In memory of T. A. Stephenson

The Formation and Characterisation of (η^2-Ethene)hydrido(η^5-pentamethylcyclopentadienyl)(trisubstituted-silyl)rhodium Complexes; Intermediates in Catalytic Dehydrogenative Silylation Reactions†

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The complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)(\text{C}_2\text{H}_4)]$ [R = Et (**4a**) or Me (**4b**)] have been detected and characterised spectroscopically [including ^{103}Rh n.m.r. spectra (*via* INEPT)] as intermediates in the thermal and photochemical reaction (i). Complex (**4d**) (R = OEt), which was isolated and fully

$$\underset{(\mathbf{1})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiR}_3)_2]} \underset{\text{SiR}_3\text{H}}{\overset{\text{C}_2\text{H}_4}{\rightleftharpoons}} \underset{(\mathbf{3})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]} \qquad \text{(i)}$$

characterised, and (**4c**) (R = Ph), were obtained from reaction of SiR_3H and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]$. Evidence for iridium analogues of (**4**) was obtained but more complex further reactions also occurred there. The complexes (**4**) were reasonably thermally robust; since (**1**) and (**3**) are active catalysts for the reaction, $\text{SiEt}_3\text{H} + \text{C}_2\text{H}_4 \longrightarrow \text{CH}_2\text{=CHSiEt}_3 + \text{SiEt}_4$, this implies significant activation is required to reorganise the ligands in (**4**). The related reaction, of SiR_3H (R = Me, Et, Ph, or OEt) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}_2]$, only proceeded as far as $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)(\text{CO})]$; this was very labile and lost SiR_3H with the formation of blue $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}\}_2]$.

During an investigation of pentamethylcyclopentadienyl rhodium complexes as catalysts for hydrosilylation of olefins, we discovered that, under certain easily reproduced conditions, the major reaction product from $\text{R}'\text{CH=CH}_2$ and SiR_3H was $\text{R}'\text{CH=CHSiR}_3$ (and isomers) plus $\text{R}'\text{CH}_2\text{CH}_3$. The normal hydrosilylation product, $\text{R}'\text{CH}_2\text{CH}_2\text{SiR}_3$, was often there as a minor component.[1] The formation of vinylic silanes in other rhodium-catalysed hydrosilylations has been reported.[2] Mechanisms for both the dehydrogenative and the normal hydrosilylation, involving olefin–hydride–silyl species such as $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)(\text{CH}_2\text{=CHR}')]$ were proposed.[1]

Work to define intermediates involved in these reactions led first to the novel rhodium(V) and iridium(V) complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{M(H)}_2(\text{SiEt}_3)_2]$ (M = Rh or Ir).[3,4] The rhodium complex (**1a**) and related compounds are surprisingly inert. Thus, it reacted only slowly with ligands (L) such as phosphines to give $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)\text{L}]$ by a process which involves reductive elimination of one triethylsilane followed by combination of the resultant 16-electron intermediate with L [equations (1) and (2)]. The first step appears to be rate-limiting overall.

$$\underset{(\mathbf{1a})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiEt}_3)_2]} \rightleftharpoons [(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)] + \text{SiEt}_3\text{H} \qquad (1)$$

$$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)] + \text{L} \rightleftharpoons \underset{(\mathbf{2a})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)\text{L}]} \qquad (2)$$

The reasons behind this type of reactivity have been considered, as has the lack of bimolecular reaction with most nucleophiles (however, see refs. 5 and 6).

We now report related reactions involving ethene– and carbonyl–rhodium complexes and some iridium analogues. A preliminary communication on part of this work has been published.[7]

Results and Discussion

(η^2-*Ethene*)*hydrido*(*trisubstituted-silyl*)*rhodium Complexes*.—The original route to the dihydrobis(triethylsilyl)rhodium complex (**1a**) was by reaction of SiEt_3H with $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\}_2\text{Cl}_4]$. An alternative, which has some advantages for the preparation of homologues of (**1a**), is the thermal or photochemical reaction of the appropriate silane with the bis-ethene complex (3). That process is reversible. Thus, reaction of (**1a**) with ethene (again, either thermally or photochemically) leads to (3), indicating the existence of the equilibrium (3). We

$$\underset{(\mathbf{1a})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiEt}_3)_2]} \underset{\text{SiEt}_3\text{H}}{\overset{\text{C}_2\text{H}_4}{\rightleftharpoons}} \underset{(\mathbf{3})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]} \qquad (3)$$

have now detected intermediates [equations (4) and (5)] such as (**4a**) in this reaction. Here too the activation is clearly

$$[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiEt}_3)_2] \underset{\text{SiEt}_3\text{H}}{\overset{\text{C}_2\text{H}_4}{\rightleftharpoons}} \underset{(\mathbf{4a})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)(\text{C}_2\text{H}_4)]} \qquad (4)$$

$$(\mathbf{4a}) \underset{\text{SiEt}_3\text{H}}{\overset{\text{C}_2\text{H}_4}{\rightleftharpoons}} \underset{(\mathbf{3})}{[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]} \qquad (5)$$

needed to create, from (**1a**), the co-ordinatively unsaturated intermediate, $[(\eta\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)]$, which then goes on to react with ethene to give (3). Haddleton and Perutz[8,9] have

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† *Non-S.I. unit employed*: atm = 101 325 N m^{-2}.

Table 1. ^1H and ^{13}C N.m.r. spectra of $[(\eta^5\text{-}C_5Me_5)M(H)(SiR_3)L]$

	^1H (δ)[a]				^{13}C (δ)[b]		
Complex	H	C_5Me_5	R	L = C_2H_4	C_5Me_5	R	L = C_2H_4
(4a)	−13.75 [35]	1.64	1.13(t) (7.5) 0.86(m)	n.o.	10.8 97.0	9.4 9.8	36.0 [10] 37.6 [13]
(4b)	−13.83 [35.5]	1.60	0.23	n.o.	9.7 98.3 [3]	9.9	37.7 [13] 41.1 [15]
(4c)	−12.69 [32.0]	1.39	7.0—7.7(m)	0.84(br) 2.00(br)	9.4 99.8 [4]	127.3 128.0 136.5 141.6	41.0(br) 42.2(br)
(4d)	−13.61 [35.5]	1.70	1.18(t) (7) 3.75(m)	2.18(br)	9.6 99.1 [n.o.]	18.7 57.4	39.6 [14] 39.3 [10]
(6d)	−17.29	1.76	1.31(t) (7) 3.88(m)	1.4(br) 2.4(br)	9.5 96.0 [n.o.]	18.8 57.7	*c*
							L = CO
(9a)	−11.56 [36]	1.76	0.95(m) 1.12(t) (7.5)	—	10.8 101.1[4]	10.3 10.6	195.2 [84]
(9b)	−11.6 [36.5]	1.75	0.55	—	10.6 101.6	7.9	193.7 [77]
(9c)	−10.41 [32.5]	1.53	7.1—7.9(m)	—	10.1 101.0	128.4 130.0 136.6 142.0	193.5 [77]
(9d)	−11.06 [35.5]	1.96	1.38(t) (7.5) 3.85(m)	—	10.5 101.8	18.6	192.4 [77]

[a] ^1H N.m.r. spectra in C_6D_6 or C_7D_8 at 25 °C; [] coupling to Rh in Hz; () coupling to H, in Hz; n.o. = not observed. [b] ^{13}C N.m.r. spectra for complexes **(4a)**—**(4d)** in C_7D_8 at −70 °C (at +25 °C the ethene signals have coalesced) and for **(6d)**, and **(9a)**—**(9d)** in C_6D_6 at +25 °C; [] coupling to Rh, in Hz; n.o. = not observed. [c] This signal remains unobservable both at +25 °C and at −70 °C.

similarly shown that $[(\eta^5\text{-}C_5R_5)Rh(C_2H_4)_2]$ will dissociate photochemically [equation (6); R = H or Me].

$$[(\eta^5\text{-}C_5R_5)Rh(C_2H_4)_2] \underset{+C_2H_4}{\overset{-C_2H_4}{\rightleftharpoons}} [(\eta^5\text{-}C_5R_5)Rh(C_2H_4)] \quad (6)$$

A further route to **(4a)** is by the comportionation of **(1a)** and **(3)** [equation (7)].

$$[(\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2] + [(\eta^5\text{-}C_5Me_5)Rh(C_2H_4)_2] \longrightarrow 2[(\eta^5\text{-}C_5Me_5)Rh(H)(SiEt_3)(C_2H_4)] \quad (7)$$

The trimethylsilyl complex $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiMe_3)(C_2H_4)]$ **(4b)** was analogously accessible by any of the routes for **(4a)**; in addition the triphenylsilyl complex $[(\eta^5\text{-}C_5Me_5)Rh(H)(SiPh_3)(C_2H_4)]$ **(4c)** and the triethoxysilyl complex $[(\eta^5\text{-}C_5Me_5)Rh(H)\{Si(OEt)_3\}(C_2H_4)]$ **(4d)** were made by irradiation of **(3)** and triphenylsilane or triethoxysilane respectively.

Each of these preparations suffers from the disadvantage that the complexes **(4)** are formed in admixture with **(1)** and **(3)**. Neither of the trialkylsilyl- nor the triphenylsilyl-complexes could be isolated pure. Although they are thermally reasonably robust, under the conditions needed to separate them from **(1)** and **(3)** (which have rather similar characteristics, for example on chromatography) they decompose readily. However, the n.m.r. spectroscopic identification of these complexes is unambiguous and leaves little room for doubt that they are indeed **(4)**.

Thus, for example, irradiation of a cyclohexane solution of a **(1a)** under an atmosphere of ethene (1 atm, 20 °C, 16 h) gave a mixture which, by integration of the $(C_5Me_5)Rh$ signals, showed that three components, **(1a)**, **(3)**, and **(4a)**, were present in the ratio 4:15:3. The ^{13}C n.m.r. spectrum (100.62 MHz, in perdeuteriotoluene, at −70 °C) showed, in addition to all the peaks corresponding to **(1a)** and **(3)**, other peaks not present in either of these compounds. They included a C_5Me_5 resonance at δ 97.0 and two doublets, arising from the inequivalent ends of co-ordinated ethene, at δ 36.0 [*J*(Rh–C) 10 Hz] and 37.6 [*J*(Rh–C) 13 Hz] (Table 1). Upon warming the solution, these two doublets coalesced to one doublet [30 °C, δ 38.7, *J*(Rh–C) 12 Hz]. This is in agreement with the properties expected for **(4a)**; co-ordinated ethene in such complexes shows rotation at high temperatures on the n.m.r. time-scale.[10] By contrast, and as expected, the carbon resonances for the two ethenes in **(3)** were seen as a single doublet at δ 42.9 [*J*(Rh–C) 13 Hz] even at −70 °C.[11]

The hydride in the ^1H n.m.r. spectrum appeared at δ −13.75 [d, *J*(Rh–H) 35 Hz] and was quite distinct from that of **(1a)** [δ −13.85, *J*(Rh–H) 36.9 Hz]. The observation of a normal hydride resonance for **(4a)** also rules out any significant contribution of agostic bonding to the structure.

The ^{103}Rh n.m.r. spectrum (recorded using an INEPT pulse sequence and the hydride coupling) showed signals at δ −1 375 (with respect to Ξ 3.16 MHz = 0 p.p.m.) and −1 714. The first, an out of phase doublet (ratio −1:+1) with separation [*J*(Rh–H)] of 35 Hz, was due to the *mono*hydride **(4a)**, the coupling agreeing with that found from the ^1H n.m.r. spectrum. The second, also a −1:+1 doublet, had a separation of 74 Hz, and was due to the *di*hydride, **(1a)**, *J*(Rh–H) 36.9 Hz. The final confirmation came from the ^{29}Si n.m.r. spectrum which showed a doublet at δ 38.2 [*J*(Rh–Si) 17 Hz] (Table 2), indicating the presence of a direct Rh–Si bond. In summary, the n.m.r. spectra showed the presence of an ethene with inequivalent ends, a $(C_5Me_5)Rh$ group, one hydride bonded to rhodium, and one silyl, also bonded to rhodium.

Complexes **(4a)** and **(4b)** each showed a band at 1 995 cm^{-1} in the i.r. spectrum, assigned to ν(Rh–H); this band appeared at 2 027 cm^{-1} in complex **(4c)** and at 2 011 cm^{-1} in **(4d)**.

The most stable of the silyl–ethene–hydrides so far prepared is **(4d)**, $[(\eta^5\text{-}C_5Me_5)Rh(H)\{Si(OEt)_3\}(C_2H_4)]$. In this case, it was possible to isolate a 38% yield of an oil, from the reaction of **(3)** with triethoxysilane. This material was again very air-sensitive, but it could, with care, be separated from **(3)**, **(1d)**, and

Table 2. ^{103}Rh and ^{29}Si n.m.r. and i.r. spectra of $[(\eta^5\text{-}C_5Me_5)M(H)(SiR_3)L]$

	I.r.^{a}/cm^{-1}			
Complex	ν(Rh–H)	ν(CO)	^{103}Rh (δ)^b	^{29}Si(δ)^c
(4a)	1 995		−1 375 [35]	38.2 [17]
(4b)	1 995		−1 346 [37]	
(4c)	2 027		−1 403 [32]	
(4d)	2 011		−1 451 [36]	−9.9 [45]
(6d)	2 155			
(9a)		1 985	−1 519 [36]	
(9b)	2 025	1 995	−1 453 [36]	
(9c)		1 999	−1 471 [33]	
(9d)		2 000	−1 543 [36]	

^{a} I.r. spectra measured on Perkin-Elmer 1 710 Fourier-transform spectrometer, in benzene solution [for (**9a**), (**9c**), and (**9d**)], and in cyclohexane solution [for (**4a**)—(**4d**), (**6d**) and (**9b**)]; ν(Rh–H) obscured by ν(CO) in (**9a**), (**9c**), and (**9d**). ^{b} ^{103}Rh N.m.r. spectra (*via* INEPT) measured relative to Ξ 3.16 MHz = 0 p.p.m.; [] coupling to H in Hz. ^{c} ^{29}Si N.m.r. spectra measured relative to $SiMe_4$; [] coupling to Rh in Hz.

excess $Si(OEt)_3H$ by chromatography on Florisil. The identity of the complex was confirmed by microanalysis and by a mass spectrum, which showed a peak at m/e $(M - 2)^+$. The characterisation of (**4d**) was again by n.m.r. spectroscopy. For example, in the ^{1}H n.m.r. spectrum the hydride [δ −13.61, d, J(Rh–H) 35.5 Hz] integrated as expected on the basis of the intensities of the (C_5Me_5)Rh and ethoxy protons. The ^{103}Rh n.m.r. spectrum (*via* INEPT) showed a −1 : +1 ratio doublet, at δ −1 451, separation 36 Hz, while the ^{29}Si-{^{1}H} n.m.r. showed a doublet at δ −9.9 [J(Rh–Si) 45 Hz]. These data indicated that each rhodium was also attached to one hydride and one silyl. The ^{13}C n.m.r. spectrum in perdeuteriotoluene at −70 °C showed resonances at δ 9.6 and 99.1 [(C_5Me_5)Rh], 18.7 and 57.4 [$Si(OEt)_3$], 39.3 [d, C_2H_4, J(Rh–C) 10 Hz] and 39.6 [d, C_2H_4, J(Rh–C) 14 Hz]. The ^{1}H n.m.r. spectrum at −70 °C showed signals at δ −13.34 [d, J(Rh–H) 35.5 Hz], 1.67 [(C_5Me_5)Rh], 1.31 [OEt, t, J(H–H) 7 Hz], and 3.85 [OEt, m] and 2.66 (m, C_2H_4); this last signal integrated as two of the four ethene protons, the remainder appeared to be under the (C_5Me_5)Rh resonance.

Reactions of $[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2]$ (**5**) *with* SiR_3H.—We have also tried to make the iridium analogues of (**4**), but with less success. Irradiation of $[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2]$, (**5**), with $SiEt_3H$ gave a mixture of products, as indicated by the presence of five hydride resonances in the ^{1}H n.m.r. spectrum. These products were not separable, but the resonance at δ −17.23 is indicative of the formation of $[(\eta^5\text{-}C_5Me_5)Ir(H)_2(SiEt_3)_2]$ and therefore that the desired reactions [equations (8) and (9)], have

$$SiR_3H + \underset{(\mathbf{5})}{[(\eta^5\text{-}C_5Me_5)Ir(C_2H_4)_2]} \longrightarrow \underset{(\mathbf{6})}{[(\eta^5\text{-}C_5Me_5)Ir(H)(SiR_3)(C_2H_4)]} \quad (8)$$

$$(\mathbf{6}) \longrightarrow [(\eta^5\text{-}C_5Me_5)Ir(H)_2(SiR_3)_2] \quad (9)$$

taken place. We presume that the other hydrides result from reactions such as those recently described in which the iridium inserts into the vinyl–hydrogen bond of ethylene.[12] However, no reaction at all was observed when the reactants were heated (in toluene). Mixtures of hydrides were also obtained when (**5**) was irradiated with $SiMe_3H$ or $SiPh_3H$.

Irradiation of (**5**) with triethoxysilane gave a more tractable mixture; again, as in the formation of (**4d**), the polarity differences between the various products were sufficient to allow chromatographic separation. The oil obtained appeared to be 90% of a single material, tentatively identified as (**6d**) (R = OEt). The ^{1}H n.m.r. spectrum showed the presence of a hydride (s, at δ −17.29), as well as C_5Me_5 (s, 1.76) and ethoxy resonances [t, δ 1.31; m, δ 3.88; J(H–H) = 7 Hz] in the correct relative intensities for the complex. Broad signals were seen at δ 1.4 and 2.4 which may have been due to the co-ordinated ethene.

We conclude that the reactions (10) and (11) are general, but

$$[(\eta^5\text{-}C_5Me_5)M(C_2H_4)_2] + SiR_3H \rightleftharpoons [(\eta^5\text{-}C_5Me_5)M(H)(SiR_3)(C_2H_4)] + C_2H_4 \quad (10)$$

$$[(\eta^5\text{-}C_5Me_5)M(H)(SiR_3)(C_2H_4)] + SiR_3H \rightleftharpoons [(\eta^5\text{-}C_5Me_5)M(H)_2(SiR_3)_2] + C_2H_4 \quad (11)$$

that the circumstances of each case determine whether the particular intermediate is stable enough to be detectable or isolable.

We have some indirect evidence that olefins other than ethylene can also take part in such reactions. However, the organometallic products from such reactions are very unstable {such as that between (**1a**) and but-1-ene, which we presume to give $[(\eta^5\text{-}C_5Me_5)Rh(C_4H_8)_2]$} so that no adequate characterisation has yet been possible.

Relationships to Catalytic Reactions.—A fascinating aspect of this work is the relation of complexes (**4**) to the mechanisms of the catalytic olefin hydrosilylation and the dehydrogenative silylation reactions.[1] In fact both complexes (**1a**) and (**3**) slowly catalysed the reaction of ethene and triethylsilane to give a 3 : 1 mixture of triethyl(vinyl)silane and tetraethylsilane (6 h, 60 °C, 50 atm). The involvement of (**4a**) seems inescapable.

Although the reactions of (**4**) have not yet been examined in detail, they seem surprisingly thermally robust. Thus, the relative intensities of (**4**) and the other components in the mixtures containing (**1**) and (**3**) did not change dramatically on warming the solutions to 60 °C. This implies that the further combination of silyl and olefin (and hydride) within a complex such as (**4**) when it is intermediate needs quite significant activation.

The reorganisation which takes place may involve simply a reorientation of the ethene to facilitate the migration reactions; details are under investigation. However the observation of unexpected metal hydrides (which may be associated with iridium vinyl–hydride species) in the iridium reactions suggests that a sequence of reactions of the type shown by equations (12)—(14) competes very effectively with the normal hydrosilylation reactions (15) and (16) [m = $(\eta^5\text{-}C_5Me_5)$Rh].

$$m(H)(SiR_3)(CH_2{=}CH_2) \longrightarrow m(H)_2(SiR_3)(\sigma\text{-}CH{=}CH_2) \longrightarrow m(H)_2 + CH_2{=}CH\text{-}SiR_3 \quad (12)$$

$$m(H)_2 + C_2H_4 \longrightarrow m(H)_2(C_2H_4) \longrightarrow m + C_2H_6 \quad (13)$$

$$m + SiR_3H + C_2H_4 \longrightarrow m(H)(SiR_3)(C_2H_4) \quad (14)$$

$$m(H)(SiR_3)(C_2H_4) \longrightarrow m + SiEt_4 \quad (15)$$

$$m + C_2H_4 + SiR_3H \longrightarrow m(H)(SiR_3)(C_2H_4) \quad (16)$$

Since the dehydrogenative silylation is characteristic of many of the rhodium catalysed reactions under certain conditions,[1,2] the formation of such vinyl–rhodium intermediates must be quite general and relatively facile.

Reactions of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}_2]$ *and* SiR_3H.—Closely related processes are those involving carbon monoxide in place of ethene. Thus, complex (**1a**) reacted with CO (benzene, 10 atm, 90 °C, 24 h) to give a 92% yield of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}_2]$ (**8**). Conversely, reaction of (**8**) with triethylsilane (toluene, 90 °C) gave a mixture (by n.m.r. and i.r.) of (**8**), $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}\}_2]$, and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)\text{(CO)}]$ (**9a**). No complex (**1a**) could be detected in the mixture.

Problems of instability (see below) and similarity of physical behaviour precluded separation of (**9a**), but the n.m.r. characterisation makes it clear that the complex is actually formed. Thus, the ^{1}H n.m.r. spectrum showed a doublet integrating for 1 H at δ −11.56 [J(Rh–H) 36 Hz], the (C_5Me_5)Rh at δ 1.76, and the ethyl resonances at δ 0.95 (m) and 1.12 (t, J 7.5 Hz). The ^{13}C n.m.r. spectrum confirmed this and also showed a resonance at δ 195.2, J(Rh–C) 84 Hz, due to the carbonyl carbon. The ^{103}Rh n.m.r. spectrum (*via* INEPT) showed a −1 : +1 ratio doublet of separation 36 Hz at δ −1 519 indicating that only one hydrogen was attached to the metal. These data were confirmed by the observation of ν(CO) at 1 985 cm^{-1}.

Very similar data were obtained for the related complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)\text{(CO)}]$ [R = Me (**9b**), Ph (**9c**), or OEt (**9d**)] prepared analogously.

There were two significant differences between (**9**) and (**4**). One is that the substitution of CO on rhodium stops at that point; for none of these reactions was there any sign of the formation of the rhodium(V) complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiR}_3)_2]$. Presumably the carbonyl in (**9**) is much more firmly bound than is the ethene in (**4**); this may well be a steric effect since CO is very much smaller than C_2H_4, and the ethene complexes are as a consequence rather crowded.

The other difference is that complexes (**9**) are thermally labile in a quite different sense: *in vacuo*, for example, on removal of solvent, *the silane is lost* with the formation of the blue dinuclear carbonyl (**10**) [equation (17)].

$$2[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)\text{(CO)}] \underset{(\mathbf{9})}{} \longrightarrow \underset{(\mathbf{10})}{[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}\}_2]} + 2\text{SiR}_3\text{H} \quad (17)$$

Related complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(H)(SiR}_3)\text{(CO)}]$ have previously been reported to arise from the addition of SiPh_3H or $\text{Si(CH}_2\text{Ph)}_3\text{H}$ to $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh(CO)}_2]$[13] (see also ref. 9).

Experimental

Reactions were carried out under nitrogen or argon. Irradiations were performed using a Hanovia medium-pressure mercury lamp. Typical experiments are detailed below. Spectroscopic data (n.m.r., measured on Bruker WH-400 and AM-250 spectrometers, and i.r., measured on a Perkin-Elmer 1710 Fourier-transform spectrometer) are collected in Tables 1 and 2.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiR}_3)(\text{C}_2\text{H}_4)]$ [R = Et (**4a**), Me (**4b**), *or* Ph (**4c**)].—(*i*) Irradiation of a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiEt}_3)_2]$ (**1a**) (0.1 g, 0.2 mmol) in cyclohexane (1 cm^3) under ethene (1 atm, 16 h, 20 °C) gave a mixture; after removal of volatiles, this was shown by ^{1}H and ^{13}C n.m.r. spectroscopy in deuteriobenzene to contain (**1a**) (19%), (**4a**) (15%), and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]$ (**3**) (66%).

(*ii*) A solution of SiEt_3H (0.3 cm^3) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]$ (**3**) (110 mg, 0.37 mmol) in cyclohexane (0.4 cm^3) was irradiated (2 h, 20 °C). ^{1}H N.m.r. spectroscopy showed the mixture to contain (**4a**) (25%), (**1a**) (15%), and (**3**) (60%).

(*iii*) A solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiEt}_3)_2]$ (**1a**) (0.1 g, 0.21 mmol) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]$ (**3**) (62 mg, 0.21 mmol) in cyclohexane (0.7 cm^3) was irradiated (48 h, 20 °C). Analysis as above showed the presence of (**1a**) (35%), (**3**) (35%), and (**4a**) (30%). The same composition was achieved when an identical solution was heated (14 h, 90 °C).

A similar reaction to (*iii*) but using $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiMe}_3)_2]$ (**1b**) in place of (**1a**) gave a mixture containing (**4b**) (20%), (**1b**) (40%), and (**3**) (40%), after heating (90 °C, 10 h). Longer heating did not increase the amount of (**4b**) present.

Irradiation of a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(C}_2\text{H}_4)_2]$ (**3**) (0.1 g, 0.34 mmol) and triphenylsilane (89 mg, 0.3 mmol) in cyclohexane (0.7 cm^3) gave a mixture containing (**4c**) (45%), (**3**) (50%), and (**1c**) (5%). Chromatography on neutral alumina gave a solution which, by n.m.r. analysis, contained (**4c**) (85%), and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}_2(\text{SiPh}_3)_2]$ (**1c**) (15%). This was used for the spectroscopic characterisation.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)}\{\text{Si(OEt)}_3\}(\text{C}_2\text{H}_4)]$ (**4d**).—Irradiation of a solution of (**3**) (0.25 g, 0.85 mmol) and triethoxysilane (0.22 cm^3) in cyclohexane gave a mixture of (**4d**) (60%) and (**3**) (40%) (by n.m.r.). This was chromatographed on Florisil; pentane eluted (**3**) and excess triethoxysilane and complex (**4d**) was eluted with diethyl ether. Complex (**4d**) was purified by rechromatographing as before to give a pale yellow oil (0.14 g, 38%) (Found: C, 51.0; H, 9.1. $\text{C}_{18}\text{H}_{35}\text{O}_3\text{RhSi}$ requires C, 50.2; H, 8.2%). Mass spectrum (electron impact mode): m/e 428 $(M - 2)^+$.

Attempts to Prepare $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(H)(SiR}_3)(\text{C}_2\text{H}_4)]$ [R = Et (**6a**), Me (**6b**) *or* Ph (**6c**)].—Irradiation of a solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(C}_2\text{H}_4)_2]$ (**5**) (0.1 g, 0.26 mmol) with triethylsilane (0.17 cm^3) in cyclohexane (0.5 cm^3) gave a mixture which, after removal of volatiles and examination by ^{1}H n.m.r. spectroscopy in deuteriobenzene, showed the presence of (**5**), and at least five other hydrido-complexes (resonances at δ −16.95, −17.04, −17.23, −17.63, and −18.20). The resonance at δ −17.23 corresponds to that of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(H)}_2(\text{SiEt}_3)_2]$.[4] No reaction occurred on heating a toluene solution of (**5**) and SiEt_3H (130 °C, 2 d).

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(H)}\{\text{Si(OEt)}_3\}(\text{C}_2\text{H}_4)]$ (**6d**).—Irradiation of a solution of (**5**) (0.1 g) and triethoxysilane (0.1 cm^3) in cyclohexane (0.5 cm^3) (14 h, 20 °C) gave a solution which was shown by ^{1}H n.m.r. spectroscopy to contain some 50% of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir(H)}\{\text{Si(OEt)}_3\}(\text{C}_2\text{H}_4)]$. After chromatography (neutral alumina) a solution containing 90% of this complex was obtained for which the spectra were measured.

Preparation of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(H)(SiEt}_3)\text{(CO)}]$ (**9a**).—A solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}_2]$ (**8**) (90 mg, 0.31 mmol) and triethylsilane (0.3 cm^3) in toluene (1 cm^3) was stirred (6 h, 90 °C). After removal of volatiles *in vacuo* the residue was shown by ^{1}H n.m.r. spectroscopy to be a mixture of (**9a**) (30%), (**8**) (60%), and $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh(CO)}\}_2]$ (10%). All attempts to purify (**9a**) led to increased amounts of the blue dimer. Neither this reaction nor those of (**8**) with other silanes were improved on irradiation.

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