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THE STRUCTURES AND DYNAMIC BEHAVIOR OF SOME POLYNUCLEAR ALKYNE-RHODIUM COMPLEXES

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Summary

The known complex, trans-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is formed in high yield from $(\eta\text{-}C_5H_5)Rh(CO)_2$ and $CF_3C{\equiv}CCF_3$ at 100°. The less stable cis-isomer of the complex is obtained in low yield from the same reaction. The infrared, ^1H, ^{19}F and ^{13}C NMR spectra of the two isomers are compared. The trans-isomer undergoes CO scrambling in solution at room temperature, and the variable temperature ^{13}C NMR spectra are consistent with a pairwise bridge opening and closing mechanism. The mechanism is extended to account for the isomerization of cis to trans isomer, which has a half-life of 12 h at room temperature. The ^{13}C spectrum indicates that the cis-isomer is static in solution at room temperature. The trans-isomer is reversibly protonated by protonic acids, and BF_4^- and PF_6^- salts of the protonated species can be isolated. The spectroscopic properties of these salts are consistent with protonation at one of the alkynyl-carbons, but it is not possible to distinguish between two alternative structures for the complex cation.

Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ with $(\eta\text{-}C_5H_5)Rh(CO)_2$ gives the trinuclear complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ in 80% yield. The analogous but-2-yne complex is formed from $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ and $MeC{\equiv}CMe$. The infrared, ^1H, ^{19}F and ^{13}C NMR spectra indicate that the hexafluorobut-2-yne complex exists in two different structural arrangements in solution. One has an edge bridging, and the other a face bridging carbonyl. The proportion of the isomers is affected by

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the solvent polarity. The spectra of the but-2-yne complex indicate it is fluxional at room temperature, and has a face bridging structure in solution regardless of the polarity of the solvent. Reversible protonation of the hexafluorobut-2-yne complex occurs in protonic acids, and the salt $[(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)H]^+[BF_4]^-.H_2O$ can be isolated. The spectroscopic properties of this complex are consistent with a structure incorporating an edge-bridging carbonyl, and probably, an edge-bridging hydride ligand.

Our investigations of the reactions between alkynes and $(\eta\text{-}C_5H_5)Rh(CO)_2$ [1-8], and complementary studies by Rausch and his co-workers [9-11], have provided a wide range of organo-rhodium complexes. These complexes incorporate the alkyne unit in several different structural arrangements. Recent interest in the binding of small molecules to metal clusters [12, 13] has prompted us to extend an earlier study [14] on the dynamics and solution structures of polynuclear alkyne-rhodium complexes. In this paper, we shall discuss the nature of the complexes cis- and trans-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$, $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CH_3C_2CH_3)$. Additionally, we report on the protonation of the two hexafluorobut-2-yne complexes in acidic media.

(a) $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$

In a previous paper [2] we reported formation of the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ in 54% yield* from the reaction between $(\eta\text{-}C_5H_5)Rh(CO)_2$ and $CF_3C{\equiv}CCF_3$ at 100°. We now find that a better yield of the complex is obtained if the $(\eta\text{-}C_5H_5)Rh(CO)_2$ is replaced by $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$; this procedure gives $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ in 60-70% yield under comparable conditions. Determination of the structure of the complex by single crystal X-ray diffraction [15] has revealed a σ-bridging alkyne-dimetal arrangement, and a trans geometry for the two carbonyls. A representation of the molecular structure is given in Fig. 1 which also lists some important bond parameters.

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* Reported incorrectly in reference [2] as 27% yield.

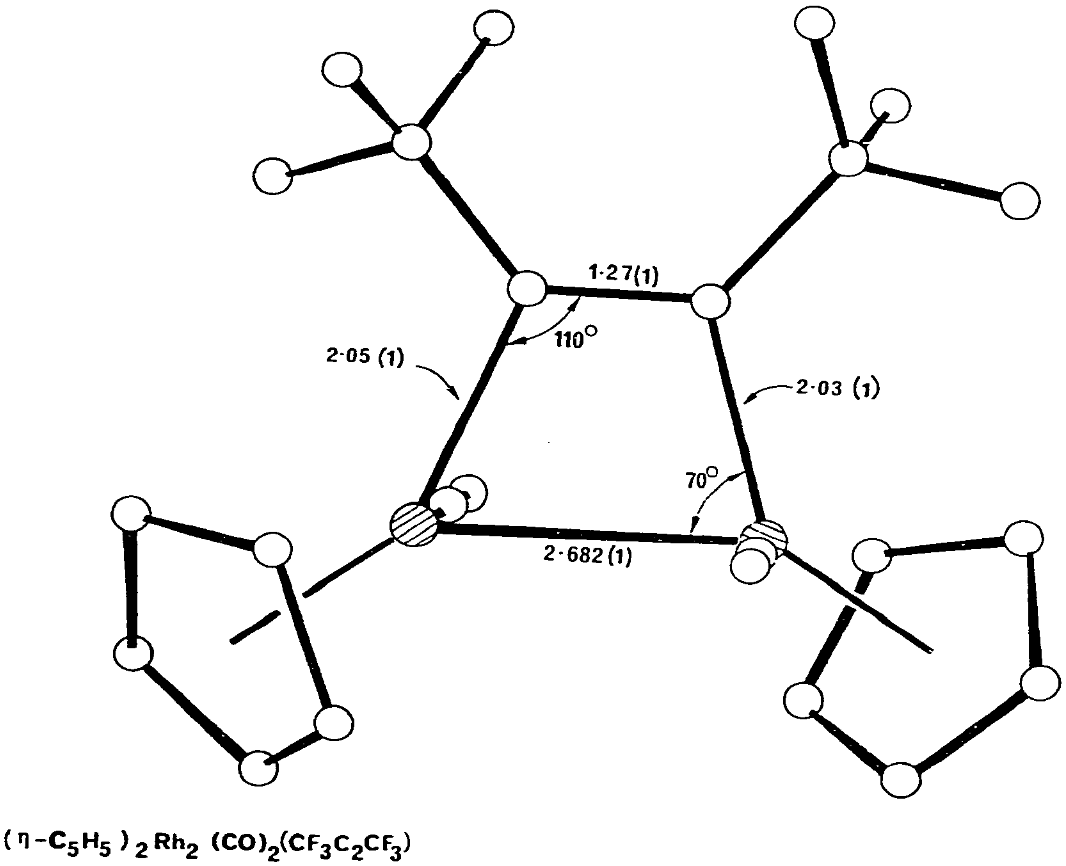


Fig. 1. Molecular structure of <u>trans</u>-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$

Formation of <u>trans</u>-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ in high yield, and purification of the complex by repeated thin layer chromatography, has enabled us to detect a very small amount ($<$ 1% yield) of a second species of identical formula. We suggest that the second isomer retains the σ-bridging alkyne group, but has a <u>cis</u>-arrangement of the two carbonyls and consequently of the two cyclopentadienyl groups. The infrared spectra of the complex are consistent with this. Two strong terminal carbonyl absorptions are observed at 2040 and 1993 cm^{-1} for solutions of the complex in $CHCl_3$, and at 2002 and 1966 cm^{-1} for the complex in the solid state (KBr disc). The two absorptions are assigned to the symmetric and asymmetric stretching modes for a <u>cis</u>-dicarbonyldimetal arrangement [16, 17].

In contrast, the spectra of solutions of the trans isomer show only one strong terminal carbonyl peak at 1992 ($CHCl_3$) or 2004 cm^{-1} (C_6H_{12}). This can be assigned to the asymmetric stretch of the trans-$M_2(CO)_2$ moiety. The symmetric stretching mode for this arrangement is expected to be weak. The infrared spectrum of solid samples of the trans complex shows two terminal carbonyl bands at 2022 and 1994 cm^{-1}. According to the rules developed by Adams [18] for the vibrational analysis of solids, two bands can be expected in the solid state spectrum of the trans isomer because of intermolecular interactions. Monitoring of the infrared spectrum of the cis isomer indicates it is unstable with respect to isomerization. Thus, in 12 hours at room temperature, a solution of pure cis isomer is converted to a 1:1 mixture of cis and trans isomers.

Unexpectedly, we have obtained substantial amounts of cis-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ from an experiment that was designed for a different purpose. In extending our previous investigation [19] of the reaction between $[Rh(CO)_2Cl]_2$ and $CF_3C{\equiv}CCF_3$, we treated the intractable products with thallous cyclopentadienide at room temperature and obtained high yields of cis-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$. This has enabled us to extend our spectroscopic study of this species.

The ^1H NMR data on the two isomers are similar, with the C_5H_5 resonance being observed at δ 5.54 and 5.59 for $CDCl_3$ solutions of the trans and cis isomers respectively. We reported previously [14] on the ^{13}C spectrum of the trans isomer. At room temperature, the carbonyl resonance is observed as a triplet (J Rh-C, 39.3 Hz) centred at δ 190.8 ppm, which is in the normal region for terminal carbonyls. At -40°, the multiplicity is reduced to a doublet (J Rh-C, 78.7 Hz), but there is no significant change in chemical shift (δ 190.8 ppm). These results can be interpreted in terms of the carbonyls being scrambled rapidly and non-dissociatively over the two sites at room temperature whereas CO site exchange is slow or stopped at -40°. We assume that the pathway for site exchange involves pairwise bridge closing and opening coupled with small concerted shifts of the cyclopentadienyl groups. A scheme is shown in Fig. 2. We suggest that the species A can be converted to B by pairwise bridge closing, and B can then open to regenerate A (- no site exchange) or to form C (- site exchange). The suggested pathway can be extended to cover the isomerization process. Thus, it is possible for the cis isomer D to bridge close stepwise to give B, which can then open to form the trans isomer A. Presumably, the thermodynamic

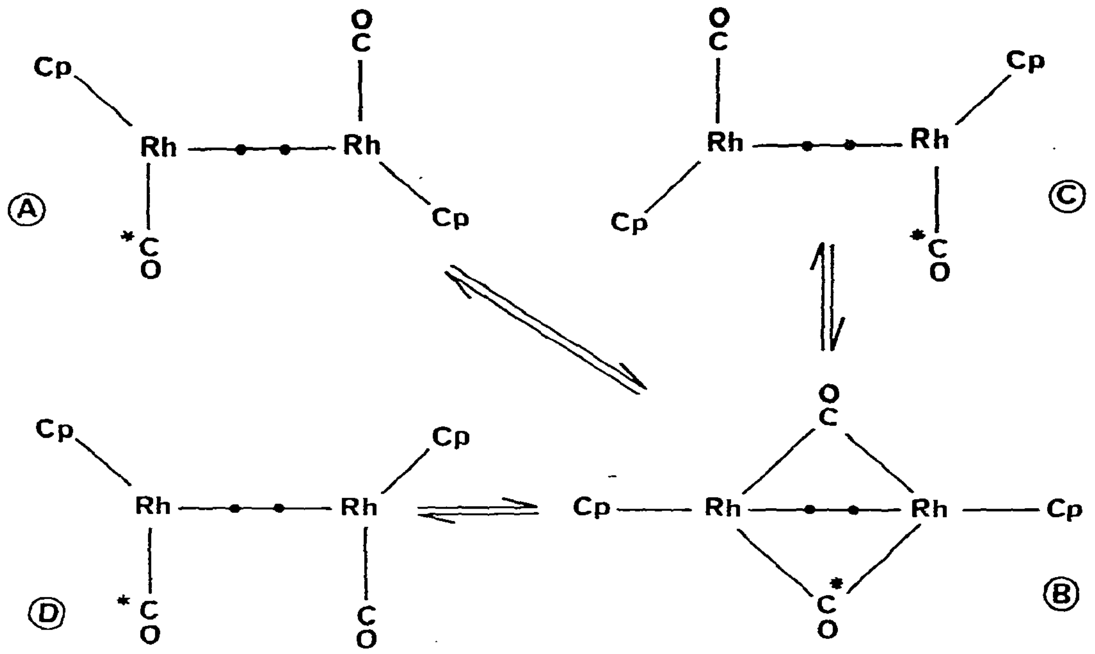


Fig. 2. Proposed pathway for carbonyl site exchange and for cis → trans isomerization in the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$. The molecule is viewed along the $\overset{\diagdown\quad\diagup}{\underset{Rh\diagup\quad\diagdown Rh}{C{=}C}}$ plane, and the CF_3 groups are removed for clarity.

stability of D is intrinsically low and hence we can isolate it only in very low yield. Overall, the pathway we suggest is closely related to those proposed by Cotton et al. [20] for isomerization and scrambling in complexes such as $(\eta\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta\text{-}C_5H_5)_2Mo_2(CO)_5(CNR)$. An important difference with our system is that rotation about the metal-metal bond is inhibited by the σ-attachment of the bridging alkyne unit. We have recorded the ^{13}C spectrum of a ^{13}CO-enriched sample of trans-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ at temperatures between room temperature and -40°. The results seem to be consistent with the suggested pathway. As the temperature is lowered, the centre peak of the triplet is observed to broaden while a sharp "doublet" pattern is retained at the extremities of the original triplet. As the doublet grows in intensity, the central peak continues to broaden until it finally merges into the background. The peak profile at various temperatures is shown in Fig. 3. This is a particularly interesting example of carbonyl

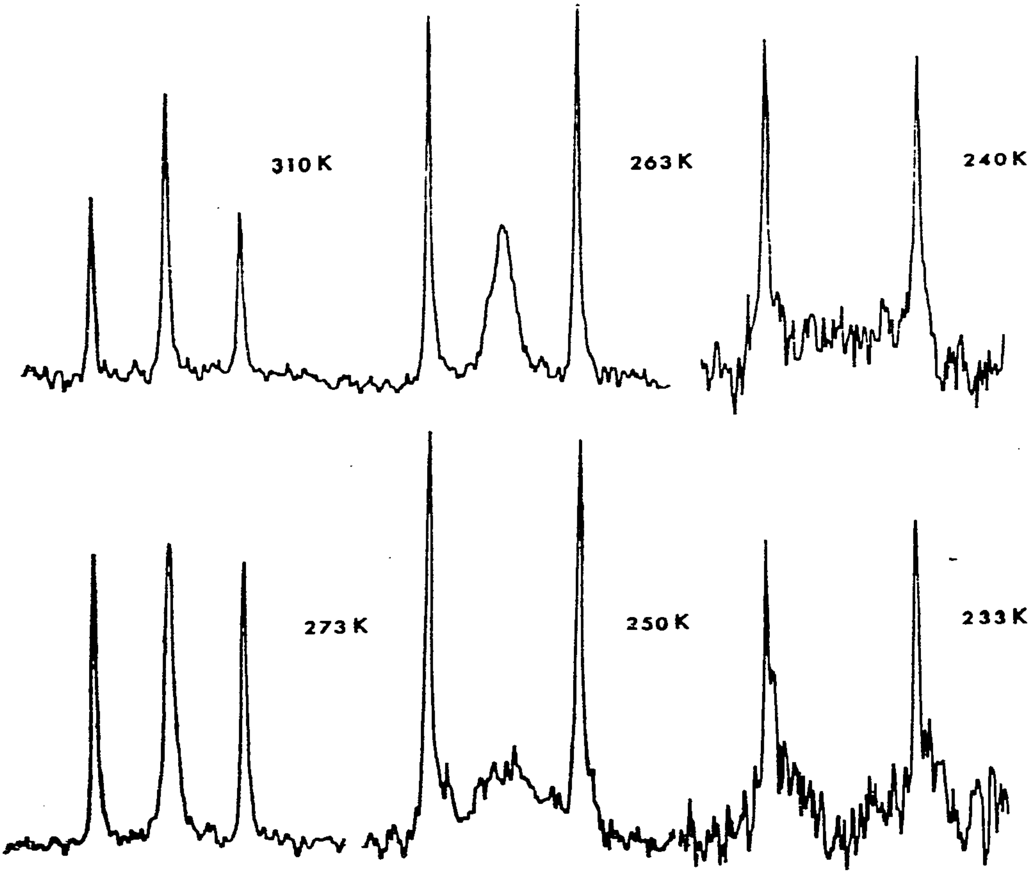


Fig. 3. ^{13}C NMR spectrum of trans-(η-$C_5H_5)_2Rh_2(^{13}CO)_2(CF_3C_2CF_3)$ at various temperatures.

scrambling because we are able to detect site exchange for carbonyls which are in identical chemical environments.

We have recorded the ^{13}C spectrum of a ^{13}C-enriched sample of cis-(η-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ at room temperature, using a freshly prepared sample so that isomerization was minimal. The carbonyl resonance is observed as a doublet (J Rh-C, 78.7 Hz) centred at δ 190.4 ppm. This result indicates that the cis isomer is static at room temperature.

The CF_3 resonance in the ^{19}F NMR spectrum of (η-$C_5H_5)_2Rh_2$-$(CO)_2(CF_3C_2CF_3)$ is observed at δ 55.09 and 55.12 ppm for the trans- and cis-isomers respectively. On an expanded scale, the resonance for the trans-isomer is seen as a 1:2:1 triplet. We believe this can be analyzed as a doublet of doublets with J Rh-F ~ J Rh'-F = 1.3 Hz, or alternatively, as a deceptively simple X_3X_3' ($AA'X_3X_3'$) spectrum [21]. We have excluded the possibility that the triplet pattern is related to the fluxional behavior of the molecule by recording the ^{19}F spectrum at low temperature. There is no change in the spectrum down to -100° where we know the structure is static.

(b) $[(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)H]^+$

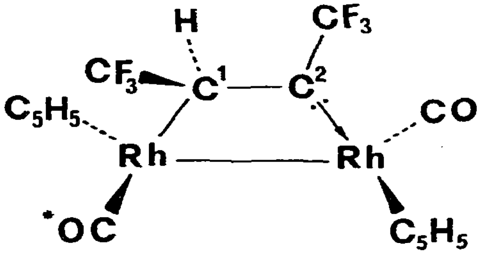
An interesting property of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ is its ability to undergo reversible protonation when dissolved in protonic acids such as H_2SO_4, CF_3CO_2H and aqueous HBF_4. We have isolated analytically pure samples of the protonated species as the PF_6^- and hydrated BF_4^- salts. The spectroscopic properties of these complex salts are consistent with protonation at one of the 'alkyne' carbons. Consequently, the protonation reaction can be written as follows:

$$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3) + HA \rightleftharpoons [(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3CC(H)CF_3)]^+ A^-$$

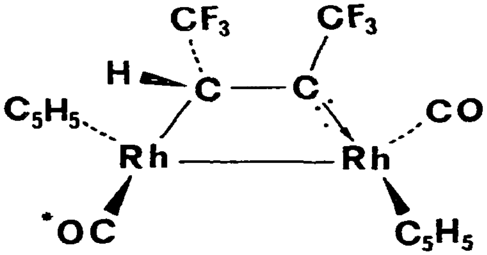
The ^1H spectrum of solutions of $[(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3CC(H)CF_3)]^+A^-$ in acetone (and of solutions of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ in H_2SO_4) indicates inequivalent $(\eta\text{-}C_5H_5)$ rings, and shows a peak of relative intensity 1H at δ 4.32. This resonance is split into a well resolved quartet of doublets with J F-H ~ 8.5 and J Rh-H ~ 2.0 Hz. The spectrum of the BF_4^- salt shows an additional line at δ 2.94 of relative intensity 2 H, and this is assigned to a molecule of coordinated water. The infrared spectrum and elemental analysis are also consistent with formulation of this complex salt as a monohydrate.

The ^{19}F spectrum of $[(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3CC(H)CF_3)]^+$ shows two CF_3 signals of equal intensity at δ 51.3 and 54.4 ppm. The peak at lower field is a well resolved quartet of doublets with J F-F' ~ 12.5 and J Rh-F ~ 1.5 Hz; we assign this peak to the CF_3 on the unprotonated carbon. The higher field peak has the appearance of a 1:4:6:4:1 pentuplet - however, we believe it is better viewed as two overlapping 1:3:3:1 quartets with J F-F' ~ 12.5 and J F-H ~ 8.5 Hz. There is additional splitting of the peaks (J ~ 1.5 Hz) due to Rh-F coupling. Thus, this is an AB_3X system which can be assigned to the CF_3 group which is attached to the protonated carbon.

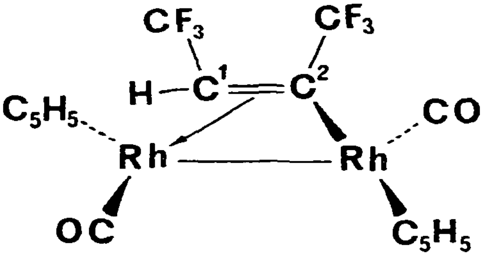
The ^1H and ^{19}F magnetic resonance data are consistent with both of the alternative structures I and II. In I, C1 is aliphatic and C2 is



Ia



Ib



II

carbenoid in nature. By contrast, C1 and C2 are both olefinic in II. Each type of carbon atom should be readily distinguished in the ^{13}C spectrum of the complex. In particular, a carbenoid carbon should be easily recognized because such carbons are generally very strongly deshielded (e.g. δ 250-370 ppm [22-24]) in transition metal complexes. Unfortunately, it is not easy to obtain a clean spectrum of $[(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3CC(H)(CF_3)]^+$ because the complex slowly decomposes in solution. We have recorded reasonable spectra of ^{13}CO enriched samples at -40°, but none reveals a very low field line. Rather, we observe a resonance in the normal olefinic region at δ 69.6, and another in the aliphatic region at δ 31.1 ppm. Both signals are observed as quartets with J F-C ~ 45 Hz. These results are probably more consistent with structure I although doubt remains about the precise nature of C2. A three-dimensional, single crystal X-ray diffraction study of the complex is planned.

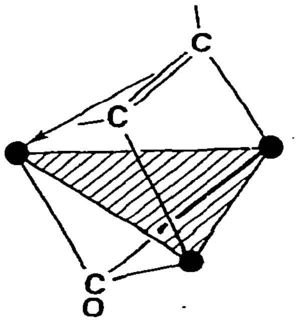
The remainder of the ^{13}C spectrum is certainly consistent with structure I (and structure II). Signals for the carbons of two $(\eta\text{-}C_5H_5)$, two CF_3, and two CO groups are found in the normal regions. The CO resonances are observed as a doublet at δ 188.2 (J Rh-C ~ 72 Hz) and two overlapping doublets at δ 186 ppm (J Rh-C ~ 80 Hz; separation

~ 4 Hz). We attribute the appearance of the latter band to the presence of two isomers (Ia and Ib) in solution. The small difference in the chemical environments of the carbonyls we have labelled CO* would account for the duplication of δ CO for this group.

(c) $(\eta\text{-}C_5H_5)_3Rh_3(CO)(RC_2R)$, R = CF_3 or Me

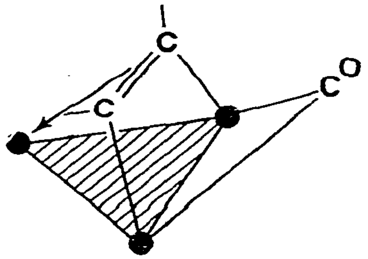
Our previous work on the reaction between $(\eta\text{-}C_5H_5)Rh(CO)_2$ and $CF_3C{\equiv}CCF_3$ gave the complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ in very low yield [2]. This trinuclear complex can be obtained in almost 25% yield from the reaction between $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ and $CF_3C{\equiv}CCF_3$. An even better synthesis involves treatment of the binuclear complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ with additional $(\eta\text{-}C_5H_5)Rh(CO)_2$; this procedure gives the trinuclear complex in approx. 80% yield. We suggest this reaction is the major pathway for formation of $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ in the direct reaction between $(\eta\text{-}C_5H_5)Rh(CO)_2$ and $CF_3C{\equiv}CCF_3$.

Previously, we found no evidence for formation of the related complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(MeC_2Me)$ in the reaction between $(\eta\text{-}C_5H_5)Rh(CO)_2$ and MeC≡CMe [2]. However, we have now isolated this complex in good yield from the reaction between $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ and MeC≡CMe. Analogous complexes with $RC_2R = PhC_2Ph$ or $C_6F_5C_2C_6F_5$ have been isolated by Rausch et al. [9, 10] from the reactions of $(\eta\text{-}C_5H_5)Rh(CO)_2$ with the appropriate alkyne. The structures of these two complexes have been determined by Dahl et al. [25], and two different structure types are found. In $(\eta\text{-}C_5H_5)_3Rh_3(CO)(PhC_2Ph)$, the carbonyl is in a face-bridging position (IIIa) whereas it is edge-bridging (IIIb) in



$(\eta\text{-}C_5H_5)_3Rh_3(CO)(PhC_2Ph)$

IIIa



$(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_6F_5C_2C_6F_5)$

IIIb

TABLE

CARBONYL STRETCHING FREQUENCIES (cm^{-1}) AND ASSIGNMENTS FOR THE COMPLEXES (η-C_5H_5)$_3$Rh$_3$(CO)(RC$_2$R)

RC$_2$R	Phase	ν(CO)		Assignment		
$CF_3C_2CF_3$	KBr		1710	IIIa		
$CF_3C_2CF_3$	$CHCl_3$	1820w,	1720m	IIIa	$\rightleftharpoons$	IIIb
$CF_3C_2CF_3$	acetone	1822m,	1720m	IIIa	$\rightleftharpoons$	IIIb
$CH_3C_2CH_3$	$CHCl_3$		1674	IIIa		
PhC$_2$Ph	KBr		1675	IIIa		
$C_6F_5C_2C_6F_5$	KBr	1810				IIIb

(η-C_5H_5)$_3$Rh$_3$(CO)($C_6F_5C_2C_6F_5$). Spectroscopic data indicate that the solid state structures are preserved in solution at room temperature [14, 26].

Our spectroscopic results for (η-C_5H_5)$_3$Rh$_3$(CO)($CF_3C_2CF_3$) (see Table) indicate that this complex is delicately poised between the alternative structure types. In the solid state and in relatively non-polar solvents, the face-bridging structure (IIIa) is preferred. However, with increasing solvent polarity, the concentration of the edge-bridging form (IIIb) increases. The infrared data are complemented by our NMR results. The ^{1}H spectrum of a solution of (η-C_5H_5)$_3$Rh$_3$(CO)($CF_3C_2CF_3$) in $CDCl_3$ or CS_2 shows a single C_5H_5 signal at δ 5.38. This is consistent with a face-bridged structure provided that the three rhodium environments are averaged by rapid rotation of the alkyne. The spectrum of the complex in CS_2 does not change when the solution is cooled to -100°, indicating that there is an exceedingly low barrier to rotation of the alkyne. This contrasts with the temperature dependence of the spectrum of (η-C_5H_5)$_3$Rh$_3$(CO)(PhC$_2$Ph) in CD_2Cl_2. The single C_5H_5- line in this spectrum becomes two lines of relative intensity 2:1 at -88° [14, 26]. This is consistent with freezing out of the alkyne - Rh$_3$ arrangement into the bonding conformation which is found in the solid state structure.

For solutions of (η-C_5H_5)$_3$Rh$_3$(CO)($CF_3C_2CF_3$) in acetone, the ^{1}H spectrum is more complex. Three C_5H_5 signals are observed at room temperature. A peak at δ 5.46 can be assigned to the face bridging form, and two doublets at δ 5.42 and 5.66 of relative intensity 2:1 can then be assigned to the edge bridging form. At -70^{o}, the spectrum becomes even more complex in that two new peaks are added to those observed in the room temperature spectrum. We assign one peak at δ 5.55 to the time averaged face-bridging isomer, and a pair of peaks at δ 5.48 and 5.77 of relative intensity 2:1 can then be assigned to the edge-bridging form. The remaining two peaks at δ 5.50 and 5.85 are weaker than the others. We suggest that these latter two peaks are due to partial freezing out of the face-bridging form to a conformation similar to that found for $(\eta\text{-}C_5H_5)_3Rh_3(CO)(PhC_2Ph)$ in the solid state, and in solution at low temperatures. The fact that this conformation is not observed for $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ in CS_2 at -100^{o} indicates that it is stabilized somewhat by the more polar solvent, acetone.

In the ^{19}F spectrum, a single CF_3 resonance is observed for solutions in $CDCl_3$, but two lines are observed in acetone. Integration of the ^{19}F spectrum in acetone indicates that the proportion of face to edge bridging isomers is about 45:55 at room temperature. On an expanded scale, the ^{19}F spectrum in $CDCl_3$ is observed as a quartet which is consistent with time averaged coupling to all three rhodium nuclei. The two lines observed in acetone are a quartet and a complex five line multiplet with peak heights in the approximate ratio 1:1:2:1:1. Although this might be treated as a doublet of two overlapping doublets, it is probably better regarded as an $A_3A'_3XX'Y$ spin system. The multiplet cannot be resolved further with our instrument.

The ^{13}C spectrum of $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ in $CDCl_3$ shows a single C_5H_5 line at δ 89 and a single carbonyl resonance at δ 234.3. The carbonyl resonance appears as a 1:3:3:1 quartet (J Rh-C ~ 37 Hz) and this confirms the face-bridging nature of the carbonyl group. The observation of a single C_5H_5 resonance is consistent with a fluxional alkyne-Rh_3 arrangement. The ^{13}C spectrum in acetone supports our interpretation of the ^{1}H and ^{19}F spectra in this solvent, showing three C_5H_5 signals, one carbonyl quartet (J Rh-C ~ 36.8 Hz) at δ 231.7, and a carbonyl triplet (J Rh-C ~ 46.0 Hz) at δ 215.3.

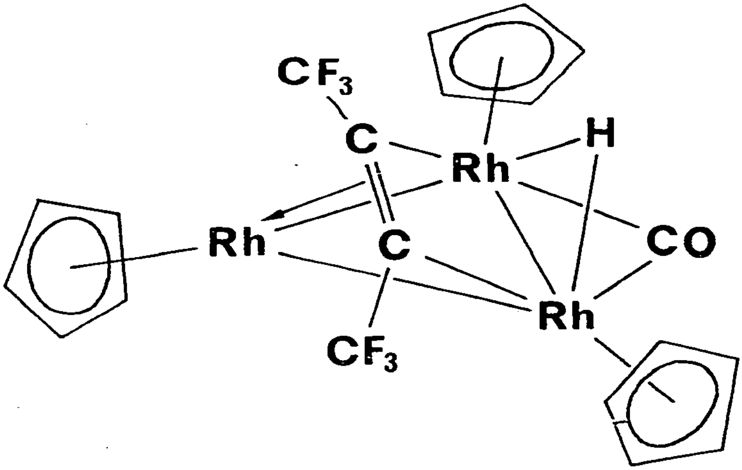
Spectroscopic data indicate that the but-2-yne complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(MeC_2Me)$ is fluxional at room temperature and has a face bridging structure in solution regardless of the polarity of the solvent. The infrared spectra in various media show ν(CO) near 1680 cm^{-1}, and the ^{13}C resonance for the carbonyl is observed as a quartet ($CDCl_3$; δ 242.1, J Rh-C ~ 39.7 Hz) at room temperature; these results indicate a triply bridging carbonyl. The ^1H NMR spectrum for solutions in $CDCl_3$ shows a single C_5H_5 signal at δ 5.25 and one singlet resonance for the methyl groups at δ 2.69. For the complex dissolved in acetone, both resonances are shifted slightly to higher field but there is no real change in the appearance of the spectrum. Thus, the but-2-yne complex does not exhibit the solvent-dependent behavior of its $CF_3C_2CF_3$ homologue.

(d) $[(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)H]^+$

The complex $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ is reversibly protonated when dissolved in protonic acids. An unstable green salt was isolated with BF_4^-, and elemental analysis agrees with its formulation as $[(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)H]^+[BF_4]^-, H_2O$. Protonation of $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ might occur at one of the alkyne carbons as for $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$, or alternatively at the rhodium atoms. It has been shown [27] that protonation of the trinuclear osmium-alkyne complex $Os_3(CO)_{10}(HC_2Me)$ yields the cation $[HOs_3(CO)_{10}(HC_2Me)]^+$ which exists as a mixture of two isomers, each possessing a proton occupying an Os-Os edge.

Spectroscopic data for the protonated Rh_3 complex indicate the presence of an edge-bridging carbonyl, and probably of an edge-bridging hydride. The complex rapidly deprotonates when dissolved in water or organic solvents, but NMR data were obtained by recording spectra of $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ dissolved in concentrated H_2SO_4. The ^1H spectrum shows two C_5H_5 signals of relative intensity 2:1 at δ 6.02 and 6.13, but no other proton signal could be observed. The ^{19}F spectrum exhibits a single, broad, unresolved multiplet at δ 51.84. The ^{13}C spectrum of a ^{13}CO enriched sample showed a triplet (J Rh-C, 39.7 Hz) at δ 197.7, and this is assigned to an edge-bridging carbonyl.

The presence of an edge-bridging carbonyl is also indicated by a band at 1880 cm^{-1} in the infrared spectrum of the salt. No absorption which could be assigned to a M-H stretching frequency could be observed in the infrared spectrum. However, if the complex contains an edge-bridging hydride, this band would be expected [28] in the range 1200-1000 cm^{-1} which is obscured by strong C-F stretching frequencies. We have therefore recorded the spectrum of the complex dissolved in D_2SO_4 - D_2O, and we observe a broad, strong peak at 725 cm^{-1}. Since the expected H-D shift is



IV

about 1.40, this would correspond to a M - H - M stretching frequency of 1015 cm^{-1}. Thus, we tentatively assign the structure (IV) to the protonated complex. Our inability to observe the expected high field hydride line in the NMR spectrum may be due to broadening resulting from Rh-H coupling and/or to fluxional behavior of the metal-hydride link.

Experimental

(a) General:

Dicarbonyl(η-cyclopentadienyl)rhodium, (η-C_5H_5)Rh(CO)$_2$, was prepared from tetracarbonyldi-μ-chlorodirhodium and thallous cyclopentadienide [1]. Tricarbonylbis(η-cyclopentadienyl)dirhodium, (η-C_5H_5)$_2$-Rh$_2$(CO)$_3$, was obtained by ultraviolet irradiation of a hexane solution of (η-C_5H_5)Rh(CO)$_2$ [29]. Tricarbonyltris(η-cyclopentadienyl)trirhodium, (η-C_5H_5)$_3$Rh$_3$(CO)$_3$, was obtained by reaction of (η-C_5H_5)Rh(CO)$_2$ with trimethylamine-N-oxide dihydrate [30]. But-2-yne was obtained from Farchan Research Laboratories and hexafluorobut-2-yne from P.C.R. Inc.

Reactions were performed in evacuated Pyrex Carius tubes (55-90 ml capacity) fitted with Quickfit Rotaflo Teflon taps. Thin layer chromatography was carried out on 20 by 20 cm plates with a 1:1 silica gel G-HF$_{254}$ mixture as adsorbent. Microanalyses were performed by the Australian Microanalytical Service, Melbourne.

Infrared spectra (4000-400 cm^{-1}) were recorded with a Perkin-Elmer 521 spectrometer. Only bands of medium or greater intensity are listed. An

Hitachi Perkin-Elmer RMU 6E mass spectrometer was used to record the mass spectra. Nuclear magnetic resonance spectra were obtained with a Bruker WH-90 spectrometer. The proton magnetic resonance spectra are reported as δ values, the fluorine chemical shifts are reported upfield from trichlorofluoromethane internal reference, and the carbon chemical shifts are downfield from tetramethylsilane. Tris(acetylacetonato)chromium(III) was added to ^{13}C NMR samples to reduce T_1 relaxation times [31].

(b) Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ with hexafluorobut-2-yne:

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ (0.100 g), hexafluorobut-2-yne (0.3 g, mole ratio c. 1:8) and hexane (5 ml) were heated at 100° for 24 h. The product mixture was dissolved in chloroform, filtered and concentrated under reduced pressure. Thin layer chromatography with hexane-chloroform (9:1) as eluent separated minor amounts of $(\eta\text{-}C_5H_5)Rh(CO)_2$, $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$, $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$, $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)$ and cis-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2$-$(C_4F_6)$ from the major band, trans-$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ (0.082 g, 62%). All products were identified by spectroscopic analysis.

(c) Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ with H^+; isolation of the complexes $[(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6H)]^+X^-$, X = BF_4 or PF_6:

(i) The hexafluorophosphate salt

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ was dissolved in the minimum quantity of conc. H_2SO_4, and this solution was added dropwise to a saturated aqueous solution of NH_4PF_6 (threefold excess). The orange precipitate was collected by filtration and washed with water and then hexane to give $[(\eta\text{-}C_5H_5)_2$-$Rh_2(CO)_2(C_4F_6H)]^+[PF_6]^-$ (c. 95% yield), m.p. 162-163°, (Found: C, 27.1; H, 1.6; F, 32.3. $C_{16}H_{11}F_{12}O_2Rh_2P$ calcd.: C, 27.45; H, 1.6; F, 32.6%). Infrared absorption (KBr disk): 2075vs, 2046vs, 1434m, 1410m, 1324s, 1253s, 1184vs, 1158sh, 1143vs, 860sh, 848vs, 825vs, 690m, 655m, 558s. PMR spectrum (acetone-d_6): δ 6.39 (s, 5H, C_5H_5), 6.16 (s, 5H, C_5H_5), 4.32 (q of d, J F-H = 8.5 Hz and J Rh-H = 2.0 Hz, 1H). ^{19}F NMR spectrum (acetone-d_6): δ 51.18 (q of d, J F-F = 12.5 Hz and J Rh-F = 1.5 Hz, 3F), 54.4 (m, J F-F = 12.5 Hz, J F-H = 8.5 Hz and J Rh-F = 1.5 Hz, 3F), 71.2 (d, J F-P = 708 Hz, 6F).

(ii) The tetrafluoroborate salt

Similarly, with 43% HBF_4 aqueous solution, a red precipitate was isolated. This was washed with water and hexane to give $[(\eta\text{-}C_5H_5)_2Rh_2$-$(CO)_2(C_4F_6H)]^+[BF_4]^-,(H_2O)$, m.p. 193-194°, (Found: C, 28.9; H, 1.9; F, 28.7. $C_{16}H_{13}BF_{10}O_3Rh_2$ calcd.: C, 29.1; H, 2.0; F, 28.8%).

Infrared absorption (KBr disc): 3122m, 2066sh, 2047vs, 1630br, 1432m, 1412m, 1328s, 1253s, 1182vs, 1162s, 1142vs, 1127vs, 1085vs, 1053s, 1015s, 850s, 690m, 658m, 410m. PMR spectrum (acetone-d_6): δ 6.39 (s, 5H, C_5H_5), 6.16 (s, 5H, C_5H_5), 4.33 (q of d, J F-H = 8.5 Hz and J Rh-H = 2.0 Hz, 1H), 2.98 (s, 2H, H_2O). ^{19}F NMR spectrum (acetone-d_6): δ 51.3 (q of d, J F-F = 12.5 Hz and J Rh-F = 1.5 Hz, 3F), 54.4 (m, J F-F = 12.5 Hz, J F-H = 8.5 Hz and J Rh-F = 1.5 Hz, 3F), 150.1 (s, 4F).

(d) Reaction of $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ with hexafluorobut-2-yne:

$(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ (0.08 g, 0.14 mmol) and hexafluorobut-2-yne (0.05 g, 0.31 mmol) in hexane were heated at 135° for 66 h. The contents of the tube were dissolved in acetone, filtered and concentrated under reduced pressure. Thin layer chromatography with hexane-dichloromethane (1:3) as eluent separated minor amounts of $(\eta\text{-}C_5H_5)Rh(CO)_2$, $(\eta\text{-}C_5H_5)_3\text{-}Rh_3(CO)_3$, hexakis(trifluoromethyl)benzene, and $(\eta\text{-}C_5H_5)Rh[\eta^4\text{-}C_6(CF_3)_6]$ from the major products $(\eta\text{-}C_5H_5)_2Rh_2(C_4F_6)_2$ (0.022 g, 24%) and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)$ (0.022 g, 23%). All products were identified by spectroscopic analysis.

(e) Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ with $(\eta\text{-}C_5H_5)Rh(CO)_2$:

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ (0.098 g, 0.18 mmol) and $(\eta\text{-}C_5H_5)Rh(CO)_2$ (0.176 g, 0.79 mmol) in hexane (5 ml) were heated at 120° for 62 h. Purple crystals were deposited on the cooler parts of the tube. These were isolated by filtration and were washed with n-pentane to give $(\eta\text{-}C_5H_5)_3Rh_3(CO)\text{-}(C_4F_6)$ (0.090 g, 73%). The supernatant and washings were concentrated and chromatographed by t.l.c. with hexane-dichloromethane (1:1) as eluent. This separated $(\eta\text{-}C_5H_5)Rh(CO)_2$ (0.100 g), $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(C_4F_6)$ (0.006 g, 6%), $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ (0.010 g), and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)$ (0.019 g, 15% - total yield, 88%). All products were identified by spectroscopic analysis.

(f) Reaction of $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ with but-2-yne:

$(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ (0.340 g, 0.81 mmol) and but-2-yne (1.1 ml, 14.1 mmol) in hexane (10 ml) were heated at 110° for 48 h. Purple crystals were deposited on the tube walls. These were collected by filtration and washed with hexane and methanol to give $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4H_6)$ (0.030 g, 6%), m.p. 225° (dec.) (Found: C, 40.83; H, 3.74; mol. wt. (M^+, m/e), 586. $C_{20}H_{21}ORh_3$ calcd.: C, 40.98; H, 3.61%; mol. wt. 586). Infrared absorption (KBr disk): 2925m, 1686sh, 1680vs, 1105m, 1051m, 829m, 803m, 792s, 513m. PMR spectrum: $(CDCl_3)$: δ 5.25 (s, 15H, C_5H_5) 2.69 (s, 6H, CH_3); (acetone-d_6): δ 5.21 (s, 15H, C_5H_5), 2.67, (s, 6H, CH_3). Thin layer chromatography of the supernatant solution with hexane-dichloromethane (1:1) as eluent separated $(\eta\text{-}C_5H_5)Rh(CO)_2$ (0.070 g, 19%), hexamethylbenzene (0.050 g), $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3$ (0.010 g, 3%), $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ (0.015 g, 5%) and $(\eta\text{-}C_5H_5)_2Rh_2[(C_4H_6)_2CO]$ (0.011 g, 3%). All products were identified by spectroscopic analysis.

(g) Reaction of $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ with but-2-yne:

$(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ (1.50 g, 2.55 mmol) and but-2-yne (2 ml, 25.5 mmol) in toluene were heated at 145° for 48 h. The contents of the tube were filtered and the residue was washed with cold $CHCl_3$. Extraction of the residue with CH_2Cl_2 yielded unchanged $(\eta\text{-}C_5H_5)_3Rh_3(CO)_3$ (0.250 g, 16%). The supernatant and washings were concentrated and the residue was washed with n-pentane and then MeOH. Extraction of the residue with $CHCl_3$ yielded $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4H_6)$ (0.430 g, 29%). The n-pentane washings were concentrated and chromatographed by t.l.c. with hexane as eluent. This separated $(\eta\text{-}C_5H_5)Rh(CO)_2$ (0.050 g) and C_6Me_6 (0.085 g). Chromatography of the MeOH washings by t.l.c. with hexane-dichloromethane (1:1) as eluent separated many coloured bands. Repeated t.l.c. of the major bands using hexane-dichloromethane and acetone-methanol mixtures separated $(\eta\text{-}C_5H_5)_2Rh_2[(C_4H_6)_2CO]$ (0.018 g), $(\eta\text{-}C_5H_5)Rh[(C_4H_6)_2CO]$ (0.055 g) and $(\eta\text{-}C_5H_5)Rh[(C_4H_6)_2(CO)_2]$ (0.063 g). All products were identified by spectroscopic analysis.

(h) Reaction of $(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)$ with H^+;

Isolation of the complex $[(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)H][BF_4],H_2O$:

$(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)$ was dissolved in the minimum quantity of conc. H_2SO_4 and this solution was added dropwise to 43% HBF_4 aqueous solution. The green precipitate was washed with water and then hexane to give $[(\eta\text{-}C_5H_5)_3Rh_3(CO)(C_4F_6)H]^+[BF_4]^-, H_2O$ (c. 90% yield), m.p. 280° (dec.) (Found: C, 29.95; H, 2.18; F, 23.0. $C_{20}H_{18}BF_{10}O_2Rh_3$ calcd.: C, 30.03; H, 2.27; F, 23.75%). Infrared absorption (nujol): 1884s, 1874s, 1396s, 1188vs, 1143s, 1123s, 1075s, 1036s, 843m, 695m. PMR spectrum (conc. H_2SO_4): δ 6.13 (s, 5H, C_5H_5), 6.02 (s, 10H, C_5H_5). ^{19}F NMR spectrum: δ 51.84 (s, br).

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