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The addition of small molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$

X *. Addition of terminal alkynes; the formation of bridging carbonyl cyclobutenyl intermediates $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\eta^1,\eta^3\text{-}C_4(CF_3)_2HR\}$ and their facile conversion to binuclear metalladiene complexes $(\eta\text{-}C_5H_5)_2Rh_2\{\eta^2,\eta^4\text{-}C_4(CF_3)_2HR\}$

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Abstract

Reaction occurs immediately when solutions of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**1**) in hexane are treated with $HC{\equiv}CR$ ($R = H$, CF_3 or Ph), and the cyclobutenyl complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C_4(CF_3)_2HR\}$ (**2**) separate in near quantitative yield. CO is lost fairly rapidly from solutions of **2** in polar organic solvents, and the metallacyclopentadiene complexes $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^2,\eta^4\text{-}C_4(CF_3)_2HR\}$ (**3**) are formed. The reactions between $HC{\equiv}CR$ ($R = Pr$ or CH_2CO_2Me) and **1** in hexane are also fast, but no precipitate is formed; infrared spectroscopy indicates that **2** ($R = Pr$ or CH_2CO_2Me) is present in the reaction solution, but there is rapid conversion into **3** (ca. 80% yield after TLC work up). Slower reactions (2–5 min) occur between **1** and $HC{\equiv}CR$ ($R = CH_2CH_2CH_2C{\equiv}CH$ or $CMe{=}CH_2$) in hexane, and again all the products remain in solution. It is possible to separate **2** ($R = CH_2CH_2CH_2C{\equiv}CH$ or $CMe{=}CH_2$) (up to 65% yield obtained) from the corresponding **3** by immediate TLC, but **2** is converted fairly rapidly into **3** when left in solution. The reaction between **1** and $HC{\equiv}CSiMe_3$ is significantly slower (ca. 15 min), and gives **3** ($R = SiMe_3$) (64% yield) and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (21%) as major products. Another product, spectroscopically identified as $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(O)C(CF_3)C(CF_3)\}(\mu\text{-}HC_2SiMe_3)$

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* For Part IX, see ref. 1.

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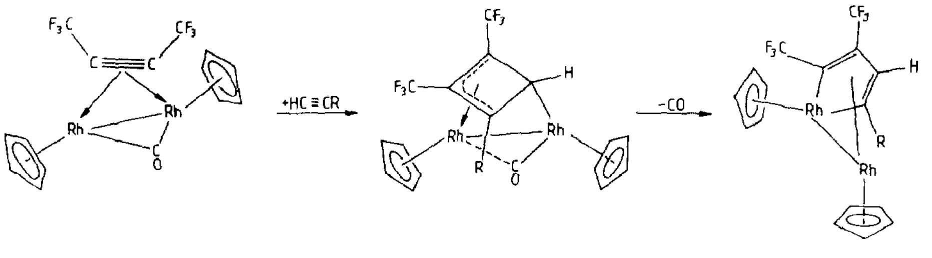
(7) can be isolated in significant amount only when TLC of the reaction solution is performed within 10 min of mixing the reactants. Spectroscopic analysis indicates complete regioselectivity in the formation of all metallacyclopentadiene complexes **3**, with the H and R groups (from HC≡CR) located in the 3- and 2-positions respectively of the 1-metallacyclopentadiene ring.

Introduction

In previous work [2,3] we established that reactions between $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ and disubstituted alkynes can proceed by two alternative pathways, and that the substituents on the alkyne influence the course of the reaction. The substituents also have a regioselective influence in that there is often a strong preference for a particular arrangement of the substituents within the organometallic products obtained from each reaction pathway. Although reactions with a wide range of disubstituted alkynes were investigated, the reasons for the observed specificities did not emerge. In an attempt to improve our understanding of the substituent effects, we have extended our study to include some terminal alkynes. The reaction with t-butylacetylene gives a variety of products, and the results of this work have already been published [4]. With other terminal alkynes, the reactions are highly specific; this work is described here.

Results

The complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (**1**) has been treated with a variety of terminal alkynes HC≡CR. A reaction occurs instantaneously at room temperature when R = H, Pr, CH_2CO_2Me, CF_3 or Ph; somewhat slower reactions take place when R is $CH_2CH_2CH_2C{\equiv}CH$, $CMe{=}CH_2$ or $SiMe_3$. Without exception, the major end product is a binuclear metallacyclopentadiene complex of formula $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^2,\eta^4\text{-}C_4(CF_3)_2HR\}$ (**3**); in some cases, a small amount of the dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$ is obtained also. An intermediate step in the formation of the metalladiene complexes has been recognised. Thus, complexes of formula $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2HR\}$ (**2**) are formed initially, and for some R groups the intermediate has been isolated and subjected to full spectroscopic analysis. In solution, conversion of **2** to the metalladiene complex **3** (Scheme 1) can be followed spectroscopically and it is found that the rate of transformation is markedly dependent on the nature of R. Further details of the characterization of these complexes and their interconversion is presented below.



(1) (2) (3)

Scheme 1

The complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{C_4(CF_3)_2HR\}$ (**2**)

In three reactions, the complexes **2** (R = H, CF_3 or Ph) separated out as soon as the reactants were mixed in hexane at room temperature. These complexes were isolated in at least 95% yield, and were obtained analytically pure.

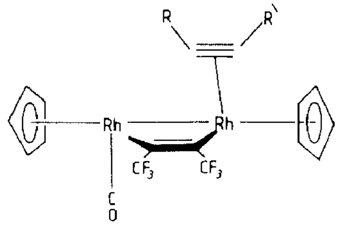
The reactions with HC≡CR (R = $CH_2CH_2CH_2C{\equiv}CH$ or CMe=CH_2) occurred more slowly, and no precipitate was formed. TLC monitoring revealed that all of the starting material **1** had been consumed after 2 min for the diyne or 5 min for the enyne system. Preparative TLC of the diyne system after 2 min separated the dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$ (22% yield) and the metalladiene complex **3** (R = $CH_2CH_2CH_2C{\equiv}CH$) (28%) from the major product **2** (R = $CH_2CH_2CH_2C{\equiv}CH$) (49%). Similarly, complex **2** (R = CMe=CH_2) was isolated in 66% yield by preparative TLC after 5 min reaction time. The metalladiene complex **3** (R = CMe=CH_2) (30% yield) was also obtained, but no dicarbonyl complex was detected in this system. It was not possible to isolate the complexes **2** (R = $CH_2CH_2CH_2C{\equiv}CH$ and CMe=CH_2) analytically pure because they underwent conversion continuously to the corresponding metalladiene complexes **3** in solution. Each conversion was sufficiently slow, however, to enable a full set of spectroscopic data to be obtained for the intermediate complexes **2**.

In a further two reactions, infrared data on the fresh reaction solutions indicated that the complexes **2** (R = Pr or CH_2CO_2Me) were formed rapidly. However, these complexes are soluble in hexane and they convert very quickly to the metalladiene complexes **3**. They could not be isolated by TLC.

The fairly rapid **2** → **3** conversions in solution made it impossible to obtain good crystals of any of the complexes **2** that could be used in X-ray structure determination. Consequently, characterization of these complexes depended on interpretation of the spectroscopic data. Mass spectroscopic analysis showed a weak molecular ion signal for two of the complexes **2** (R = H or CF_3) but not for the others. The base peak corresponds to $[M - CO]^+$ in each spectrum, and the intensity of this peak gives notice that these complexes will readily undergo decarbonylation. We commented earlier on the relatively fast decarbonylation of the complexes **2** in solution. Decarbonylation also occurs in the solid state; for example, after 5 days at $-20\,^\circ C$, there is 15% conversion of **2** to **3** (R = CMe=CH_2).

The infrared spectra establish that the carbonyl group is bridging; for solutions in dichloromethane, ν(CO) is observed between 1850 (**2**, R = Ph) and 1875 cm^{-1} (**2**, R = CF_3). Further information about the bridging arrangement comes from the ^{13}C NMR spectrum of a ^{13}CO-enriched sample of **2** (R = $CH_2CH_2CH_2C{\equiv}CH$); δ(CO) is detected as a doublet of doublets at 212.6 ppm. The observation of two very different Rh–C coupling constants (63 and 28 Hz) is consistent with an asymmetrical or semi-bridging carbonyl arrangement.

Two cyclopentadienyl environments are indicated in the ^1H NMR spectra ($CDCl_3$ solutions) of all complexes except **2** (R = CF_3 and Ph). It seems likely that all complexes are unsymmetrical, and that the C_5H_5 resonances are accidentally degenerate in the latter systems. This was confirmed by re-recording the spectrum of **2** (R = CF_3) in acetone-d_6 and observing separate C_5H_5 signals. The ^1H spectrum of **2** (R = H) shows additional peaks at δ 11.2 and 4.67 ppm which are assigned to the two protons of the coordinated acetylene. For the other complexes **2** (R ≠ H), the alkyne proton resonance is observed near δ 4.6 ppm. The absence of a low field peak near δ 11 ppm indicates high regioselectivity in the orientation of the "alkyne". The very disparate chemical shifts for the "acetylene-protons" in **2** (R = H), together with the other spectroscopic results, indicate **2** as the probable structure.



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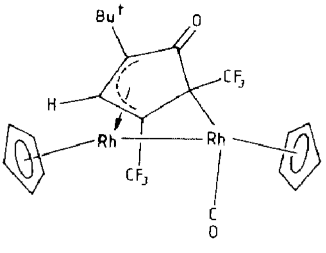


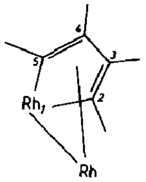
(5)

Structures with independently coordinated alkynes, (e.g. **4**) are inconsistent with the IR and NMR data. The chemical shifts of the acetylene protons in binuclear complexes with recognizable acetylene ligands cover a considerable range. For example, δ is below 4 ppm in $(\eta\text{-}C_5H_5)_2W_2(CO)_4(HC_2H)$ [5] but above 11 ppm in $W_2(OR)_6(\mu\text{-}C_4H_4)(HC_2H)$ [6]. This makes it extremely difficult to predict δ (≡CH) for a complex such as **4**; regardless of the magnitude of the chemical shift, it seems inconceivable that the two acetylene protons in **4** (R = R′ = H) would have chemical shifts separated by almost 7 ppm.

We are not aware of previous examples of complexes with bridging $\eta^1\eta^3$-cyclobutenyl groups. However, we recently isolated and structurally characterized [4] a closely related complex **5** (R = Bu^t), which was formed in the reaction between **1** and HC≡CBu^t. Unfortunately, **5** is not a good model for predicting the NMR spectrum of **2** because it has a CF_3 group, rather than H, on the σ-bonded carbon of the ring. There is another notable difference between **2** (R = $SiMe_3$) and **5** (R = Bu^t). Thus, the bonding mode of the carbonyl is semi-bridging in **2** but terminal in **5**, and this presumably results from slight differences in the metal *d*-electron density for the two complexes [7].

The conversion of 2 → 3, and characterization of the complexes 3

Infrared monitoring established that all complexes **2** were unstable in solution, the decay being slowest when R = Ph, $CH_2CH_2CH_2C{\equiv}CH$ or $CMe{=}CH_2$. TLC of the aged solutions indicated near quantitative conversion to metalladiene complexes of formula $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^2,\eta^4\text{-}C_4(CF_3)_2HR\}$ (**3**). Spectroscopic data for these complexes is detailed in the Experimental Section. In the ^1H NMR spectrum of **3** (R = H), resonances for the two metalladiene ring protons are found at δ 7.75 and 6.04 with $J(H\text{-}H)$ 5.3 Hz. The lower field peak is assigned to H in the 2-position of the 1-metalladiene ring (see **6**); there is further discussion of the basis for this assignment below. Interestingly, the H in the 3-position shows additional coupling to rhodium ($J(Rh\text{-}H) \approx 5$ Hz) whereas that in the 2-position does not. Formation of the complexes **3** (R ≠ H) is completely regioselective, with the proton located in the 3-position of the 1-metalladiene ring.



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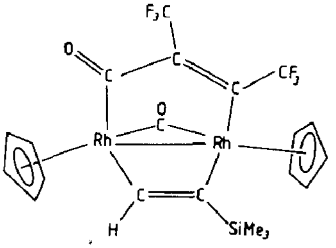


(7)

The above assignments are dependent upon the chemical shift for H^2 being at lower field than that for H^3. The same trend has been suggested previously for some related complexes including the bridging dienone complex $(\eta^5\text{-}C_9H_7)_2Rh_2(\mu\text{-}\eta^2,\eta^4\text{-}C_4H_4CO)$ [8] and the bridging enone species $(\eta\text{-}C_5H_5)_2M_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1\eta^1\text{-}CHCHCO)$ (M = Fe, Ru) [9], and has been confirmed by lanthanide shift experiments on $(\eta\text{-}C_5H_5)_2Rh_2\{\mu\text{-}\eta^1,\eta^3\text{-}C_4(CF_3)_2HBu^tCO\}$ [4] and by spin decoupling analysis for $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CHCH_2)\{\mu\text{-}C(CF_3)C(CF_3)H\}$ [10]. However, an opposite assignment has been suggested for some ditungsten metalladiene complexes on the basis of W–C and C–H coupling constant data [6]. If the expectation, expressed in the latter paper, that $J(M^1\overset{\sigma}{-}C^2) > J(M^2\overset{\pi}{-}C^2)$ or $J(M^2\overset{\pi}{-}C^3)$ is wrong, then the whole basis for the assignment is removed. On the basis of our own results, we believe that this is the case.

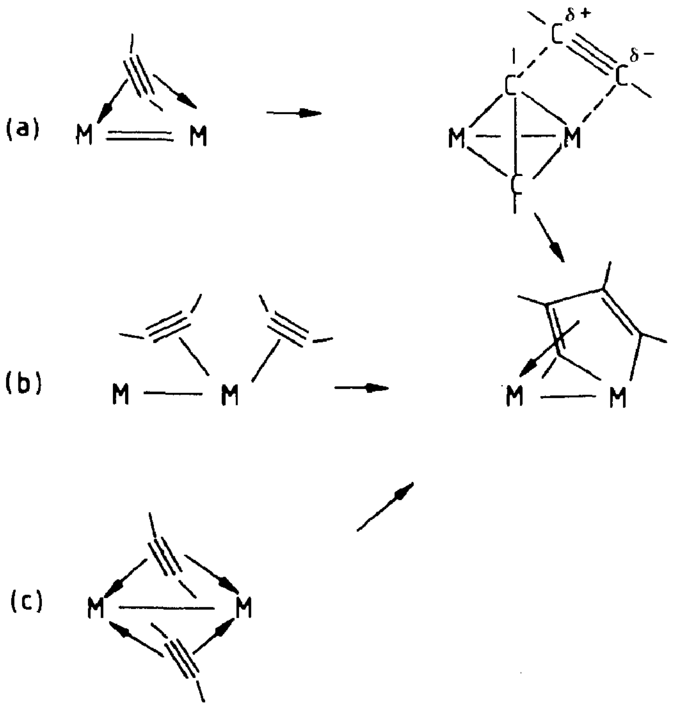
The reaction with HC≡CSiMe₃

This was by far the slowest of the terminal alkyne reactions. TLC monitoring showed that **1** was absent after ca. 15 min. Preparative TLC after this time separated **3** (R = $SiMe_3$) (64% yield) and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (21%) from a minor product **7**. The yield of **7** was significantly greater if the reaction was worked up after only 5–10 min. Spectroscopic monitoring established that **7** transforms rapidly to **3** (R = $SiMe_3$) plus $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ if left in solution. This made it impossible to obtain analytically pure samples of **7**, but the complex was characterized spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)(HC_2SiMe_3)$.

A weak molecular ion was detected in the mass spectrum, and peaks corresponding to stepwise loss of two carbonyls were also observed. The infrared spectrum indicates that one carbonyl is bridging (ν(CO) at 1870 cm^{-1}) and the other is ketonic (ν(CO) at 1705 cm^{-1}). Two cyclopentadienyl environments and one trimethylsilyl group are seen in the ^1H NMR spectrum together with a lone proton singlet at δ 7.26 ppm. The two CF_3 signals in the ^{19}F NMR spectrum are at relatively high field, and the F–F coupling is relatively small; in addition, one CF_3 group shows coupling to rhodium. These features of the ^{19}F spectrum are very similar to those reported previously for the complex $(\eta\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CO)\{\mu\text{-}C(O)C(CF_3)C(CF_3)\}$ [11], and it seems likely that a related bridging group exists in the present compound. The structure **7** is consistent with all the spectroscopic data.

Discussion

The cyclization of alkynes to substituted arenes on Co–Co bonds has been investigated extensively [12]. It has been suggested [13] that the nickel catalyzed

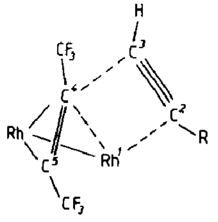


Scheme 2

"Reppe" [14] cyclization of alkynes to cyclooctatetraenes may also involve binuclear intermediates. Some support for this idea comes from recent work on the sequential coupling of four alkynes at Cr–Cr and Mo–Mo centres [15,16]. In all of these reactions, there is a stage where two alkyne units are coordinated and coupled. Numerous binuclear metallacyclopentadiene complexes are known [2–4,6,9,17], and these are regarded [18] as likely intermediates in the formation of $M_2(\text{alkyne})_n$ ($n = 3$ or 4) complexes which degrade to the cyclic organic products.

Relatively little is known about how the alkynes are arranged prior to formation of a metallacyclopentadiene ring. Two ideas have been presented. A theoretical study [19] on the formation of ferroles indicates that the second alkyne engages in side on attack of a $M_2(\mu\text{-}RC_2R)$ system (see Scheme 2a). Requirements for this reaction are that the metal system has a low energy orbital and that the C≡C bond is polarized by an electron-withdrawing group. Experimental work with the indenyl systems $(\eta\text{-}C_9H_7)_2Mo_2(CO)_4$ [16] indicates that the key step is initial coordination of two alkynes to the same metal followed by condensation to give the metallacyclopentadiene (see Scheme 2b). It is possible to contemplate related intermediates in which the two alkynes both occupy bridging positions. There are certainly a number of well characterized complexes of this type. Examples include $Fe_2(CO)_4(Bu^tC_2Bu^t)_2$ [20], $MoCo(\eta\text{-}C_5H_5)(CO)_3(\mu\text{-}CF_3C_2CF_3)_2$ [21] and $Pt_2(COD)_2(\mu\text{-}CF_3C_2CF_3)_2$ [22], and the heteronuclear MoCo complex is known to undergo conversion into a metallacyclopentadiene complex.

In our work, we have been able to isolate some examples of different binuclear 'bis-alkyne' intermediates, and monitor their conversion to binuclear metallacyclopentadiene complexes. We have proposed the structure **2** for the intermediates, and we visualize its formation in terms of: (i) displacement of $CF_3C^4{\equiv}C^5CF_3$ away from Rh^1 (see **8**); (ii) insertion of $RC^2{\equiv}C^3H$ into the Rh^1–C^4 bond; and (iii) subsequent formation of the C^2–C^5 bond. This is closely related to the "side on attack" intermediate proposed by Hoffmann rather than to the complexes with two coordinated alkynes proposed by Green and others. Thus, there is now experimental evidence for a variety of different intermediates in the formation of binuclear metallacyclopentadiene complexes. Presumably, different pathways can be followed depending upon the nature of the initial M_2 species.



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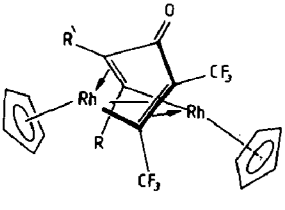
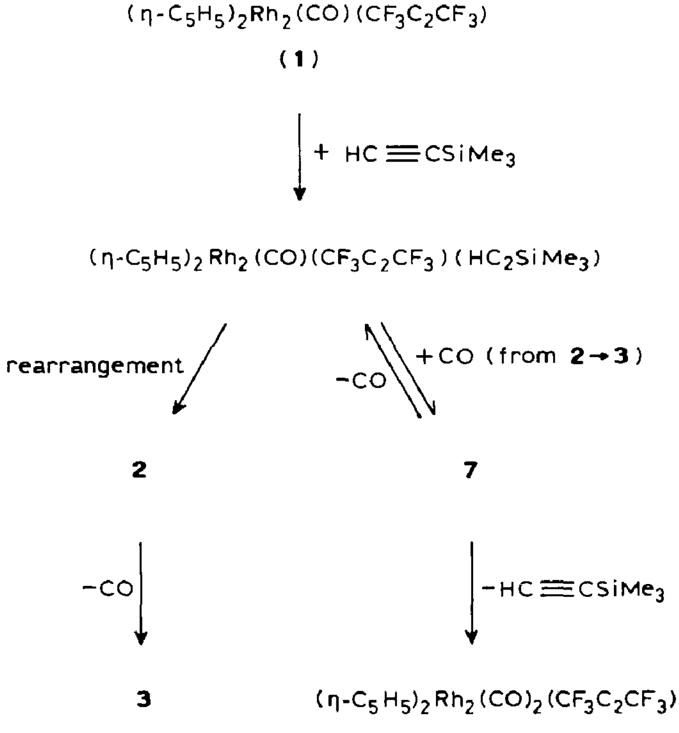


(9)

We observe very facile decarbonylation of our intermediate **2** in solution, and this is accompanied by rearrangement of the η^1,η^3-cyclobutenyl ring to generate the metallacyclopentadiene ring. This occurs with complete regioselectivity, the H and R group occupying the 3- and 2-positions respectively. Stereo-electronic factors are expected to contribute to the regioselectivity of formation of metalladiene ring systems. Small substituents should favour formation of the C^3–C^4 bond (see **6**), and



Scheme 3

electron-withdrawing substituents should stabilize Rh–$C^{2,5}$ σ-bond formation [19]. It has been argued [23] that steric factors alone will control the selectivity when substituents are bulky and steric and electronic influences are in competition. In reactions with terminal alkynes, there is clearly no steric or electronic inhibition to C^3–C^4 bond formation when H is attached to C^3, and we suggest this is the over-riding influence in controlling the regioselectivity in our reactions.

It is interesting to reflect further on the reactions involving terminal alkynes with bulky substituents. In the reaction of **1** with $HC{\equiv}CSiMe_3$, a different intermediate **7** is detected and the formation of **3** (R = $SiMe_3$) is relatively slow. An even slower reaction occurs between **1** and $HC{\equiv}CBu^t$ [4], and there is formation of a variety of products, one of which is **3** (R = Bu^t). Formation of the trimethylsilyl complex **7** is not easy to explain because it involves the addition of CO as well as $HC{\equiv}CSiMe_3$ to **1**. It seems unlikely that the reaction sequence is CO addition followed by alkyne addition because $HC{\equiv}CSiMe_3$ does not add to $(\eta\text{-}C_5H_5)_2Rh(CO)_2(\mu\text{-}CF_3C_2CF_3)$ under the reaction conditions. Alkyne addition followed by CO insertion to relieve steric strain is a possible pathway (see Scheme 3), and would account for all the products detected.

All the reactions between **1** and HC≡CR have given **3** as the major, and sometimes the only, end product. By comparison, the corresponding reactions with internal alkynes RC≡CR′ gave dimetallacycloheptadienone complexes (**9**) except when at least one aryl or electron-withdrawing substituent was present on the alkyne. With the latter systems, metalladiene complexes equivalent to **3** were obtained together with an equal amount of the dicarbonyl complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$; in a few instances (R = R′ = Me_3Si, CF_3 or CN), there was formation of **9** as well as **3** plus $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)$. It seems reasonable to suggest that the differences in product distribution are a reflection of the relative rates of formation of **2** or other intermediates to **3** or **9**, and reactions of released CO with any unchanged **1**.

In all cases where formation of metalladiene complexes is dominant, the reactions are fast. With terminal alkynes, little $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is obtained presumably because **1** reacts with HC≡CR much more quickly than it adds CO. With internal alkynes, the formation of approximately equal amounts of **3** and $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ probably indicates that CO addition to **1** is relatively fast compared to the reaction of **1** with RC≡CR′.

The reactions with non-polar, internal alkynes, which lead to **9**, are much slower. This can be explained if the normally fast C^3–C^4 bond formation which gives **3** is severely inhibited to steric and/or electronic factors in these cases, and there is then preference for an alternative pathway involving prior reaction between one alkyne and CO and subsequent condensation of the bridging ene-one with the second alkyne. Overall, a dominant factor in the formation of **3** or **9**, and in the regioselectivity observed in the formation of **3** from terminal alkynes, is the ease with which the C^3–C^4 bond in the metalladiene ring is formed.

Experimental

General

The general procedures and instruments used are described in previous papers in this series (see ref. 4). Preparative radial chromatography was carried out on a "chromatotron" model 7924T using Merck Silica Gel with gypsum (60 PF/UV-254, No. 7749). Acetylene was purchased as a solution in acetone from Commonwealth Industrial Gases Lt., Melbourne, Australia; the acetone was removed by bubbling the vapour through concentrated H_2SO_4. Other alkynes were obtained from Farchan Laboratories, Albany International Chemicals Division, Ohio, USA, and were used as obtained.

Reactions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ with alkynes

(i) HC≡CH. An excess of acetylene (0.10 g) was condensed at −196 °C into an evacuated Carius tube containing a green solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.085 g, 0.16 mmol) in hexane (10 ml). By the time the solution had attained room temperature the reaction was complete. The solution was dark red in colour, and a dark red precipitate was present. Filtration of the mixture and subsequent washing of the residue with pentane gave dark red needles of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2H)$ (0.087 g, 98%) m.p. 123°C (Found: C, 36.9; H, 2.3; F, 20.9. $C_{17}H_{12}F_6ORh_2$ calcd.: C, 37.0; H, 2.2; F, 20.7%). Mass spectrum: 552 (2%, M), 524 (100%, $M-CO$), 505 (5%, $M-CO-F$), 459 (28%, $M-CO-C_5H_5$). Infrared spectrum (CH_2Cl_2): $\nu(CO)$ at 1864vs cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 11.2 (dm, J(H–H) 3.7 Hz, 1H, HC_2H), 5.59 (s, 5H, C_5H_5), 5.55 (d, J(Rh–H) 0.9 Hz, 5H, C_5H_5), 4.67 (m, 1H, HC_2H). ^{19}F NMR ($CDCl_3$): δ (ppm) −53.4 (q, J(F–F) 13 Hz, 3F, CF_3), −57.8 (q, J(F–F) 13 Hz, 3F, CF_3).

When left in solution (CH_2Cl_2, $CHCl_3$ or acetone), or applied to a TLC plate (silica), the above complex was transformed rapidly into $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H_2\}$ (> 95% conversion) m.p. 113°C (Found: C, 36.3; H, 2.3; F, 22.0. $C_{16}H_{12}F_6Rh_2$ calcd.: CC, 36.7; H, 2.3; F, 21.8%). Mass spectrum: 524 (100%, M), 505 (6%, $M-F$), 459 (21%, $M-C_5H_5$), 233 (71%, $C_{10}H_{10}Rh^+$). Infrared spectrum: no $\nu(CO)$ absorptions. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 7.75 (d, J(H–H) 5.3 Hz, 1H, =CH), 6.04 (t or dd, $J(H\text{–}H) \approx J(Rh\text{–}H) \approx 5$ Hz, 1H, =CH), 5.52 (d, J(Rh–H) 0.9 Hz, 5H, C_5H_5), 5.28 (d, J(Rh–H) 0.6 Hz, 5H, C_5H_5). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) −49.8 (q, J(F–F) 12 Hz, 3F, CF_3), −52.5 (q, J(F–F) 12 Hz, 3F, CF_3).

(ii) HC≡CCF₃. An excess of 1,1,1-trifluoropropyne (0.12 g) was condensed at −196°C into an evacuated Carius tube containing a solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.068 g, mole ratio 10/1) in hexane (10 ml). When warmed to room temperature, the colour of the solution changed from green to orange, and orange crystals were deposited rapidly. These were filtered off and washed with hexane to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2CF_3)$ (0.077 g, 95%) m.p. 111°C (Found: C, 34.9; H, 1.8; F, 27.3. $C_{18}H_{11}F_9ORh_2$ calcd.: C, 34.9; H, 1.8; F, 27.6%). Mass spectrum: 620 (3%, M), 592 (100%, $M-CO$), 527 (30%, $M-CO-C_5H_5$), 187 (30%, $C_5H_5FRh^+$), 168 (58%, $C_5H_5Rh^+$). Infrared spectrum: $\nu(CO)$ at 1895 (Nujol) or 1875 cm^{-1} (CH_2Cl_2). ^1H NMR spectrum ($CDCl_3$) *: δ (ppm) 5.65 (s, 10H, $2\times C_5H_5$); 4.68 (m, 1H, =CH). ^{19}F NMR

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* In solution, this complex is transformed very rapidly to $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_3H\}$, and the NMR spectra invariably contain peaks for both complexes. When the ^1H spectrum is recorded for solutions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}CF_3C_2CF_3)(HC_2CF_3)$ in acetone-d_6, two $\delta(C_5H_5)$ resonances are detected at 5.83(s) and 5.80(s) ppm.

spectrum ($CDCl_3$): δ (ppm) -51.9 (q, J(F–F) 11 Hz, 3F, CF_3), -56.6 (q, J(F–F) 11 Hz, 3F, CF_3), -60.4 (s, 3F, CF_3).

The compound was dissolved in $CHCl_3$ or CH_2Cl_2, and the solutions were kept for 30 min. Subsequent TLC with a 8/3 mixture of pentane/dichloromethane as eluent separated small amounts of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2CF_3)$ from a major dark red band. Extraction with dichloromethane and evaporation of solvent gave dark red crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_3H\}$ (> 90% conversion) m.p. 173 °C (Found: C, 34.3; H, 2.0; F, 28.9. $C_{17}H_{11}F_9Rh_2$ calcd.: C, 34.5; H, 1.9; F, 28.9%). Mass spectrum: 592 (100%, M), 573 (10%, $M - F$), 527 (32%, $C_{12}H_6F_9Rh_2$), 405 (14%, $C_{12}H_6F_8Rh^+$), 233 (78%, $C_{10}H_{10}Rh^+$). Infrared spectrum: no ν(CO) absorptions. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 6.23 (d, J(Rh–H) 6.5 Hz, 1H, =CH), 5.60 (d, J(Rh–H) 0.6 Hz, 5H, C_5H_5), 5.33 (s, 5H, C_5H_5). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) -50.1 (q, J(F–F) 12 Hz, 3F, CF_3), -52.6 (q, J(F–F) 12 Hz, 3F, CF_3), -55.9 (s, 3F, CF_3).

(iii) HC≡CPh. When $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.080 g) and phenylacetylene (0.16 g, mole ratio 1/10) were mixed in hexane (10 ml), there was an immediate colour change and deposition of dark red crystals. These were filtered off and washed with hexane to give $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2Ph)$ (0.080 g, 94%) m.p. 113 °C (Found: C, 44.2; H, 2.6; F, 17.9. $C_{23}H_{16}F_6ORh_2$ calcd.: C, 44.0; H, 2.6; F, 18.1%). Mass spectrum: 600 (100%, $M - CO$), 581 (2%, $M - CO - F$), 535 (12%, $M - CO - C_5H_5$), 233 (46%, $C_{10}H_{10}Rh^+$). Infrared spectrum (CH_2Cl_2): ν(CO) at 1850vs cm^{-1}. ^1H NMR spectrum (acetone-d_6): δ (ppm) 7.7–7.2 (multiplets, 5H, C_6H_5), 5.56 and 5.55 ($2 \times$ s, 10H, $2 \times C_5H_5$), 4.63 (d(br), 1H, CH). ^{19}F NMR spectrum (acetone-d_6): δ (ppm) -51.6 (q, J(F–F) 12 Hz, 3F, CF_3), -56.4 (q, J(F–F) 12 Hz, 3F, CF_3).

In solution (CH_2Cl_2, $CHCl_3$, or acetone), this complex was transformed relatively slowly at room temperature to a new species. TLC of the aged solution with a 8/3 mixture of pentane/dichloromethane as eluent separated unchanged $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2Ph)$ from a small amount of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2$-$(CF_3C_2CF_3)$ and a major orange band. Extraction of the latter gave orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2HPh\}$ m.p. 135 °C (Found: C, 44.2; H, 2.8; F, 19.3. $C_{22}H_{16}F_6Rh_2$ calcd.: C, 44.0; H, 2.7; F, 19.0%). Mass spectrum: 600 (100%, M), 581 (2%, $M - F$), 535 (26%, $M - C_5H_5$). Infrared spectrum: no ν(CO) absorption. ^1H NMR spectrum (acetone-d_6): δ (ppm) 7.4–7.1 (multiplets, 5H, C_5H_5), 5.98 (d, J(Rh–H) 3.5 Hz, 1H, CH), 5.68 (d, J(Rh–H) 1 Hz, 5H, C_5H_5), 5.14 (d, J(Rh–H) 0.6 Hz, 5H, C_5H_5). ^{19}F NMR spectrum (acetone-d_6): δ -48.5 (q, J(F–F) 11 Hz, 3F, CF_3), -51.3 (q, J(F–F) 11 Hz, 3F, CF_3).

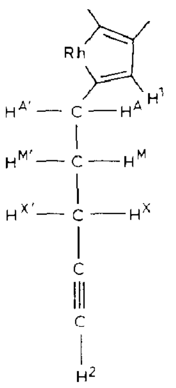
(iv) $HC{\equiv}CCH_2CH_2CH_3$. An excess of 1-pentyne (0.09 g) was added to a solution of $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.071 g, mole ratio 10/1) in hexane (10 ml) at 20 °C. There was an immediate colour change from green to orange-red, but no precipitate separated. Concentration of the mixture, followed by TLC, with a 2/3 mixture of pentane/dichloromethane as eluent, separated three major bands from some trace bands; the latter were not identified. The major bands were extracted with CH_2Cl_2. The first yellow band gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.009 g, 17%). The second yielded orange-red crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2$-$HPr\}$ (0.056 g, 74%) m.p. 124 °C (Found: C, 40.2; H, 3.3; F, 19.8. $C_{19}H_{18}F_6Rh_2$ calcd.: C, 40.3; H, 3.2; F, 20.1%). Mass spectrum: 566 (55%, M), 511 (16%, $M - C_4H_7$), 233 (100%, $C_{10}H_{10}Rh^+$). Infrared spectrum: no ν(CO) absorption. ^1H

NMR spectrum ($CDCl_3$): δ (ppm) 5.75 (br, 1H, =CH), 5.50 (d, J(Rh–H) 0.9 Hz, 5H, C_5H_5), 5.26 (d, J(Rh–H) 0.6 Hz, 5H, C_5H_5), 2.7–2.2 and 1.6–1.3, complex multiplets, 4H, CH_2CH_2), 0.94 (overlapping dd, J(H–H) $\approx$ J(H–H′) $\approx$ 7 Hz, 3H, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) -49.9 (q, J(F–F) 12 Hz, 3F, CF_3), -52.4 (q, J(F–F) 12 Hz, 3F, CF_3). The final orange-red band gave a solution which showed ν(CO) at 1850 cm^{-1} in the infrared spectrum. There was rapid conversion of this complex into $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2HPr\}$ when the solution was allowed to stand for 5–10 min, or during re-chromatography.

(v) $HC_2CH_2CO_2Me$. $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.050 g) and 2-propynyl acetate (0.09 g, mole ratio 1/10) were mixed in hexane (10 ml). There was an immediate colour change to red, and a red oil formed and adhered to the sides of the flask. The infrared spectrum of the hexane solution showed a strong carbonyl band at 1850 cm^{-1}; the intensity of this absorption decreased rapidly with time. Hexane was evaporated from the mixture and the oily residue was dissolved in dichloromethane. TLC of this solution with a 1/2 mixture of hexane/CH_2Cl_2 as eluent separated $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.005 g, 9%) and several trace bands from one major orange band. The latter yielded orange crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H(CH_2CO_2Me)\}$ (0.048 g, 84%) m.p. 74–75 °C (Found: C, 38.0; H, 2.6; F, 19.5. $C_{19}H_{16}F_6O_2Rh_2$ calcd.: C, 38.3; H, 2.7; F, 19.1%). Mass spectrum: 596 (58%, M), 577 (4%, $M-F$), 537 (16%, $M-CO_2Me$), 471 (28%, $M-C_5H_5-CF_3-H$), 233 (100%, $C_{10}H_{10}Rh^+$). Infrared spectrum (CH_2Cl_2): ν(CO) at 1730 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 5.99 (d, J(Rh–H) 3 Hz, 1H, =CH), 5.52 (d, J(Rh–H) 1.2 Hz, 5H, C_5H_5), 5.29 (s, 5H, C_5H_5), 5.12 and 4.86 ($2\times$d, J(H–H′) 15 Hz, 2H, H–C–H′), 2.10 (s, 3H, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) -50.1 (q, J(F–F) 12 Hz, 3F, CF_3), -52.4 (q, J(F–F) 12 Hz, 3F, CF_3).

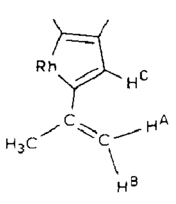
(vi) $HC{\equiv}CCH_2CH_2CH_2C{\equiv}CH$. A solution containing $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ (0.060 g) and 1,6-heptadiyne (0.105 g, mole ratio 1/10) in hexane (20 ml) was stirred for 2 min, during which the colour changed from green to red. Evaporation of some solvent followed by TLC with a 1/1 mixture of hexane/CH_2Cl_2 (plates) or hexane/Et_2O ('chromatotron') as eluent separated three main bands from several minor bands which were rejected. The first major band gave $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (0.014 g, 22%). The second gave red crystals of $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H(CH_2CH_2CH_2C_2H)$ (0.018 g, 28%) m.p. 114–115 °C (Found: C, 43.0; H, 3.2; F, 19.3. $C_{21}H_{18}F_6Rh_2$ calcd.: C, 42.7; H, 3.1; F, 19.3%). Mass spectrum: 590 (10%, M), 336 (22%, $C_{10}H_{10}Rh_2{}^+$), 233 (100%, $C_{10}H_{10}Rh^+$). Infrared spectrum: no ν(CO) absorptions. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 5.76 (d, J 2.8 Hz, 1H, H^2), 5.52 (d, J(Rh–H) 1.0 Hz, 5H, C_5H_5), 5.28 (s, 5H, C_5H_5), 2.77 (ddd, $J(H^X-H^{X'})$ 13 Hz, $J(H^X-H^M)$ 9 Hz, $J(H^X-H^{M'})$ 5 Hz, 1H, H^X), 2.41 (ddd, $J(H^X-H^{X'})$ 13 Hz, $J(H^X-H^{M'})$ 9 Hz, $J(H^{X'}-H^M)$, 6 Hz, 1H, $H^{X'}$), 2.23 (m, 2H, $H^A+H^{A'}$), 2.02 (t, J(Rh–H) $\approx$ $J(Rh-H^1)$ $\approx$ 2 Hz, 1H, H^1), 1.7 (m, 2H, $H^M+H^{M'}$). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) -49.8 (q, J(F–F) 11 Hz, 3F, CF_3), -52.3 (q, J(F–F) 11 Hz, 3F, CF_3).

The final major band gave a red solid identified spectroscopically as $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)(HC_2CH_2CH_2CH_2C_2H)$ (0.033 g, 49%). Spectroscopic data showed that attempts to purify this compound by recrystallization inevitably led to some contamination with $(\eta\text{-}C_5H_5)_2Rh_2\{C_4(CF_3)_2H(CH_2CH_2CH_2C_2H)\}$. Mass spectrum: 618 (5%, M), 590 (10%, $M-CO$), 336 (15%, $C_{10}H_{10}Rh_2{}^+$), 233



(100%, $C_{10}H_{10}Rh^+$). Infrared spectrum (CH_2Cl_2): ν(CO) at 1850vs cm^{-1}. ^1H NMR spectrum ($CDCl_3$): 5.59 (s, 5H, C_5H_5), 5.50 (s, 5H, C_5H_5), 4.31 (d, J 3.1 Hz, 1H, H^2), 3.98 (ddd, $J(H^X–H^{X'})$ 13.5, $J(H^{X'}–H^M)$ 10, $J(H^{X'}–H^{M'})$ 7.5 Hz, 1H, H^X), 2.35 (m, 1H, $H^{A'}$), 2.25 (m, 1H, H^A), 2.06 (t, $J(Rh–H) \approx J(Rh'–H) \approx J(Rh'–H) \approx 2$ Hz, 1H, H^1), 1.97 (m, 1H, $H^{M'}$), 1.82 (m, 1H, H^M). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) −53.4 (q, J(F–F) 10 Hz, 3F, CF_3) and −57.8 (q, J(F–F) 10 Hz, 3F, CF_3). ^{13}C NMR spectrum (^{13}CO-enriched sample, $CDCl_3$, Cracac$_3$ added): δ (ppm) (CO) 212.6 (dd, J(Rh–C) 63 Hz, J'(Rh–C) 28 Hz).

(vii) $HC{\equiv}CCMe{=}CH_2$. A solution of (η-C_5H_5)$_2$Rh$_2$(CO)($CF_3C_2CF_3$) (0.060 g) in hexane (30 ml) was treated with 2-methylbut-1-ene-3-yne (0.075 g, mole ratio 1/10); within 5 min, the solution was a deep red colour. Some solvent was removed under reduced pressure. Subsequent TLC with a 1/1 mixture of hexane/CH_2Cl_2 as eluent separated a small amount of unchanged (η-C_5H_5)$_2$Rh$_2$(CO)($CF_3C_2CF_3$) (0.002 g) from two major products. The first was a red solid which was recrystallized from CH_2Cl_2/pentane to give red crystals of (η-C_5H_5)$_2$Rh$_2${$C_4(CF_3)_2$-H(CMeCH$_2$)} (0.019 g, 30%) m.p. 118°C dec. (Found: C, 40.9; H, 2.7; F, 19.9. $C_{19}H_{16}F_6Rh_2$ calcd.: C, 40.5; H, 2.9; F, 20.2%). Mass spectrum: 564 (100%, M), 499 (10%, $M - C_5H_5$), 233 (65%, $C_{10}H_{10}Rh^+$). Infrared spectrum: no ν(CO) absorptions. ^1H NMR spectrum ($CDCl_3$): δ (ppm) 5.87 (d, $J(H^A–H^B)$ 1.5 Hz, 1H, H^A or H^B), 5.54 (s, 5H, C_5H_5), 5.21 (s, 5H, C_5H_5), 4.83 (d, $J(H^A–H^B)$ 1.5 Hz, 1H, H^A or H^B), 4.73 (t, $J(Rh–H^C) \approx J(Rh'–H^C) \approx 1.5$ Hz, 1H, H^C), 1.96 (s, 3H, CH_3). ^{19}F NMR spectrum ($CDCl_3$): δ (ppm) −50.1 and −52.1 (2 × q, J(F–F) 9 Hz, 2 × 3F, 2 × CF_3).



The second major product was also a red crystalline solid. It could not be obtained analytically pure because it was converted in solution into (η-C_5H_5)$_2$Rh$_2${$C_4(CF_3)_2$H(CMeCH$_2$)}. However, spectroscopic data indicated it was (η-C_5H_5)$_2$Rh$_2$(CO)($CF_3C_2CF_3$)(HC_2CMeCH_2) (0.043 g, 66%). Mass spectrum: 564

(100%, $M-\mathrm{CO}$), 499 (10%, $M-\mathrm{CO}-\mathrm{C_5H_5}$), 233 (65%, $\mathrm{C_{10}H_{10}Rh^+}$). Infrared spectrum ($\mathrm{CH_2Cl_2}$): ν(CO) at 1858vs $\mathrm{cm^{-1}}$. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$): δ (ppm) 5.55 (s, 5H, $\mathrm{C_5H_5}$), 5.48 (s, 5H, $\mathrm{C_5H_5}$), 5.07 (d, $J(\mathrm{H^A}$-$\mathrm{H^B})$ 2 Hz, 1H, $\mathrm{H^A}$ or $\mathrm{H^B}$), 4.93 (s(br), 1H, $\mathrm{H^C}$), 4.45 (d, $J(\mathrm{H^A}$-$\mathrm{H^B})$ 2 Hz, 1H, $\mathrm{H^A}$ or $\mathrm{H^B}$), 2.30 (s, 3H, $\mathrm{CH_3}$). ^{19}F NMR spectrum ($\mathrm{CDCl_3}$): δ (ppm) -53.2 and -57.7 ($2\times$q, J(F–F) 14 Hz, 2×3F, $2\times\mathrm{CF_3}$).

(viii) HC≡CSiMe$_3$. A solution of (η-$\mathrm{C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)}$ (0.067 g) in hexane (10 ml) was treated with trimethylsilylacetylene (0.13 g, mole ratio 1/10); the colour of the solution changed from green to orange during about 15 min at 20 °C. TLC of the solution with a 8/3 mixture of hexane/$\mathrm{CH_2Cl_2}$ as eluent separated one major orange band from (η-$\mathrm{C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)}$ (0.015 g, 21%) and numerous trace bands which were rejected.

Evaporation of solvent from the major orange band gave orange-red crystals of (η-$\mathrm{C_5H_5)_2Rh_2\{C_4(CF_3)_2H(SiMe_3)\}}$ (0.049 g, 64%) m.p. 118 °C (Found: C, 39.0; H, 3.1; F, 19.0. $\mathrm{C_{19}H_{20}F_6Rh_2Si}$ calcd.: C, 38.3; H, 3.4; F, 19.1%). Mass spectrum: 596 (100%, M), 581 (32%, $M-\mathrm{CH_3}$), 233 (100%, $\mathrm{C_{10}H_{10}Rh^+}$). Infrared spectrum: no ν(CO) absorptions. ^{1}H NMR spectrum (acetone-d_6): δ (ppm) 6.05 (d, J(Rh–H) 3.5 Hz, 1H, =CH), 5.68 (d, J(Rh–H) 0.9 Hz, 5H, $\mathrm{C_5H_5}$), 5.28 (s, 5H, $\mathrm{C_5H_5}$), 0.15 (s, 9H, $\mathrm{SiMe_3}$). ^{19}F NMR spectrum ($\mathrm{CDCl_3}$): δ (ppm) -50.1 and -52.0 ($2\times$q, J(F–F) 12 Hz, 2×3F, $2\times\mathrm{CF_3}$).

When the procedure was repeated but the mixture was worked up within 5×10 min, a significant amount (10–25% yield, depending on reaction time) of a second complex was isolated. This transformed to (η-$\mathrm{C_5H_5)_2Rh_2\{C_4(CF_3)_2H(SiMe_3)\}}$ when left in solution, and it could not be recrystallized. Spectroscopic data indicated the formulation (η-$\mathrm{C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)(HC_2SiMe_3)}$. Mass spectrum: 652 (1%, M), 624 (4%, $M-\mathrm{CO}$), 596 (88%, $M-2\mathrm{CO}$), 581 (36%, $M-2\mathrm{CO}-\mathrm{CH_3}$), 387 (85%, $M-\mathrm{C_4F_6}-\mathrm{Rh}$), 168 (100%, $\mathrm{C_5H_5Rh^+}$). Infrared spectrum ($\mathrm{CH_2Cl_2}$): ν(CO) at 1870s, 1705 vs $\mathrm{cm^{-1}}$. ^{1}H NMR spectrum ($\mathrm{CDCl_3}$): δ (ppm) 7.26 (s, 1H, CH), 5.58 (s, 5H, $\mathrm{C_5H_5}$), 5.45 (s, 5H, $\mathrm{C_5H_5}$), 0.19 (s, 9H, $\mathrm{SiMe_3}$). ^{19}F NMR spectrum ($\mathrm{CDCl_3}$): δ (ppm) -58.1 (q, J(F–F) 8 Hz, 3F, $\mathrm{CF_3}$) and -60.3 (qd, J(F–F) 8 Hz, J(Rh–F) 4 Hz, 3F, $\mathrm{CF_3}$).

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