

Photochemical displacement of co-ordinated ethene from [Rh(η^5 -C₅H₅)(PPh₃)(C₂H₄)]

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The rhodium (triphenylphosphine)(ethene) complex [Rh(η^5 -C₅H₅)(PPh₃)(C₂H₄)], was synthesized by reaction of [Rh(C₂H₄)₂Cl]₂ with triphenylphosphine and thallium cyclopentadienide. Like in [Rh(η^5 -C₅H₅)(PMe₃)(C₂H₄)], the co-ordinated ethene ligand may be displaced photochemically. Photoreaction of [Rh(η^5 -C₅H₅)(PPh₃)(C₂H₄)] with SiR₃H (R = Prⁱ or Et) and hexafluorobenzene yielded [Rh(η^5 -C₅H₅)(PPh₃)(SiR₃)H] and [Rh(η^5 -C₅H₅)(PPh₃)(η^2 -C₆F₆)], respectively. Oxidative addition of the C–H bonds of partially fluorinated arenes, C₆F₅H and 1,3-C₆F₂H₄, was demonstrated by NMR spectroscopy to result in formation of [Rh(η^5 -C₅H₅)(PPh₃)(R)H] (R = C₆F₅ or 2,6-C₆F₂H₃). Oxidative addition of benzene may be detected following photolysis in benzene–thf mixtures at 233 K, but the product decomposes on warming. The molecular structure of [Rh(η^5 -C₅H₅)(PPh₃)(SiPrⁱ₃)H] has been determined crystallographically. The disorder of the isopropyl groups was modelled with two orientations of the SiPrⁱ₃ with equal occupancies. The Rh–Si bond length is 2.386(2) Å, the first example of measurement of such a distance at cyclopentadienyl rhodium(III).

Photochemical displacement of co-ordinated ethene from the trimethylphosphine complex, [Rh(η^5 -C₅H₅)(PMe₃)(C₂H₄)], has proved to be a valuable method of achieving oxidative addition of carbon–hydrogen bonds, and of co-ordinating unusual ligands such as hexafluorobenzene at the metal.^{1–5} In parallel studies of the C₅Me₅ analogues, two additional entry routes to the [Rh(η^5 -C₅Me₅)(PMe₃)] intermediate have been employed, photolysis of the dihydride complex and thermal displacement of benzene from the phenyl hydride complex.^{2–6} The need to generate the 16-electron intermediate in order to effect oxidative addition, *i.e.* the need for a dissociative mechanism, is emphasised by studies involving matrix isolation^{7–10} laser flash photolysis,^{11–15} and quantum yield measurements^{16,17} on these complexes and related carbonyl systems such as [Rh(η^5 -C₅H₅)(CO)₂] and [Rh(η^5 -C₅H₅)(CO)(C₂H₄)]. Electron-releasing ligands such as PMe₃ and C₅Me₅ are not essential for C–H and Si–H bond activation, as is evident from the reactivity of the carbonyl complexes, but they certainly influence the stability of the products {compare [Rh(η^5 -C₅H₅)(CO)(alkyl)H] and [Rh(η^5 -C₅Me₅)(PMe₃)(alkyl)H]}.^{6,11} The comparisons between the Rh(η^5 -C₅H₅) and Rh(η^5 -C₅Me₅) systems show that the electron-releasing abilities of the ligands influence the position of equilibrium between Rh(η^2 -arene) and Rh^{III}(aryl)H species in those cases where such equilibria can be observed [*e.g.* arene = C₆H₄(CF₃)₂-1,4 or naphthalene].^{2,4}

In this study we report that the triphenylphosphine complex [Rh(η^5 -C₅H₅)(PPh₃)(C₂H₄)] **1** can be employed as a precursor for Si–H bond activation and for co-ordination of hexafluorobenzene. We also present NMR evidence for C–H bond activation of partially fluorinated arenes. These results may also be compared with studies of related triphenylphosphine complexes, especially [Ir(η^5 -C₅H₅)(PPh₃)(C₂H₄)] and [Rh(η^5 -C₅Me₅)(PPh₃)H₂].^{18,19}

Results

Synthesis of [Rh(η^5 -C₅H₅)(PPh₃)(C₂H₄)] **1**

The synthesis of complex **1** from [Rh(MeCOCHCOMe)(C₂H₄)₂] has been reported previously.^{20a} The original NMR

spectrum was later supplemented by a ¹⁰³Rh–¹H two-dimensional spectrum.^{20b} Complex **1** was also observed as a product of photolysing [Rh(η^5 -C₅H₅)(C₂H₄)₂] in the presence of PPh₃.²¹ We synthesized **1** by reaction of [Rh(C₂H₄)₂Cl]₂ with 2 equivalents of PPh₃, and subsequent reaction with Tl(η^5 -C₅H₅), a similar procedure to that used for [Rh(η^5 -C₅H₅)(PMe₃)(C₂H₄)].¹⁵ The complex exhibits the expected doublet in the ³¹P–{¹H} NMR spectrum. The value of *J*_{RhP} of 209 Hz provides a marker for rhodium(I) complexes of this type.

Photochemical reactions with trialkylsilanes, SiR₃H (R = Prⁱ or Et)

Irradiation of complex **1** in triisopropylsilane at 283 K generates a single stable product identified as [Rh(η^5 -C₅H₅)(PPh₃)(SiPrⁱ₃)H] **2** on the basis of the spectra described below. The ¹H NMR spectrum in the high field region shows a hydride resonance as a doublet of doublets at δ –13.60 (*J*_{PH} = 29.9, *J*_{RhH} = 28.2 Hz). In the low field region there are resonances for the η^5 -C₅H₅ ligand at δ 5.10, the PPh₃ ligand at δ 7.76–7.70 and two resonances at δ 1.14 (pseudo t) and 0.85 (septet) which are assigned to the CH₃ and CH groups of the isopropyl group respectively.† The ³¹P–{¹H} NMR spectrum shows a doublet at δ 56.8 (*J*_{RhP} = 185 Hz). The photochemical synthesis of the PMe₃ analogue of **2** from [Rh(η^5 -C₅H₅)(PMe₃)(η^2 -C₆F₆)] has been described previously.³

Irradiation of complex **1** in triethylsilane at 283 K proceeds similarly to generate [Rh(η^5 -C₅H₅)(PPh₃)(SiEt₃)H] **3** as the sole product (see Experimental section for NMR data). The ¹H NMR spectrum shows a triplet at δ 1.07 for the CH₃ groups and multiplets at δ 0.68 and 0.56 for the CH₂ protons. On heating in C₆D₆ the multiplets at δ 0.68 and 0.56 first coalesced (*T*_c = 316 K) and then sharpened to form one poorly resolved quartet at 341 K. This behaviour was reversed on cooling and did not affect the other resonances in the spectrum. The coalescence temperature and low-temperature limiting NMR data yield, *via*

† The pseudo-triplet splitting of the methyl resonances arises from an overlapping pair of doublets. Complex **2** is chiral at rhodium and the methyl groups are prochiral and therefore inequivalent {compare [Rh(η^5 -C₅Me₅)Cl(CO)(SbPrⁱ₃)]}.²²

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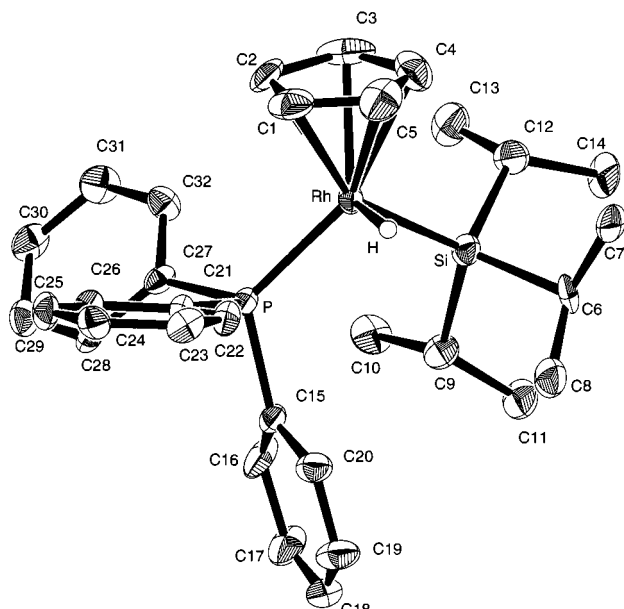


Fig. 1 An ORTEP²³ diagram (30% ellipsoids) of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{-(PPh}_3\text{)}_3\text{(SiPr}_3\text{)}_3\text{H}] \mathbf{2}$. Only one of two disordered sets of isopropyl groups is shown for simplicity and only the hydridic hydrogen is shown

equation (1), an estimate of the free energy of activation for the

$$\Delta G^\ddagger = -RT_c \ln \pi h \Delta \nu_o / k_B T_c \sqrt{2} \quad (1)$$

exchange process, $\Delta G^\ddagger = 66 \text{ kJ mol}^{-1}$ (the symbols have their standard meanings). The inequivalence of the two CH_2 resonances at room temperature may be attributed to restricted rotation about the Si–C bonds in this congested molecule.

Crystal structure of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3(\text{SiPr}_3)_3\text{H}] \mathbf{2}$

Crystals of complex **2** were grown from toluene at 253 K and investigated by X-ray diffraction. The resulting data confirm the identity of **2** and provide useful data in spite of complications of disorder of the isopropyl groups. The structure (Fig. 1, Table 1) reveals a Rh–Si bond length of 2.386(2) Å and a Rh–P bond length of 2.231(2) Å. The hydride was located in a difference map, yielding a Rh–H bond length of 1.50(9) Å after refinement. Two orientations of the SiPr_3 group were refined with equal occupancy. One orientation places the Si–C bonds in an approximately staggered orientation with respect to Rh–P, Rh–H and Rh– C_5H_5 bonds. The second orientation lies *ca.* 60° with respect to the first and eclipses the bonds to rhodium (Fig. 2).

Although the $\text{Rh}(\eta^5\text{-C}_5\text{R}_3)(\text{SiR}'_3)$ functionality has been investigated extensively,^{11,16,17,24,25a} the only crystal structure reported is for the rhodium(v) complex $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{-(SiEt}_2)_2\text{H}_2]$.^{25a} This neutron structure gives a Rh–Si bond length of 2.379(2) Å and a mean Rh–H distance of 1.581(3) Å. The crystal structure of an octahedral rhodium(III) metallacyclic complex, $[\text{Rh}(\text{PMe}_3)_3(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)\text{H}]$, gives a mean Rh–Si distance of 2.386(2) Å.^{25b} Further comparison can be gained from the four-co-ordinate rhodium(I) complex $[\text{Rh}(\text{PMe}_3)_3(\text{SiPh}_3)]$ with a Rh–Si distance of 2.317(1) Å.^{25c}

Photochemical reaction of complex **1**

With hexafluorobenzene. Irradiation of complex **1** in hexafluorobenzene at 283 K yielded, on purification, a lemon-yellow solid which was characterised by ³¹P and ¹⁹F NMR spectroscopy. The ³¹P–{¹H} NMR spectrum shows a doublet of triplets at δ 45.8 with $J_{\text{RhP}} = 203$ and $J_{\text{FP}} = 54$ Hz, which is indicative of a rhodium(I) complex in which the ³¹P nucleus is also coupled to two equivalent fluorine nuclei. The ¹⁹F NMR spectrum contains three multiplets at δ –147.1, –158.2 and

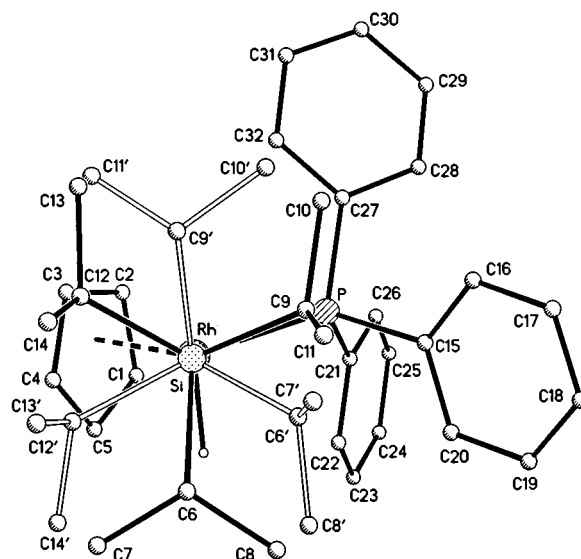


Fig. 2 Diagram showing the disorder in the isopropyl groups of complex **2**, looking down the Si–Rh vector. One set of bonds of the isopropyl group is shown in black, the other set as open lines

Table 1 Selected bond lengths (Å) and angles (°) for $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)\text{-(PPh}_3\text{)}_3\text{(SiPr}_3\text{)}_3\text{H}] \mathbf{2}$

Rh–C(1)	2.278(9)	P–Rh–C(1)	104.4(3)
Rh–C(2)	2.272(9)	P–Rh–C(2)	100.8(3)
Rh–C(3)	2.270(10)	P–Rh–C(3)	129.0(4)
Rh–C(4)	2.204(10)	P–Rh–C(4)	160.0(3)
Rh–C(5)	2.280(10)	P–Rh–C(5)	134.0(3)
Rh–Si	2.386(2)	P–Rh–Si	102.08(8)
Rh–P	2.231(2)	Si–Rh–C(1)	153.6(3)
Si–C(6')	1.854(11)	Si–Rh–C(2)	137.3(4)
Si–C(9')	1.927(12)	Si–Rh–C(3)	103.0(3)
Si–C(12')	1.930(12)	Si–Rh–C(4)	95.9(3)
Si–C(6)	1.940(12)	Si–Rh–C(5)	120.6(3)
Si–C(9)	1.933(12)	C(6')–Si–Rh	116.5(4)
Si–C(12)	1.885(12)	C(9')–Si–Rh	113.3(5)
P–C(15)	1.842(8)	C(12')–Si–Rh	105.6(5)
P–C(21)	1.847(7)	C(6)–Si–Rh	112.1(5)
P–C(27)	1.833(8)	C(9)–Si–Rh	117.7(5)
Rh–H	1.50(9)	C(12)–Si–Rh	111.4(5)

–173.9 with integrations in the ratio 1:1:1 enabling the complex to be identified as $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^2\text{-C}_6\text{F}_6)] \mathbf{4}$ by comparison with the PMe_3 analogue.³

With partially fluorinated arenes. Complex **1** was irradiated in pentafluorobenzene at *ca.* 273 K in an ampoule. The solution was pumped to dryness and redissolved in $[\text{}^2\text{H}_8]\text{toluene}$ for NMR spectroscopy. The ¹H NMR spectrum shows a hydride resonance for the product with a doublet of doublets pattern characteristic of coupling to rhodium and phosphorus. The ³¹P–{¹H} NMR spectrum shows a doublet resonance at δ 57.8 with $J_{\text{RhP}} = 155$ Hz which is indicative of a rhodium(III) complex. The ¹⁹F NMR spectrum contains three signals at δ –104.1, –164.6 and –165.8 with integrations in the ratio 2:1:2. The product is readily assigned as the C–H activation product $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_6\text{F}_5)\text{H}] \mathbf{5}$ and may be compared to its PMe_3 analogue.⁵ Attempts to isolate analytically pure material did not prove successful.

Irradiation of complex **1** in 1,3-difluorobenzene was investigated in a similar way. After photolysis, the high field region of the ¹H NMR spectrum contains a hydride resonance at δ –11.51 which appears as a doublet of doublets, and in the low field region there were resonances at δ 6.60 and 6.49. The ³¹P–{¹H} NMR spectrum shows a doublet resonance at δ 57.4 ($J_{\text{RhP}} = 159$ Hz) indicative of a rhodium(III) complex. The ¹⁹F NMR spectrum contains one signal at δ –76.15. The spectra

Table 2 The NMR spectroscopic data [δ (J/Hz)] for products of photolysis of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ in benzene–thf mixtures at 233 K

	Product A	Product B
^1H , hydride	–12.90 (dd, $J_{\text{PH}} = 41.9$, $J_{\text{RH}} = 27.1$)	–13.70 (ddd, $J_{\text{PH}} = 34.9$, $J_{\text{RH}} = 27.9$, $J_{\text{HH}} = 6.1$)
^1H , C_5H_5	5.11 (s)	5.21 (s)
^{31}P - $\{^1\text{H}\}$	58 (d, $J_{\text{RHP}} = 166$)	63 (d, $J_{\text{RHP}} = 165$)

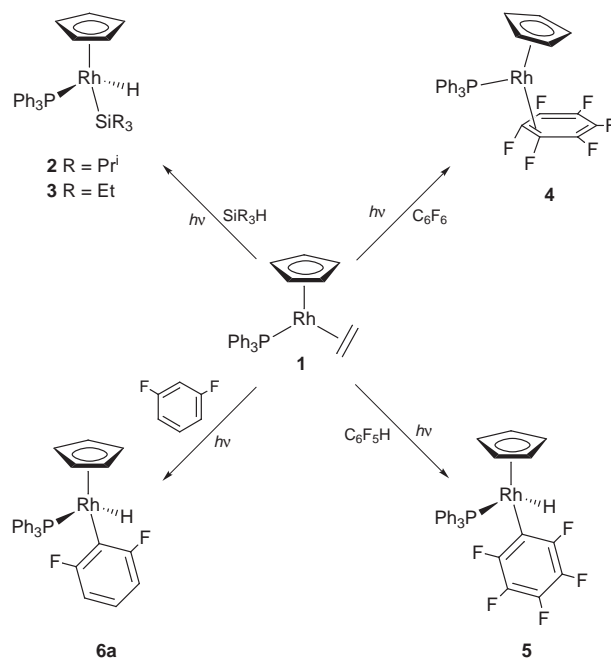
clearly identify the product as a single isomer of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_6\text{F}_2\text{H}_3)\text{H}]$ **6a**. The equivalence of the fluorine nuclei excludes the 2,4- $\text{C}_6\text{F}_2\text{H}_3$ isomer from consideration. The low field shift of the ^{19}F resonance is characteristic of *ortho* substitution and a clear indicator that the 2,6- $\text{C}_6\text{F}_2\text{H}_3$ isomer has been generated (*cf.* the PMe_3 analogue).⁵ The product was not isolated.

The reaction of complex **1** with 1,3-difluorobenzene was also investigated by photolysis of a $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ solution at 233 K. Spectra were measured at the same temperature and in 10 K steps up to room temperature. In addition to **6a**, three further rhodium(III) species were generated. One of them was also formed in a control experiment with no fluoroarene (species B, see below) and was converted at room temperature into **6a**. The remaining two species have very similar NMR parameters to those of **6a** and are tentatively assigned to $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(2,4\text{-C}_6\text{F}_2\text{H}_3)\text{H}]$ **6b** and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(3,5\text{-C}_6\text{F}_2\text{H}_3)\text{H}]$ **6c**. Related behaviour was observed for the PMe_3 analogue, but in that case the 2,4 and 3,5 isomers converted into the thermodynamic 2,6 isomer below room temperature.⁵

With benzene. Irradiation of complex **1** in benzene at 283 K caused considerable precipitation but generated no products stable enough for NMR observation in C_6D_6 solution. In order to observe labile products, samples of **1** dissolved in mixtures of deuteriated and undeuteriated benzene and thf (1:1 benzene–thf by volume) were irradiated at 233 K in NMR tubes and NMR spectra were acquired *in situ* at the same temperature. Hydride resonances were invariably observed in the ^1H NMR spectrum, providing evidence that the photoreactions are complicated by H/D exchange, as has been observed with the iridium analogue of **1**.¹⁸ Two species were observed on irradiation of **1** in a fully deuteriated benzene–thf mixture. Species A has one cyclopentadienyl resonance and a hydride resonance in the ^1H NMR spectrum and a doublet characteristic of Rh^{III} in the ^{31}P NMR spectrum (Table 2). Species B has similar characteristics, but an extra doublet splitting in the hydride resonance. On photolysis of **1** in $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ alone at 233 K, species B is retained but A is eliminated. All the photoproducts disappear on warming to 300 K. Species A is tentatively assigned as the product of C–H activation of benzene, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Ph})\text{H}]$. Species B has not been identified conclusively, but cyclometallation at triphenylphosphine can be excluded since that would result in a large high field shift of the ^{31}P NMR resonance.

Discussion

Irradiation of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)(\text{C}_2\text{H}_4)]$ in solution provides a convenient source of the unsaturated fragment $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)]$, which reacts by oxidative addition with the C–H bonds of aromatic hydrocarbons and the Si–H bonds of trialkylsilanes.^{2–5,26} With naphthalene and with hexafluorobenzene, η^2 co-ordination is observed.^{1,2,4} In contrast, the solution photochemistry of $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{C}_2\text{H}_4)]$, both for $\text{R} = \text{Me}$ and Ph , is dominated by intramolecular C–H activation of co-ordinated ethene.^{18,27} Activation of benzene is not observed at iridium when $\text{R} = \text{Me}$ and represents only about 12% of the products when $\text{R} = \text{Ph}$. The current work shows that



Scheme 1 Photochemical reactions of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ **1**

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ **1** undergoes photochemical displacement of ethene and yields products of Si–H activation and C_6F_6 co-ordination (Scheme 1) similar to those obtained from its PMe_3 analogue.^{1,3,26} Carbon–hydrogen bond activation is more limited, however. Partially fluorinated benzenes react to form C–H activation products which may be observed at room temperature: the C–F bonds probably enhance the strength of the rhodium–carbon bonds (compare the PMe_3 analogues).⁵ The product of reaction with benzene $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Ph})\text{H}]$ may be observed at low temperature, but decomposes on warming to room temperature. It appears to be even less stable than its $\eta^5\text{-C}_5\text{Me}_5$ analogue which has been reported previously.¹⁹ The latter, $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)(\text{Ph})\text{H}]$, undergoes reductive elimination of benzene *ca.* 1100 times faster than $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)(\text{Ph})\text{H}]$ at 296 K.¹⁹ Complex **1** shows no signs of undergoing photoinduced cyclometallation. The lack of cyclometallation is in keeping with the properties of $[\text{Ir}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ ¹⁸ and of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{H}_2]$,¹⁹ but contrasts with $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{H}_2]$.²⁸ The destabilisation of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{Ph})\text{H}]$ compared with its PMe_3 analogue contrasts with the stability of the $\text{Rh}^{\text{I}}(\eta^2\text{-C}_6\text{F}_6)$ complexes both with PPh_3 and PMe_3 coligands. Complex **4** joins the growing number of complexes of $\eta^2\text{-C}_6\text{F}_6$.^{1,3,29,30}

Conclusion

Photolysis of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ provides an effective method of forming Si–H activation products, or of substituting C_2H_4 by hexafluorobenzene, but only C–H bond activation products from fluoroaromatics are sufficiently stable for room temperature observation. The determination of the Rh–Si bond length of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SiPr}_3)\text{H}]$ is the first for a cyclopentadienyl rhodium(III) complex, but the difference in bond length compared to that of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)(\text{SiEt}_3)_2\text{H}_2]$ is barely significant.^{25a}

Experimental

All operations were performed under a nitrogen or argon atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a glove-box. Benzene was distilled from a dark purple solution of benzophenone ketyl. $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$, Benzene, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ toluene and $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ thf were all distilled from dark purple solutions of benzophenone ketyl and stored in ampoules

with Teflon seals. The complex $[\{\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}\}_2]$ was synthesized by the literature procedure.³¹ Pentafluorobenzene, 1,3-difluorobenzene and hexafluorobenzene from Aldrich were dried over molecular sieves. Triethylsilane and trisopropylsilane from Flurochem Ltd. were used without further purification. All NMR spectra were recorded on Bruker MSL300 or AMX500 spectrometers in tubes fitted with Young's polytetrafluoroethylene (ptfe) stopcocks. All ^1H and ^{13}C chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced using the chemical shifts of residual protio solvent resonances (benzene, δ 7.13; toluene, δ 2.1; thf, δ 3.7). The ^{19}F NMR spectra were referenced to external CFCl_3 , ^{31}P NMR spectra to external H_3PO_4 . Solutions were irradiated in Pyrex ampoules fitted with ptfe taps with an Applied Photophysics 250 W high pressure mercury arc or with an ILC 300 W xenon arc fitted with a mirror reflecting 250–400 nm. Mass spectra were measured with a VG Autospec instrument.

Syntheses

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ 1. An ampoule was charged with $[\{\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}\}_2]$ (1.38 g, 3.56 mmol) and thf (30 mL). To this solution was added PPh_3 (1.89 g, 7.20 mmol) and the resulting mixture stirred at ambient temperature for 2 h. The salt $\text{Tl}(\text{C}_5\text{H}_5)$ (2.38 g, 8.83 mmol) was added to the mixture and stirring continued for 2 h. All volatiles were distilled from the reaction vessel, the residue was dissolved in toluene and the solution was filtered. The filtrate was eluted through an alumina column with further toluene. All volatiles were removed to give complex **1** as an orange crystalline solid in 69.7% yield, based on rhodium. NMR (C_6D_6 , 296 K): ^1H , δ 7.63–6.75 (m, 15 H, PPh_3), 5.06 (s, 5 H, C_5H_5), 2.83 (m, 2 H, C_2H_4) and 1.31 (m, 2 H, C_2H_4); ^{31}P - $\{^1\text{H}\}$, δ 58.9 (d, $J_{\text{RHP}} = 209$ Hz, PPh_3); ^{13}C - $\{^1\text{H}\}$, δ 133.8 [d, $J_{\text{PC}} = 11$, $\text{P}(\text{C}_6\text{H}_5)_3$, *ortho*], 129.8 [d, $J_{\text{PC}} = 2$, $\text{P}(\text{C}_6\text{H}_5)_3$, *para*], 127.3 [d, $J_{\text{PC}} = 10$, $\text{P}(\text{C}_6\text{H}_5)_3$, *meta*], 86.7 (dd, $J_{\text{PC}} \approx J_{\text{RHC}} = 3$, C_5H_5) and 26.6 (dd, $J_{\text{RHC}} = 15$, $J_{\text{PC}} = 2$ Hz, C_2H_4) (Found: C, 65.09; H, 5.26. Calc. for $\text{C}_{25}\text{H}_{24}\text{PRh}$: C, 65.52; H, 5.24%).

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SiPr}_3\text{H})]$ 2. A degassed solution of complex **1** (43 mg, 93.9 μmol) in neat SiPr_3H (3 mL) was irradiated for 4 h at 283 K. All volatiles were removed under vacuum to give a clear yellow oil (^1H NMR spectroscopy was used to confirm that the oil contained no starting material). The oil was dissolved in neat toluene and eluted through an alumina column. Toluene was distilled from the eluent *in vacuo* to give a clear yellow oil, which was dissolved in Et_2O and again all volatiles were removed giving a yellow solid. Complex **2** was isolated as a dark yellow crystalline solid in 60% yield, based on rhodium. NMR ($[\text{C}_6\text{D}_6]$ toluene, 296 K): ^1H , δ 7.76–7.00 (m, 15 H, PPh_3), 5.10 (t, $J_{\text{RHH}} = J_{\text{PH}} = 0.5$, 5 H, C_5H_5), 1.14 [t, $J_{\text{HH}} = 7.3$, 18 H, $\text{CH}(\text{CH}_3)_2$], 0.85 [septet, $J_{\text{HH}} = 7.3$, 3 H, $\text{CH}(\text{CH}_3)_2$] and -13.60 (dd, $J_{\text{PH}} = 29.9$, $J_{\text{RHH}} = 28.2$ Hz, 1 H, RhH); ^{31}P - $\{^1\text{H}\}$, δ 56.8 (d, $J_{\text{RHP}} = 185$ Hz, PPh_3); ^{29}Si , δ 47.4 (dd, $J_{\text{PSi}} = 31.6$, $J_{\text{RHSi}} = 9.8$ Hz); ^{13}C - $\{^1\text{H}\}$, δ 134.1 [d, $J_{\text{PC}} = 11$, $\text{P}(\text{C}_6\text{H}_5)_3$, *ortho*], 129.1 [d, $J_{\text{PC}} = 2$, $\text{P}(\text{C}_6\text{H}_5)_3$, *para*], 127.0 [d, $J_{\text{PC}} = 9$, $\text{P}(\text{C}_6\text{H}_5)_3$, *meta*], 89.2 (t, $J_{\text{PC}} = J_{\text{RHC}} = 3$ Hz, C_5H_5), 21.0 [s, $\text{CH}(\text{CH}_3)_2$], 20.4 [s, $\text{CH}(\text{CH}_3)_2$] and 18.8 [s, $\text{CH}(\text{CH}_3)_2$] (Found: C, 65.30; H, 7.76. Calc. for $\text{C}_{32}\text{H}_{42}\text{PRhSi}$: C, 65.3; H, 7.14%). Electron-impact mass spectrum: m/z 545 ($M^+ - 43$, 3), 501 ($M^+ - 87$, 1), 458 ($M^+ - 130$, 1) and 430 $[\text{Rh}(\text{C}_5\text{H}_5)(\text{PPh}_3)^+$, 100%].

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{SiEt}_3\text{H})]$ 3. A degassed solution of $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_2\text{H}_4)]$ **1** (37 mg, 80.8 μmol) in neat SiEt_3H (2 mL) was irradiated for 5 h at 283 K. All volatiles were removed under vacuum to give a clear yellow oil (^1H NMR spectroscopy was used to confirm that the oil contained no starting material). The oil was dissolved in neat toluene and eluted dropwise through an alumina column. Toluene was distilled from the eluent *in vacuo* to give a clear yellow oil, which

was dissolved in Et_2O and again all volatiles were removed to give complex **3** as a yellow oil isolated in 68% yield, based on rhodium. NMR (C_6D_6 , 296 K): ^1H , δ 7.70–6.90 (m, 15 H, PPh_3), 5.10 (s, C_5H_5), 1.07 (t, $J_{\text{HH}} = 7.7$, 9 H, CH_2CH_3), 0.68 (m, $J_{\text{HH}} = 7.7$, 3 H, CH_2CH_3), 0.56 (m, $J_{\text{HH}} = 7.7$, 3 H, CH_2CH_3) and -13.49 (t, $J_{\text{PH}} = J_{\text{RHH}} = 29.1$ Hz, 1 H, RhH); ^{31}P - $\{^1\text{H}\}$, δ 59.6 (d, $J_{\text{RHP}} = 188$, PPh_3); ^{29}Si , δ 36.1 (dd, $J_{\text{PSi}} = 28.1$, $J_{\text{RHSi}} = 12.7$ Hz); ^{13}C - $\{^1\text{H}\}$, δ 134.9 [d, $J_{\text{PC}} = 12$, $\text{P}(\text{C}_6\text{H}_5)_3$, *ortho*], 130.2 [s, $\text{P}(\text{C}_6\text{H}_5)_3$, *para*], 128.5 [d, $J_{\text{PC}} = 10$, $\text{P}(\text{C}_6\text{H}_5)_3$, *meta*], 90.1 (t, $J_{\text{PC}} = J_{\text{RHC}} = 3$ Hz, C_5H_5), 13.4 (s, CH_2CH_3) and 10.7 (s, CH_2CH_3). Electron-impact mass spectrum: m/z 518 (M^+ , 1), 487 ($M^+ - 31$, 1), 458 ($M^+ - 60$, 1) and 430 $[\text{Rh}(\text{C}_5\text{H}_5)(\text{PPh}_3)^+$, 100%].

The NMR spectra of complex **3** were monitored as a function of temperature using the following method. An NMR tube was charged with **3** (25 mg, 45.8 μmol), C_6D_6 (0.5 mL) and $\text{C}_6\text{D}_5\text{CD}_3$ (0.1 mL) (used as chemical shift calibrant). The tube was placed in the probe of an NMR spectrometer and ^1H NMR spectra were acquired at temperatures in the range 296–341 K. To achieve thermal equilibrium the solution was maintained at the desired temperature for at least 10 min prior to each acquisition.

$[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^2\text{-C}_6\text{F}_6)]$ 4. An ampoule was charged with complex **1** (60 mg, 0.13 mmol) and neat C_6F_6 (2 mL). The contents were degassed and then warmed to 35 $^\circ\text{C}$ in order to dissolve **1** completely. This solution was irradiated for 6 h at 283 K. All volatiles were removed *in vacuo* to give a dark brown oily residue, which was dissolved in toluene and loaded onto an alumina column. The column was first eluted with neat toluene to remove unchanged starting material. Subsequent elution with toluene–thf (90:10 v/v) afforded a bright yellow eluent from which all volatiles were removed to give a lemon yellow solid. Recrystallisation from the minimum volume of toluene and hexane (2 mL) at -20 $^\circ\text{C}$ yielded yellow needle crystals of **4** in 29% yield, based on rhodium. NMR ($[\text{C}_6\text{D}_6]$ toluene, 296 K): ^1H , δ 7.72–6.92 (m, 15 H, PPh_3) and 4.39 (t, $J_{\text{PH}} = 0.5$ Hz, 5 H, C_5H_5); ^{31}P - $\{^1\text{H}\}$, δ 45.8 (dt, $J_{\text{RHP}} = 203.1$, $J_{\text{FP}} = 54.4$ Hz, PPh_3); ^{19}F , δ -147.14 (m, 2 F, F^2), -158.20 (m, 2 F, F^1) and -173.86 (m, 2 F, F^3); F^1 represents fluorine atoms bound to the co-ordinated carbon atoms, F^2 and F^3 are labelled sequentially; ^{13}C - $\{^1\text{H}\}$ (C_6D_6), δ 135.9 [d, $J_{\text{PC}} = 9.7$, $\text{P}(\text{C}_6\text{H}_5)_3$, *ortho*], 131.2 [d, $J_{\text{PC}} = 2.4$, $\text{P}(\text{C}_6\text{H}_5)_3$, *para*], 128.9 [d, $J_{\text{PC}} = 7.3$, $\text{P}(\text{C}_6\text{H}_5)_3$, *meta*], 90.6 (dd, $J_{\text{PC}}/J_{\text{RHC}} = 4.5$, 3.1 Hz, C_5H_5) (Found: C, 56.71; H, 3.34. Calc. for $\text{C}_{29}\text{H}_{20}\text{F}_6\text{PRh}$: C, 56.49; H, 3.25%). Electron-impact mass spectrum: m/z 597 ($M^+ - 19$, 1), 429 ($M^+ - 186$, 15) and 168 $[\text{Rh}(\text{C}_5\text{H}_5)^+$, 100%].

Spectroscopic investigations of photoreactions

With pentafluorobenzene and 1,2-difluorobenzene. In a typical experiment an ampoule was charged with complex **1** (*ca.* 30 mg, 66 μmol) and fluoroarene (2 mL). The resulting solution was thoroughly degassed and irradiated for 8 h at *ca.* 273 K. The solution darkened and some precipitation occurred. The volatiles were removed *in vacuo* and $[\text{C}_6\text{D}_6]$ toluene was added to the residue. The suspension was transferred to an NMR tube through a filter. Spectroscopic data for $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{C}_6\text{F}_5)\text{H}]$ **5**. NMR ($[\text{C}_6\text{D}_6]$ toluene, 296 K), ^1H , δ 7.40–6.90 (m, 15 H, PPh_3), 5.04 (t, $J_{\text{RHH}} = J_{\text{PH}} = 0.8$, 5 H, C_5H_5) and -11.50 (dd, $J_{\text{PH}} = 43.9$, $J_{\text{RHH}} = 21.6$ Hz, RhH); ^{31}P - $\{^1\text{H}\}$, δ 57.8 (d, $J_{\text{RHP}} = 154.9$ Hz, PPh_3); ^{19}F , δ -104.10 (d, $J_{\text{FF}} = 30.5$, 2 F, F_{ortho}), -164.59 (t, $J_{\text{FF}} = 21$, 1 F, F_{para}) and -165.80 (t, $J_{\text{FF}} = 23$ Hz, 2 F, F_{meta}); ^{13}C - $\{^1\text{H}\}$, δ 133.2 [d, $J_{\text{PC}} = 11$, $\text{P}(\text{C}_6\text{H}_5)_3$, *ortho*], 129.6 [s, $\text{P}(\text{C}_6\text{H}_5)_3$, *para*], 127.5 [d, $J_{\text{PC}} = 11$, $\text{P}(\text{C}_6\text{H}_5)_3$, *meta*] and 88.2 (t, $J_{\text{PC}} = J_{\text{RHC}} = 3$ Hz, C_5H_5); electron-impact mass spectrum m/z 598 (M^+ , 0.4), 458 ($M^+ - 140$, 1), 430 ($M^+ - 168$, 56) and 168 $[\text{Rh}(\text{C}_5\text{H}_5)^+$, 100%].

Spectroscopic data for $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(2,6\text{-C}_6\text{F}_2\text{H}_3)\text{H}]$ **6a**: NMR ($[\text{C}_6\text{D}_6]$ toluene, 296 K), ^1H , δ 7.50–6.90 (m, 15 H,

Table 3 Crystallographic parameters for complex 2

Empirical formula	C ₃₂ H ₄₂ PRhSi
<i>M</i>	588.63
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4
<i>a</i> /Å	10.596(4)
<i>b</i> /Å	16.730(6)
<i>c</i> /Å	17.049(6)
β /°	105.76(3)
<i>U</i> /Å ³	2908.4(17)
<i>D</i> _c /g cm ⁻³	1.344
μ (Mo-K α)/mm ⁻¹	0.702
<i>T</i> /K	220(2)
No. reflections measured	6694
No. independent reflections	5111 (<i>R</i> _{int} = 0.1697)
Data/restraints/parameters	5111/249/398
Reflection to parameter ratio	12.84
Residuals [<i>F</i> > 4 σ (<i>F</i>)]	<i>R</i> 1 = 0.0677 (3134 data)
Residuals (all data, <i>F</i> ²)	<i>wR</i> 2 = 0.1849

PPh₃, 6.60 (m, 1 H, H_{para}), 6.49 (t, *J* = 7.4, 2 H, H_{meta}), 5.13 (s, 5 H, C₆H₅) and -11.51 (dd, *J*_{PH} = 40.4, *J*_{RhH} = 20.9 Hz, 1 H, RhH); ³¹P-¹H}, δ 57.4 (d, *J*_{RhP} = 158.9 Hz, PPh₃); ¹⁹F, -76.15 (s, 2 F, F_{ortho}); ¹³C-¹H}, δ 168.2 (ddt, *J*_{FC} = 228, 18, *J*_{PC} = *J*_{RhC} = 2, C₆F₂H₃, CF), 133.5 [d, *J*_{PC} = 11.4, P(C₆H₅)₃, *ortho*], 129.3 [s, P(C₆H₅)₃, *para*], 127.4 [d, *J*_{PC} = 10, P(C₆H₅)₃, *meta*], 123 (t, *J*_{FC} = 10, C₆F₂H₃, CH, *para*), 108.7 (dd, *J*_{FC} = 35, 3, C₆F₂H₃, CH, *meta*) and 88.6 (t, *J*_{PC} = *J*_{RhC} = 3 Hz, C₅H₅).

Low temperature irradiation of complex 1 in [²H₈]thf in the presence of an excess 1,3-C₆F₂H₄ was performed as for the reaction with benzene (see below). Spectroscopic data for [Rh(η^5 -C₅H₅)(PPh₃)(2,4-C₆F₂H₃)H] **6b** and [Rh(η^5 -C₅H₅)(PPh₃)(3,5-C₆F₂H₃)H] **6c**. We cannot distinguish which resonance belongs to **6b** and which to **6c**. NMR ([²H₈]thf, 296 K): ¹H, δ -11.62 (*J*_{PH} = 36, *J*_{RhH} = 27) and -11.76 (*J*_{PH} = 41, *J*_{RhH} = 22 Hz); ³¹P-¹H}, δ 56.4 (*J*_{RhP} = 162) and 54.9 (*J*_{RhP} = 158 Hz).

With benzene. (a) *Room temperature experiments.* An ampoule was charged with complex 1 (30 mg, 66 μ mol) and benzene (2 mL). The resulting solution was thoroughly degassed and irradiated for 15 h at 283 K. All volatiles were removed under vacuum and the resulting dark brown residue was dissolved in C₆D₆. This solution was filtered prior to loading into an NMR tube.

(b) *Low temperature irradiation of complex 1 in thf and/or benzene.* A range of experiments were performed in which complex 1 was irradiated in either neat [²H₈]thf, or mixtures of C₆D₆-thf, C₆D₆-[²H₈]thf and C₆H₆-[²H₈]thf. In a typical experiment an NMR tube was charged with 1 (37 mg, 81 μ mol), C₆D₆ (0.3 mL) and [²H₈]thf (0.3 mL). This solution was thoroughly degassed and the tube was suspended in a thermally insulated Pyrex tube through which flowed a stream of cold nitrogen vapour. The solution was cooled to 233 K and irradiated with a xenon arc at <400 nm for 5 h. The tube was then placed in the precooled probe of an NMR spectrometer (233 K) and multinuclear NMR spectra were acquired (see Table 2).

Crystallography

Data were collected on a Stoe Stadi-4-diffractometer equipped with an Oxford Cryosystems low-temperature device. Crystallographic parameters are listed in Table 3. The diffraction profiles were characterised by rather uneven backgrounds, tailing off slowly towards low angle. In addition, one reflection out of 22 located in a random search had non-integral Miller indices relative to the remainder, suggesting a small amount of multiplicity in the sample. Other crystals in the sample showed similar features. Possibly for these reasons, an absorption correction

based on ψ -scans was rather unsatisfactory, leading to no significant improvement in data-fitting parameters compared with a refinement performed against uncorrected data. A correction was therefore applied using the program DIFABS,³² but even here the range of transmission factors (0.233–0.695) was larger than anticipated from the size of the crystal and μ . It is most likely that, in addition to correcting for absorption, DIFABS has compensated for systematic errors in the intensity measurements which arise from the factors described above. While the geometry of this molecule has been determined with little cause for doubt, little credence should be given to the displacement parameters. The structure was solved by Patterson methods (DIRDIF)³³ and completed by iterative cycles of least-squares refinement and Fourier-difference syntheses (SHELXL 97).³⁴ Hydrogen atoms (with the exception of the hydride) were placed in idealised positions and subsequently allowed to ride on their parent atoms. The hydride was located in a difference map. During refinement, the direction of the Rh–H vector was fixed, but the distance allowed to refine. The SiPr₃ group is disordered by a *ca.* 60° rotation about the Rh–Si bond. The two orientations were refined with equal occupancies of 50% and restrained to be geometrically similar with local threefold symmetry in chemically equivalent bond lengths and angles (but not torsions). All non-H atoms were modelled with anisotropic displacement parameters; for neighbouring partial weight atoms the parameters were restrained to have equal *U*_{ij} components.

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See <http://www.rsc.org/suppdata/dt/1998/2515/> for crystallographic files in .cif format.

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