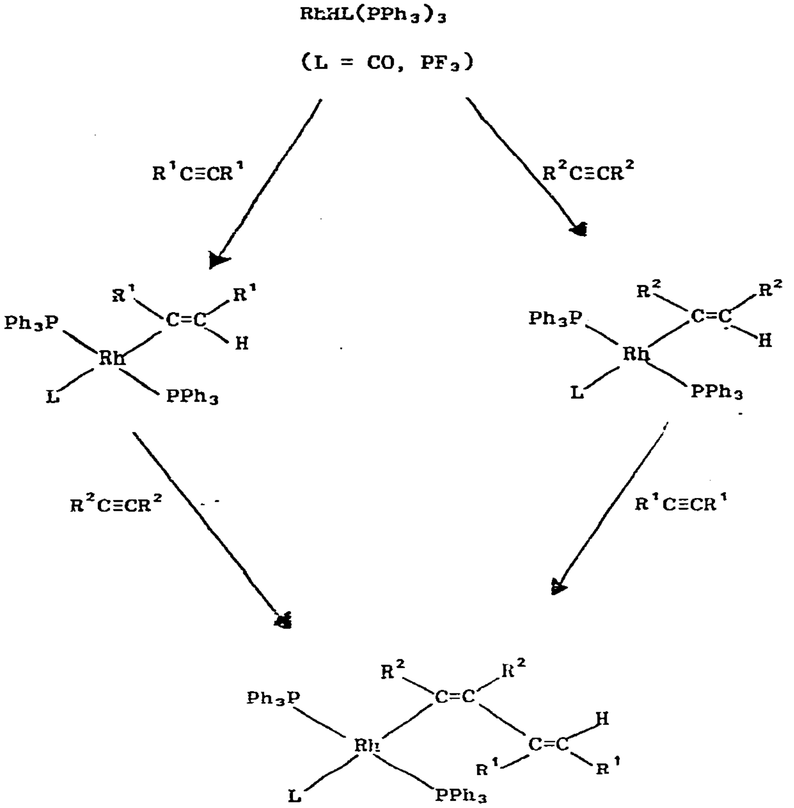
In certain cases the vinyl complexes (I) and (II) can undergo further insertion reactions (see Scheme). The reaction involving treatment of $R^2C\equiv CR^2$ with $Rh(L)(PPh_3)_2(CR^1{=}CHR^1)$; ($R^1$ = CF_3, R^2 = CO_2Me, L = CO, PF_3) takes place slowly and the products are *trans*-$Rh(L)(PPh_3)_2[C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)H]$ [(III), L = PF_3; (IV), L = CO]. The double inserted products are, of course, those expected on the accepted mechanism of acetylene insertion into the existing rhodium-carbon bond of the alkenyl metal complex. In the comparatively rapid reaction of $R^1C\equiv CR^1$ with both $Rh(L)(PPh_3)_2(CR^2{=}CHR^2)$ complexes (L = CO, PF_3), however, the products were also surprisingly identified as (III) and (IV), indicating that insertion in this case has occurred into the C-H bond of the original alkenyl complex



[R^1 = CF_3, R^2 = CO_2Me; (III) L = PF_3, (IV) L = CO]

This unusual type of insertion has only previously been reported [41] in the reaction between $Ru(h^5\text{-}C_5H_5)(PPh_3)[C(CO_2Me){=}CH(CO_2Me)]$ and $CF_3C\equiv CCF_3$, in which the acetylene inserted solely into C-H bond to give $Ru(h^5\text{-}C_5H_5)(PPh_3)[C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)H]$. X-ray crystallographic data confirmed the structure based formerly on spectroscopic assignments [54]. The interesting feature of our work is that the direction of insertion is found to be different in two cases involving closely related alkenyl complexes leading to the same double insertion product (see Scheme).

The *cis*- configuration of the CF_3 groups in the double inserted products (III) and (IV) has been established by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of $Rh(PF_3)(PPh_3)_2[C(CO_2Me){=}C(CO_2Me)C(CF_3){=}C(CF_3)H]$ exhibits a low field widely spaced doublet [$^1J(PF)$] of doublets [$^2J(\underline{F}_3P\underline{Rh})$] of triplets [$^3J(\underline{F}_3PRh\underline{P}Ph_3)$] for the PF_3 group, while the quintet pattern at higher field is assigned to the CF_3(B) group and arises from the overlap of two 1:3:3:1 quartets from spin coupling to CF_3(A) and hydrogen. The highest field resonance for the CF_3(A) is a quartet arising from coupling to CF_3(B). Coupling constant and chemical shift data are listed in the Table. The ^{19}F



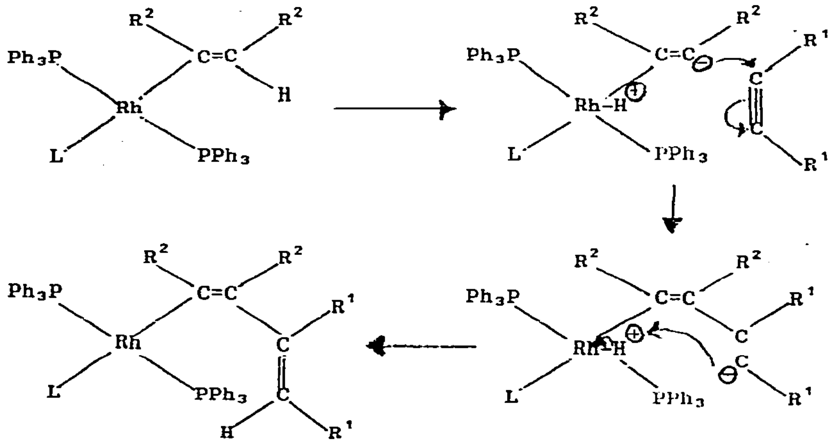
[$R^1 = CF_3$, $R^2 = CO_2Me$; (III) L = PF_3, (IV) L = CO]

(stereochemistry of the R^2 group is unknown).

Scheme

NMR spectrum of the CO analogue (IV) is very similar to (III) and the quintet pattern in the ^{19}F NMR spectrum attributable to the CF_3(B) group collapses to a quartet when the spectrum is obtained while simultaneously irradiating at the resonant frequency of the proton; the CF_3(A) resonance remains unchanged. The ^1H NMR spectra of both complexes (III) and (IV) show two singlets for the CO_2Me group and multiplets for PPh_3 ligands, but the unique hydrogen of both complexes could not be detected in the spectra.

A possible mechanism which would account for the reaction involves a dipolar intermeeiate of the typw shown below:



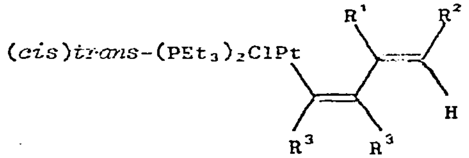
Although this type of mechanism has been proposed previously [42] to account for the unexpected product of the reaction between $Ru(h^5\text{-}C_5H_5)(PPh_3)[(CO_2Me)C{=}CH(CO_2Me)]$ and hexafluorobut-2-yne, it is difficult to understand why the insertion reactions of $R^2C{\equiv}CR^2$ into $Rh(L)(PPh_3)_2(CR^1{=}CHR^1)$ ($R^1 = CF_3$, $R^2 = CO_2Me$) proceeds in the 'normal' fashion since the electronic effects of $R = CF_3$ and $R = CO_2Me$ in disubstituted acetylenes are not expected to differ greatly.

Several further attempts were made to obtain double insertion complexes. $Rh(CO)(PPh_3)_2(CR{=}CHR)$ ($R = CO_2H$, Ph) was treated with $CF_3C{\equiv}CCF_3$ or $MeCO_2C{\equiv}CCO_2Me$ and $Rh(CO)(PPh_3)_2(CR{=}CHR)$ ($R = CF_3$, CO_2Me) with $PhC{\equiv}CPh$ and $HCO_2C{\equiv}CCO_2H$, but no evidence for double insertion products was found in any of these systems.

A recent study by Clark *et al.* [44] underlines the difficulties in obtaining double inserted products in this type of system. Only in certain cases, using $PtCl(PEt_3)_2(CMe{=}CHMe)$ and $CF_3C{\equiv}CCF_3$ in acetone in the presence of $AgPF_6$, have double insertion reactions (and these are all of the normal type) been successful, *e.g.*,

$[Pt(PEt_3)_2(acetone)(CR^1{=}CR^2]^+PF_6^-$

$$\xrightarrow[\text{(ii) } Cl^-]{\text{(i) } R^3C\equiv CR^3}$$



[*trans*, $R^1 = R^2 = Me$, $R^3 = CF_3$; *cis*, $R^1 = R^2 = Me$, $R^3 = CF_3$; *trans*, $R^1 = Me$, $R^2 = Cy$, $R^3 = CF_3$; *cis*, $R^1 = Me$, $R^2 = Cy$, $R^3 = CF_3$; *trans*, $R^1 = R^2 = Me$, $R^3 = CO_2Me$]

Although treatment of $PdX(dpp)_2(CH_3)$ (X = Cl, NO_3, solvent as the hexafluorophosphate salt) with $MeCO_2C{\equiv}CCO_2Me$ in CH_2Cl_2 has been reported [55] to yield the mono- or double insertion product, depending on the nature of X and the amount of acetylene used, attempts to extend this method in our laboratory [56] using $PtX(PPh_3)_2(RC{=}CHR)$ (X = Cl, solvent as ClO_4^- salt; R = CF_3, CO_2Me) were unsuccessful.

Very recently the production of (Et)HC=C(Et)-C(Et)=C(Et)(Ph) from the reaction of $NiBrL_2(Ph)$ with $EtC{\equiv}CEt$ in the presence of methanol indicates the likely formation of a double insertion product of the type $NiBrL_2[C(Et){=}C(Et)C(Et){=}C(Ph)(Et)]$ [57].

Experimental

General procedures were as described elsewhere [58].

Reaction of $RhH(PF_3)(PPh_3)_3$ with $CF_3C{\equiv}CCF_3$

A mixture of $RhH(PF_3)(PPh_3)_3$ (1.023 g, 1.04 mmol) in benzene (20 cm^3) and $CF_3C{\equiv}CCF_3$ (0.180 g, 1.11 mmol) was shaken in a sealed ampoule at room temperature for three days. The ampoule was opened on the vacuum line and no unreacted $CF_3C{\equiv}CCF_3$ was detected. The yellow solution was transferred to a Schlenk tube and removal of solvent gave a yellow sticky solid. The yellow residue was extracted with ether (50 cm^3) concentrated, and addition of hexane followed by cooling in the refrigerator gave yellow crystals of the complex, $Rh(PF_3)(PPh_3)_2[C(CF_3){=}CH(CF_3)]$, (I), (0.608 g, 0.69 mmol; 66%), m.p. 137-142° C (Found: C, 54.9; H, 3.7. $C_{40}H_{31}F_9P_3Rh$ requires: C, 54.68; H, 3.55%). IR spectrum: 3070vw, 3050w, 1960vw,br, 1885vw,br, 1815vw,br, 1730vw,br, 1610w, 1588w, 1572vw, 1370w, 1343m, 1313w, 1258s, 1208m, 1192w, 1187w, 1160vw, 1120vs,br, 1096s, 1075w, 1030w, 1000w, 975vw, 923vw, 890vw, 865vs, 860vs, 845m,sh, 839vs, 818w, 811w, 765w, 760w, 754m, 748m, 741m, 735w, 730m, 725s, 720w, 713w, 710m, 704vs, 700vs, 696vs, 690m,sh, 641e, 621vw, 612w, 551m, 547m, 529vs, 524s,sh, 510m, 502m, 492w,sh, 463vw, 449vw, 433w, 390vw cm^{-1} (Nujol mull). The product was fully characterised by ^{19}F, ^{1}H and ^{31}P *NMR spectroscopy (see text).*
^{1}H NMR spectrum (τ): 2-3 (mult, 30H), 4.96 (qn,1H) ($CDCl_3$ solution).

Reaction of $RhH(PF_3)(PPh_3)_3$ with $MeCO_2C{\equiv}CCO_2Me$

To $RhH(PF_3)(PPh_3)_3$ (1.304 g, 1.33 mmol) in benzene (15 cm^3) was added slowly at room temperature $MeCO_2C{\equiv}CCO_2Me$ (0.195 g, 1.37 mmol) in benzene (2 cm^3) and the red solution was stirred for 12 h. Hexane

(20 cm^3) was added and the solution placed in the refrigerator overnight to give yellow crystals of $\mathrm{Rh(PF_3)(PPh_3)_2[C(CO_2Me){=}CH(CO_2Me)]}$, (II), (1.040 g, 1.10 mmol; 83%) isolated as its hexane solvate (Found: C, 61.1; H, 5.1. $\mathrm{C_{48}H_{51}O_4F_3P_3Rh}$ requires: C, 61.02; H, 5.44%). The complex dissolves in benzene and removal of the solvent affords the benzene solvate, m.p. 110-140° C (dec) (Found: C, 62.8; H, 4.8. $\mathrm{C_{48}H_{43}O_4F_3P_3Rh}$ requires: C, 61.55; H, 4.62%). IR spectrum: 3055w, 1960vw,br, 1885vw,br, 1815vw,br, 1704s, 1688s, 1565m,br, 1369w,sh, 1318s, 1208s, 1188m, 1158s, 1150m,sh, 1100s, 1094m, 1072vw, 1035vw,sh, 1030w, 1019vw, 1003w, 975vw, 955vw, 925vw, 872m, 859s, 849vs, 834vs, 828m,sh, 758m, 753m, 748m, 742w, 724vw, 704m, 699s, 690m, 683s, 655vw, 620vw, 545w, 529vs, 527s, 513m, 500w, 493vw, 468w, 445w, 420w, 391w cm^{-1} (Nujol mull). ^{1}H NMR spectrum (τ): 2.1-3.0 (mult, 30H), 6.71 (s, 3H), 6.76 (s, 3H) ($\mathrm{CDCl_3}$ solution); 6.37 (s, 3H), 6.45 (s, 3H) ($\mathrm{C_6D_6}$ solution). The vinyl proton could not be detected.

Reaction of $\mathrm{RhH(PF_3)_2(PPh_3)_2}$ *with* $\mathrm{MeCO_2C{\equiv}CCO_2Me}$

To a suspension of $\mathrm{RhH(PF_3)_2(PPh_3)_2}$ (0.621 g, 0.77 mmol) in benzene (25 cm^3) at room temperature was added $\mathrm{MeCO_2C\ CCO_2Me}$ (0.110 g, 0.78 mmol) in benzene (10 cm^3). A very vigorous reaction occurred and the initially rather insoluble white solid dissolved instantly to form an orange solution. The reaction mixture was stirred for a further 2 h during which time the colour slightly changed to red. The solution was concentrated under vacuum (3 cm^3) and addition of hexane gave an orange sticky solid which was washed with hexane and pumped to dryness to give an orange powder (0.45 g), m.p. 125° C (softens at 78° C) (Found: C, 55.1; H, 4.7. $\mathrm{C_{42}H_{37}O_4F_3P_3Rh}$ requires: C, 58.74; H, 4.31%). The ^{19}F, ^{1}H and ^{31}P NMR spectra of the solid are discussed in the text. ^{1}H spectrum (τ): 2-3 (mult), 6.1 (s), 6.25 (s), 6.66 (s), 6.67 (s) ($\mathrm{CDCl_3}$ solution).

Reaction of $\mathrm{Rh(PF_3)(PPh_3)_2[C(CF_3){=}CH(CF_3)]}$ *with* $\mathrm{Bu^tBr}$

A mixture of $\mathrm{Rh(PF_3)(PPh_3)_2[C(CF_3){=}CH(CF_3)]}$ (0.156 g, 0.17 mmol) in $\mathrm{C_6D_6}$ (with a drop of $\mathrm{CFCl_3}$ added as ^{19}F NMR standard) and *t*-butyl bromide (0.040 g, 0.29 mmol) was sealed in an NMR tube and heated at 60° C for two days. The sealed tube was opened on the vacuum line and the volatiles condensed to another NMR tube. The residual yellow solid (0.11 g) was recrystallised from benzene/

hexane and was identified as *trans*-$RhBr(PF_3)(PPh_3)_2$ (IR). The ^1H and ^{19}F NMR spectra of the volatile fraction showed the presence of *iso*-butene and a mixture of *cis*- and *trans*-1,1,1,4,4,4-hexafluorobut-2-ene respectively.

Reaction of $Rh(PF_3)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)]$ *with* $CF_3C\equiv CCF_3$

A mixture of $Rh(PF_3)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)]$ (0.101 g, 0.12 mmol), $CF_3C\equiv CCF_3$ (0.020 g, 0.12 mmol) and benzene (10 cm^3) was shaken in a sealed tube for 12 h. The clear yellow solution was concentrated and a small amount of hexane was added. After 30 min some off-yellow solid was filtered off and more hexane was added to the filtrate and the solution placed in the refrigerator overnight. Yellow crystals of $Rh(PF_3)(PPh_3)_2[C(CO_2Me)=C(CO_2Me)-C(CF_3)=CH(CF_3)]$, (III), were obtained as its benzene solvate (0.056 g, 0.05 mmol; 47%), m.p. 90° C (dec) (Found: C, 56.3; H, 4.0. $C_{52}H_{43}O_4F_9P_3Rh$ requires C, 56.83; H, 3.91%). IR spectrum: 3055w, 1970vw,br, 1890vw,br, 1815vw,br, 1721s, 1690s, 1645vw, 1585vw, 1572vw, 1480m, 1365m, 1292m, 1260m, 1230vw, 1208m, 1185w, 1162vw, 1154s, 1145s, 1129m, 1098m, 1074vw, 1030vw, 1020vw, 1000vw, 995vw, 925w, 895vw, 881w. 865s, 859s, 851s, 839s, 835m, 756w,sh, 754m, 746m, 725vw, 703s, 698s, 689m, 678m, 543w, 525s, 513m, 500w, 464vw, 420vw, 390vw cm^{-1} (Nujol mull). The product was further identified by ^{19}F and ^1H NMR spectroscopy. ^1H NMR spectrum (τ): 6.57 (3H), 6.73 (3H) (C_6H_6 solution).

Reaction of $Rh(PF_3)(PPh_3)_2[C(CF_3)=CH(CF_3)]$ *with* $MeCO_2C\equiv CCO_2Me$

To $Rh(PF_3)(PPh_3)_2[C(CF_3)=CH(CF_3)]$ (0.088 g, 0.10 mmol) in benzene (containing a small amount of $CFCl_3$ as ^{19}F NMR standard) was added $MeCO_2C\equiv CCO_2Me$ (0.18 g, 0.12 mmol). A clear solution resulted and the reaction progress was followed by ^{19}F NMR spectroscopy. The formation of $Rh(PF_3)(PPh_3)_2[C(CO_2Me)=C(CO_2Me)(CF_3)=CH(CF_3)]$, (III), was established, but the reaction was slow and after two weeks some of the unreacted alkenyl rhodium starting material was detected in the ^{19}F NMR spectrum.

Reaction of $Rh(CO)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)]$ *with* $CF_3C\equiv CCF_3$

A mixture of $Rh(CO)(PPh_3)_2[C(CO_2Me)=CH(CO_2Me)]$ (2.394 g, 3.00 mmol), $CF_3C\equiv CCF_3$ (0.486 g, 3.00 mmol) and benzene (75 cm^3) reacted completely when shaken in a sealed tube for 2 days. The resulting yellow solution was transferred to a Schlenk tube and concentrated. Chromatographic separation on alumina (benzene eluant) followed by recrystallisation from benzene/hexane afforded $Rh(CO)(PPh_3)_2[C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)]$, (IV), as a yellow powder (2.389 g, 2.21 mmol; 83%), m.p. 152-156° C (dec) (Found: C, 58.9; H, 3.9. $C_{47}H_{37}F_6O_5P_2Rh$ requires: C, 58.75; H, 3.85%). IR spectrum: 3050vw, 1971s, 1962m,sh, 1717m, 1691s, 1687w,sh, 1663w, 1545w, 1367m, 1298s, 1274w, 1220w, 1208s, 1200w, 1180w, 1164w, 1155m, 1144s, 1120m, 1095m, 1077w, 1030w, 999w, 948vw, 890vw, 860vw, 831vw, 805vw, 790vw, 759w, 750m, 747m,sh, 724w, 708m, 703m,sh, 694m, 688w,sh, 680w,sh, 650w, 545w, 524vs, 509w, 475vw, 420vw cm^{-1} (Nujol mull). The product was also characterised by ^{19}F and ^1H NMR spectroscopy. ^1H NMR spectrum (τ): 2.10-2.76 (mult, 30H), 6.50 (s, 3H), 6.99 (s, 3H)($CDCl_3$ solution).

Reaction of $Rh(CO)(PPh_3)_2[C(CF_3)=CH(CF_3)]$ *with* $MeCO_2C{\equiv}CCO_2Me$

$Rh(CO)(PPh_3)_2[C(CF_3)=CH(CF_3)]$ (0.441 g, 0.53 mmol) in benzene (20 cm^3) and $MeCO_2C{\equiv}CCO_2Me$ (0.413 g, 2.90 mmol) were sealed in an ampoule and shaken for five days at room temperature. The colour of the solution changed from yellow to orange and then to red. Evaporation to dryness followed by extraction with ether and addition of hexane to a concentrated ether solution gave (IV), whose ^{19}F NMR spectrum was identical to that mentioned above.

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