Reactions of Co-ordinated Ligands. Part VIII.[1] The Addition of Hexafluoroacetone to Tricarbonyl(diene)iron and η-Cyclopentadienyl(diene)-rhodium Complexes †

By **Michael Green** * and **Brian Lewis,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Hexafluoroacetone (HFA) reacts on u.v. irradiation with tricarbonyl(2,3-dimethylbuta-1,3-diene)iron to form a π-allylic iron(II) complex, in which the HFA links the Fe and diene. The corresponding reaction with tricarbonyl-(isoprene)iron affords a related species, but which contains two HFA molecules linked head-to-tail. This compound undergoes a rearrangement on heating to form a π-allylic complex containing only one linking HFA, the second HFA molecule becoming a $C(CF_3)_2OH$ group. Isoprene and η-cyclopentadienyl(*trans*-pentadiene)rhodium react thermally with HFA to form related rhodium(III) π-allylic complexes containing a linking HFA molecule. The analogous reaction with η-cyclopentadienyl(2,3-dimethylbuta-1,3-diene)rhodium affords a similar adduct, which in addition has a second molecule of HFA formally inserted into a cyclopentadienyl carbon–hydrogen bond. 1,3-Disubstitution of the cyclopentadienyl ring occurs in the corresponding reaction of η-cyclopentadienyl-[hexamethyl(Dewar)benzene]rhodium.

HEXAFLUOROACETONE (HFA) is a highly reactive electrophilic ketone, which has been shown to react with a variety of low-valent transition-metal complexes. The most frequently observed reaction is for the HFA to behave as an extremely good π* acceptor and become side bonded onto the metal with a formal increase in the oxidation state of the metal of two.[2] A typical reaction[3] of this kind is the formation of $[\overline{OsC(CF_3)_2O}(CO)_2(PMe_2Ph)_2]$ from $[Os(CO)_3(PMe_2Ph)_2]$. Depending on the nature of the stabilising ligands, Ni, Pd, and Pt d^{10} species have been found to be able to undergo an additional reaction in which two HFA molecules formally link head-to-tail to form a five-membered-ring system. In this reaction the intermediacy of three-membered-ring complexes has been established as is illustrated[4] by the consecutive reactions $[Ni(Bu^tNC)_4] \longrightarrow [\overline{NiC(CF_3)_2O}(Bu^tNC)_2] \longrightarrow [\overline{NiC(CF_3)_2OC(CF_3)_2O}(Bu^tNC)_2]$. When the low-valent metal is stabilised by olefinic ligands, then a third alternative reaction path becomes available, as is demonstrated by the *exo*-1,3-addition of HFA to tricarbonyl(cycloheptatriene)iron.[5] Here, attack by HFA on the co-ordinated ligand is preferred to reaction at the metal centre. In order to understand more fully the interplay of the various factors controlling these different reactions, the reaction of HFA with tricarbonyl(diene)-iron and η-cyclopentadienyl(diene)rhodium complexes has been studied.[6] The new compounds described in this paper have been characterised by elemental analysis, i.r., and n.m.r. spectroscopy.

RESULTS

Attempts to react HFA with tricarbonyl(buta-1,3-diene)-iron were unsuccessful, however, prolonged u.v. irradiation of a hexane solution of HFA and tricarbonyl(2,3-dimethylbuta-1,3-diene)iron afforded the 1 : 1 adduct (I), isolated as orange-yellow crystals. The i.r. and mass spectrum indicated the presence of an $Fe(CO)_3$ unit, suggesting that an oxidative-linking reaction of the kind observed[7] on reaction of tetrafluoroethylene with tricarbonyl(2,3-dimethylbuta-1,3-diene)iron had occurred.

This was confirmed by the ^1H n.m.r. spectrum, which showed shifts and coupling constants fully consistent with the illustrated π-allylic structure. In contrast with the corresponding C_2F_4 adduct, the HFA adduct showed no evidence of ^1H–^{19}F coupling. As required by the structure shown, the ^{19}F n.m.r. spectrum displayed two quartets (J_{FF} 10·0 Hz) at 74·8 and 77·7 p.p.m. A comparison of ^{19}F chemical-shift data for three- and five-membered-ring HFA adducts shows that α-$C(CF_3)_2$ groups generally resonate for both types of complex over the close range of 65·0—68·0 p.p.m., whereas the β-$C(CF_3)_2$ group shows shifts at higher field (80·0 p.p.m.).[2,4] Therefore, it is suggested that the shifts observed for adduct (I) are more consistent with the

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† No reprints available.

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[3] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

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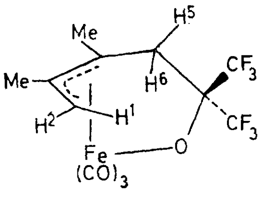
[5] M. Green, S. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

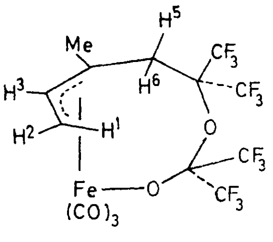
[6] M. Green and B. Lewis, *J.C.S. Chem. Comm.*, 1973,

[7] A. Bond, B. Lewis, and M. Green, *J.C.S. Dalton*, 1975, 1109.

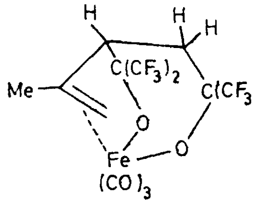
presence of the arrangement $FeOC(CF_3)_2$, as shown in the illustrated structure.



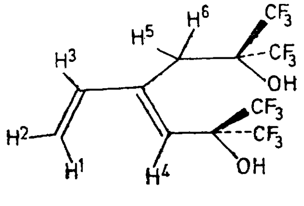
(I)



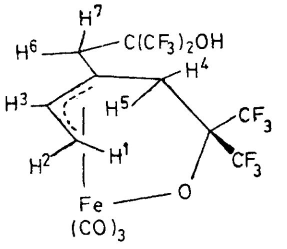
(II)



(IIa)



(III)



(IV)

In complete contrast, the room-temperature reaction of HFA with tricarbonyl(isoprene)iron in the presence of a trace amount of $[Fe(CO)_5]$ afforded a yellow crystalline 2 : 1 adduct, (II). The well-resolved ^1H n.m.r. spectrum can be analysed with the aid of decoupling, either in terms of structure (II) or (IIa), however, the chemical shifts and coupling constants of the resonances H^1, H^2, and H^3 are more consistent with the π-allylic structure. The ^{19}F n.m.r. spectrum showed four multiplets of equal intensity with shifts in the range 75·0—76·9 p.p.m., and as discussed for (I) such shifts are consistent with the presence of a $C(CF_3)_2$ group β to the iron, *i.e.* $FeOC(CF_3)_2$. The presence of ^{19}F–^{19}F coupling between $C(CF_3)_2$ groups is difficult to explain on the basis of structure (IIa), and therefore this structure will not be considered further.

The ^{19}F–^{19}F coupling is, however, explicable in terms of either a head-to-tail bonded arrangement as represented in (II), or a head-to-head, *i.e.* $FeOC(CF_3)_2O$–, bonded version of (II). It is not easy to distinguish between these two alternatives. The closeness of the ^{19}F chemical shifts makes decoupling, and hence evaluation of coupling constants, impossible. However, the adduct (II) readily undergoes a fragmentation reaction, and this can be more easily explained in terms of structure (II).

When the complex (II) is heated (80 °C/24 h) in hexane solution two products are formed, an isomeric species (IV) and an organic compound (III). Separate experiments showed that, along with some $[Fe(CO)_5]$, (III) is formed from (IV) when heated. It was also found that (II) reacts with carbon monoxide (100 atm/60 °C) to give (III).

The i.r. spectrum of (IV) showed, in addition to terminal carbonyl bands compatible with an $Fe(CO)_3$ group, a strong absorption at 3320 cm^{-1} assignable to a hydroxy-stretch. Support for this assignment was provided by the ^1H n.m.r. spectrum, which showed a broad signal at τ 5·65, double irradiation of the other signals in the spectrum having no effect on this resonance. The ^1H spectrum showed in addition six resonances with relative intensity 1 : 1 : 2 : 1 : 1 : 1, there being no evidence for the presence of a methyl group. Analysis of the spectrum with the aid of double-irradiation experiments suggested the illustrated σ,π structure. This was supported by the ^{19}F n.m.r. spectrum, which showed a singlet at 76·2 p.p.m. assignable to the equivalent trifluoromethyl groups of a $CH_2{\cdot}C(CF_3)_2OH$ side chain, and two quartet (J_{FF} 10·0 Hz) signals at 75·2 and 77·4 p.p.m., assignable, as in the case of complex (I), to a linking HFA, *i.e.* $[FeOC(CF_3)_2]$.

The organic product (III) had an analysis consistent with its formulation as $C_{11}H_8F_{12}O_2$, and this was supported by the appearance of a strong parent ion in the mass spectrum. The i.r. spectrum showed a strong hydroxylic absorption at 3340 cm^{-1}, and a band at 1622 cm^{-1} assignable to an olefinic stretch. Both these features were confirmed by the ^1H n.m.r. spectrum, which showed a broad signal at τ 4·92 (OH) and resonances fully compatible with the illustrated disubstituted isoprene structure.* In agreement the ^{19}F spectrum showed two singlet resonances at 76·1 and 77·7 p.p.m. compatible with the presence of $C(CF_3)_2OH$ groups in different environments. Thus, from a structural standpoint the formation of complex (III) from complex (IV) can be understood.

In view of these observations the reaction of HFA with the isoelectronic η-cyclopentadienyl(diene)rhodium(I) species was investigated. Hexafluoroacetone reacts thermally (60 °C) with η-cyclopentadienyl(isoprene)rhodium and η-cyclopentadienyl(*trans*-pentadiene)rhodium to form respectively the crystalline 1 : 1 adducts (V) and (VI). Examination of the ^1H n.m.r. spectrum of (V) showed this to be a mixture of the isomers (Va) and (Vb), the former predominating (2·5 : 1). Typical π-allylic chemical shifts and coupling constants were observed for both isomers, and in the case of (Va) the central allylic methyl group exhibits a coupling (1·5 Hz) to ^{103}Rh; in the isomer (Vb) the allylic proton H^3 shows a typical coupling (2·5 Hz) to the rhodium. The ^1H spectrum of the adduct (VI) obtained from the *trans*-pentadiene adduct showed similar features, but demonstrated the presence of only the one isomer, that illustrated, where addition has occurred at the unsubstituted end of the diene. In the spectrum of (Va), (Vb), and (VI) a singlet (5H) resonance at τ 4·80 is assigned to the η-cyclopentadienyl ligand.

The ^{19}F n.m.r. spectrum of each adduct showed two quartets (J_{FF} 9·5 Hz) with very similar chemical shifts to those observed for the iron adduct (I). There was no evidence of ^{19}F–^1H or ^{19}F–^{103}Rh coupling, suggesting the $RhOC(CF_3)_2$ mode of linkage. In contrast, the reaction of η-cyclopentadienyl(2,3-dimethylbuta-1,3-diene)rhodium with HFA affords the 1 : 2 adduct (VII), where one hexafluoroacetone molecule links the diene and rhodium, and a

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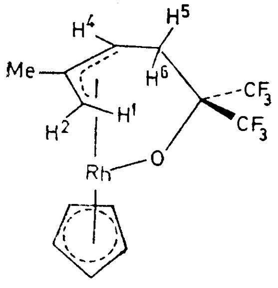
* Examination of molecular models suggests that the *cisoid* form is more stable than the *transoid* form.

second molecule of HFA has formally inserted into a cyclopentadienyl ring C–H bond.[6,8]

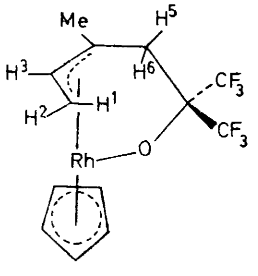
The ^1H n.m.r. spectrum of (VII) shows resonances typical of a π-allylic arrangement, the correlation with the corresponding data for adduct (I) being particularly good. However, the spectrum showed no evidence of a singlet η-cyclopentadienyl resonance, it exhibited instead five multiplets of equal intensity in the range τ 1·7—6·5. The low-field signal (τ 1·71) collapsed when (VII) was shaken with D_2O, suggesting the presence of a hydroxy-group. This was supported by the i.r. spectrum, which showed a strong band at 3155 cm^{-1}. Double-irradiation studies indicated that the remaining four hydrogens were attached to a monosubstituted cyclopentadienyl ligand.

In the ^{19}F n.m.r. spectrum the CF_3 resonances due to the linking HFA moiety appear as quartets (J_{FF} 10·0 Hz) with typical chemical shifts. Those due to the $C(CF_3)_2OH$ group appear as quartets (J_{FF} 11·0 Hz) centred at 74·3 and 77·0 p.p.m., indicating an absence of free rotation, and examination of a molecular model confirmed the presence due to steric interactions of an appreciable barrier to rotation. A possible additional barrier to rotation could be hydrogen bonding between the hydroxy-group and the oxygen of the linking HFA. This could be reflected in the low-field shift of the hydroxy-proton.

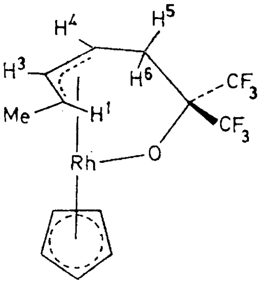
The reaction of η^5-cyclopentadienyl[hexamethyl(Dewar)-benzene]rhodium with hexafluoroacetone leads to attack only at the C_5-ring with the introduction of two $C(CF_3)_2OH$ groups 1,3 to each other. The ^1H n.m.r. spectrum of the crystalline product, (VIII), showed a broad signal at τ 6·56, which collapsed when the sample was allowed to exchange with D_2O, and which is assigned to a hydroxy-proton. The presence of a strong absorption in the i.r. at 3510 cm^{-1} confirmed the presence of a hydroxy-group. In addition the ^1H spectrum showed resonances corresponding to co-ordinated hexamethyl(Dewar)benzene, and two singlets at τ 4·72(1H) and 4·95(2H), which are assigned to the protons of a 1,3-disubstituted cyclopentadienyl group.



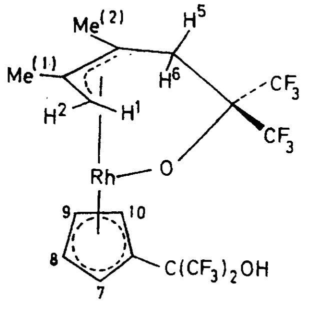
(Va)



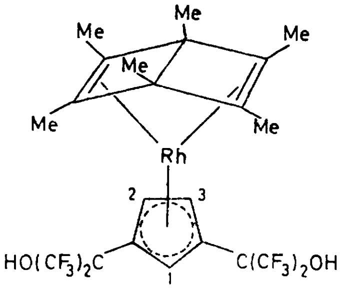
(Vb)



(VI)



(VII)



(VIII)

The ^{19}F n.m.r. spectrum showed two quartets (J_{FF} 11·0 Hz) indicating the equivalence of the two $C(CF_3)_2OH$ environments and the inequivalence of the geminal trifluoromethyl groups, arising from restricted rotation.

DISCUSSION

In considering possible reaction paths for the formation of these species, the thermal reaction leading to (Va), (Vb), and (VI) will be first considered. Protonation of both tricarbonyl(cyclohexa-1,3-diene)iron [9] and cyclohexa-1,3-diene(η-cyclopentadienyl)rhodium [10] involves *endo*-attack, and more recently acetylation of tricarbonyl(*trans,trans*-hexa-2,4-diene)iron [11] has been shown to involve a similar *endo*-approach of the electrophile. Except in the case of tricarbonyl(tropone)iron,[12] protonation of systems [13,14] where both co-ordinated and unco-ordinated olefins are available leads to *exo*-attack, suggesting that *exo*-attack occurs preferentially at the unco-ordinated olefin, the metal providing stabilisation for the generated cation.

Thus in the reaction of isoprene or η-cyclopentadienyl-(*trans*-pentadiene)rhodium with hexafluoroacetone it is reasonable to suggest that in the formation of, for

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[9] T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 1971, **93**, 5296.

[10] B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1972, 2084.

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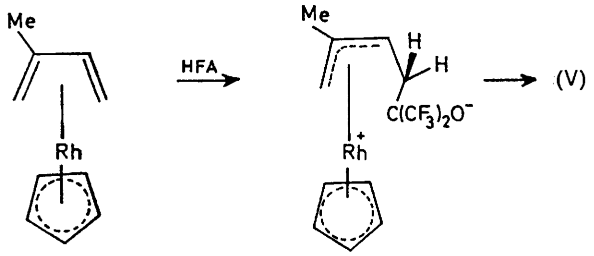
[12] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

[13] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J.C.S. Dalton*, 1972, 456.

[14] M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, 1970, **92**, 7622.

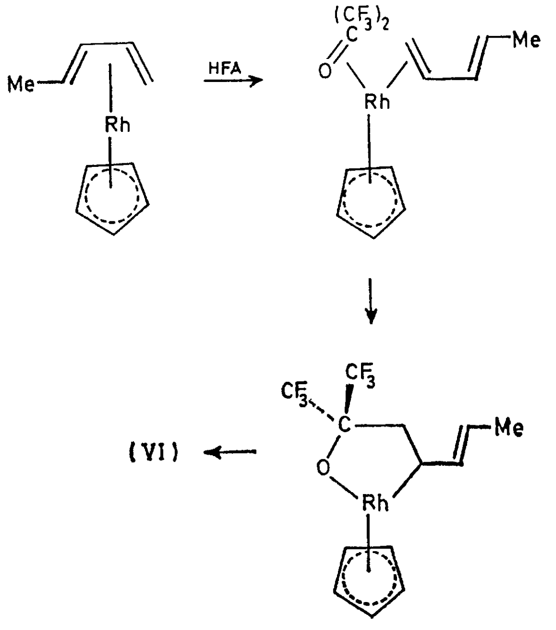
example, (VI) *endo*-attack by HFA on carbon occurs to give a dipolar π-allylic species, which rapidly undergoes charge collapse to afford the product. As in the case of acetylation [15] attack is directed towards the unsubstituted end of the co-ordinated diene (Scheme 1).



Scheme 1

This contrasts with the observed [5] *exo*-1,3-addition of tetracyanoethylene and HFA to tricarbonyl(cycloheptatriene or cyclo-octatetraene)iron. It is suggested that this difference in direction of approach of the electrophile arises from the availability in the case of the cycloheptatriene and cyclo-octatetraene systems of a lower energy *exo*-addition path.

The postulated initial formation of a dipolar species provides an explanation for the formation of the iron complex (II), in that the head-to-tail linking of two HFA molecules can be understood in terms of capture of the initially formed dipolar adduct by a second molecule of HFA prior to charge collapse.



Scheme 2

An alternative mechanism for the formation of these adducts involving nucleophilic attack by the metal on HFA seems unlikely, because such a process would be expected to afford, for example, a dipolar species $\overset{+}{\mathrm{Rh}}\mathrm{C(CF_3)_2O^-}$, leading to the formation of adducts with a different structure. A further alternative process [16] (Scheme 2) also involving an initial co-ordination of HFA onto the metal is possible, although it is difficult to see how this can provide an explanation for the formation of (II). Clearly the reactions leading to attack on the η-cyclopentadienyl ring are most readily explained in terms of the formation of dipolar species, in which proton transfer leads to the formation of the hydroxy-group.

Although the thermal decomposition of (II) is clearly a complex reaction, it is important to note that iron–oxygen bond heterolysis in (II) could lead *via* a fragmentation reaction to the observed products, whereas it is difficult to understand the formation of (IV), if (II) contained the arrangement $\mathrm{FeOC(CF_3)_2C(CF_3)_2O}$. Recently, Tsuji has reported [17,18] that the addition of HFA to buta-1,3-diene is catalysed by a mixture of $\mathrm{Pd(OAc)_2}$ and triphenylphosphine to give $\mathrm{CH_2{=}CH{\cdot}CH{=}CH{\cdot}C(CF_3)_2OH}$. It is possible that there is a relationship between the iron and palladium reactions.

EXPERIMENTAL

The spectroscopic data were obtained by the methods outlined in Part V [7] of this series.

Reaction of Tricarbonyl(2,3-dimethylbuta-1,3-diene)iron with Hexafluoroacetone.—A solution of tricarbonyl(2,3-dimethylbuta-1,3-diene)iron (0·50 g, 2·23 mmol) and hexafluoroacetone (0·67 g, 4·0 mmol) in hexane contained in a sealed Carius tube (100 ml) was subjected to u.v. irradiation (250 W, Hanovia lamp) (6 days). The volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column.

Elution with methylene chloride–hexane (1 : 1) gave, on recrystallisation (0 °C) from the same solvent system, small orange-yellow crystals of (I) (0·15 g, 17%), m.p. 108—110 °C (Found: C, 37·3; H, 2·5; F, 28·5. $\mathrm{C_{12}H_{10}F_6FeO_4}$ requires C, 37·1; H, 2·6; F, 29·3%), ν_{CO} (hexane) 2096s, 2051s, and 2001s $\mathrm{cm^{-1}}$. The mass spectrum (base *m/e* 73) showed peaks at *m/e* 360 (*P* – CO, 20%), 332 (*P* – 2CO, 31%), and 304 (*P* – 3CO, 12%). The ^{1}H n.m.r. spectrum ($\mathrm{CDCl_3}$) showed resonances at τ 5·65 (d, 1H, H^2, $J_{1,2}$ 1·0 Hz), 6·89 (d, 1H, H^1, $J_{1,2}$ 1·0 Hz), 7·62 (d, 1H, H^5, $J_{5,6}$ 14·0 Hz), 7·76 (s, 3H, Me), 7·96 (s, 3H, Me), and 8·06 (d, 1H, H^6, $J_{5,6}$ 14·0 Hz). The ^{19}F n.m.r. spectrum ($\mathrm{CH_2Cl_2}$) showed resonances at 74·8 p.p.m. [q, 3F, $\mathrm{CF_3}$, *J*(FF) 10·0 Hz] and 77·7 [q, 3F, $\mathrm{CF_3}$, *J*(FF) 10·0 Hz].

Reaction of Tricarbonyl(isoprene)iron with Hexafluoroacetone.—A Carius tube (200 ml) containing a solution of tricarbonyl(isoprene)iron (1·5 g, 7·2 mmol) and hexafluoroacetone (2·5 g, 15 mmol) in hexane (20 ml) was allowed to stand at room temperature for 3 h. Removal of volatile material *in vacuo* and recrystallisation (0 °C) of the residue from methylene chloride–hexane gave small bright yellow *crystals* of (II) (1·9 g, 50%), m.p. 105—107 °C [Found: C, 31·7; H, 1·4; F, 42·7%; *M*, 524 ($\mathrm{CDCl_3}$). $\mathrm{C_{14}H_8F_{12}FeO_5}$ requires C, 31·1; H, 1·5; F, 42·4%; *M*, 540], ν_{CO} (hexane) 2095w, 2022s, and 1992s $\mathrm{cm^{-1}}$. The mass spectrum (base *m/e* 484) showed peaks at *m/e* 540 (*P*, 3%), 512 (*P* – CO, 16%), 484 (*P* – 2CO, 100%), and 456 (*P* – 3CO, 70%).

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[15] R. E. Graf and C. P. Lillya, *J. Amer. Chem. Soc.*, 1972, **94**, 8282.

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[18] J. Tsuji, *Tetrahedron*, 1972, **28**, 3705.

The ^{1}H n.m.r. spectrum ([$^{2}H_6$]acetone) showed resonances at τ 5·57 (dd, 1H, H^3, $J_{1,3}$ 13·0, $J_{2,3}$ 8·0 Hz), 6·0 (d, 1H, H^5, $J_{5,6}$ 15·0 Hz), 6·92 (d, 1H, H^6, $J_{5,6}$ 15·0 Hz), 6·95 (dd, 1H, H^1, $J_{1,3}$ 13·0, $J_{1,2}$ 2·5 Hz), 7·31 (dd, 1H, H^2, $J_{2,3}$ 8·0, $J_{1,2}$ 2·5 Hz), and 7·92 (s, 3H, Me). The ^{19}F n.m.r. spectrum (acetone) showed resonances at 75·0 p.p.m. (m, 3F), 75·5 (m, 3F), 76·2 (m, 3F), and 76·9 (m, 3F).

Reaction of Complex (II) with Carbon Monoxide.—A solution of complex (II) (0·50 g, 0·93 mmol) in hexane (30 ml) contained in an autoclave (stainless steel, 100 ml, glass liner) under a pressure of carbon monoxide (100 atm) was heated (60 °C) for 6 h. The solution was filtered, and both solvent and [Fe(CO)$_5$] removed *in vacuo*. The residue was recrystallised (0 °C) from hexane affording white needles of (III) (0·15 g, 41%), m.p. 85—89 °C (Found: C, 32·9; H, 2·0; F, 56·7. $C_{11}H_8F_{12}O_2$ requires C, 33·0; H, 2·00; F, 56·9%), ν_{OH} (Nujol) 3340s, br; $\nu_{C=C}$ (Nujol) 1622w cm^{-1}. The mass spectrum (base *m/e* 383) showed peaks at *m/e* 400 (*P*, 31%), and 383 (*P* − OH, 100%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 3·62 (dd, 1H, H^3, $J_{1,3}$ 17·5, $J_{2,3}$ 11·0 Hz), 4·16 (s, 1H, H^4), 4·49—5·34 (broad signal, 2H, OH), 4·56 (d, 1H, H^1, $J_{1,3}$ 17·5 Hz), 4·71 (d, 1H, H^2, $J_{2,3}$ 11·0 Hz), and 6·71 (s, 2H, H^{5,6}). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 76·1 p.p.m. (s, 6F, CF$_3$) and 77·7 (s, 6F, CF$_3$).

Thermolysis of Complex (II).—A Carius tube (100 ml) containing complex (II) (0·30 g, 0·56 mmol) dissolved in hexane (12 ml) was maintained at 80 °C for 24 h. Volatile material was removed *in vacuo*, and the residue chromatographed on an alumina-packed column. Elution with hexane gave a solid which was recrystallised (0 °C) from hexane to give white *crystals* of (III) (0·06 g, 27%). Further elution with methylene chloride–hexane (1 : 1) and recrystallisation (0 °C) from hexane gave large bright yellow *prisms* of complex (IV) (0·06 g, 18%), m.p. 49—51 °C (Found: C, 30·7; H, 1·6; F, 41·1. $C_{14}H_8F_{12}FeO_5$ requires C, 31·1; H, 1·5; F, 42·2%), ν_{CO} (hexane) 2073s, 2012s, and 1999s; ν_{OH} (Nujol) 3320vs,br; $\nu_{C=C}$ (Nujol) 1614m cm^{-1}. The mass spectrum (base *m/e* 177) showed peaks at *m/e* (*P*, 5%), 512 (*P* − CO, 22%), 484 (*P* − 2CO, 62%), 465 (*P* − 2CO − F, 3%), 456 (*P* − 3CO, 77%), and 437 (*P* − 3CO − F, 7%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·45 (dd, 1H, H^3, $J_{1,3}$ 9·5, $J_{2,3}$ 7·5 Hz), 5·65 (broad signal, 1H, OH), 6·24 (d, 1H, H^4, $J_{4,5}$ 17·0 Hz), 6·51 (s, 2H, H^{6,7}), 6·73 (d, 1H, H^5, $J_{4,5}$ 17·0 Hz), 8·11 (dd, 1H, H^2, $J_{2,3}$ 7·5, $J_{1,2}$ 3·5 Hz), and 9·57 (dd, 1H, H^1, $J_{1,3}$ 9·5, $J_{1,2}$ 3·5 Hz). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 75·2 p.p.m. [q, 3F, Fe–O–C(CF$_3$), *J*(FF) 10·0 Hz], 76·2 [s, 6F, C(CF$_3$)$_2$OH], and 77·4 [q, 3F, Fe–O–C(CF$_3$), *J*(FF) 10·0 Hz].

Reaction of η-Cyclopentadienyl(isoprene)rhodium with Hexafluoroacetone.—A Carius tube (100 ml) containing a solution of η-cyclopentadienyl(isoprene)rhodium [19] (0·40 g, 1·7 mmol) and hexafluoroacetone (0·67 g, 4·0 mmol) was heated (60 °C) for 24 h. Volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with acetone–hexane (1 : 4) followed by recrystallisation from hexane gave orange *crystals* of (Va) and (Vb) (2·5 : 1) (0·20 g, 30%), m.p. 109—111 °C (Found: C, 38·7; H, 3·4; F, 29·6. $C_{13}H_{13}F_6ORh$ requires C, 38·8; H, 3·3; F, 29·4%), $\nu_{max.}$ (Nujol) 3101w, 3050m, 1408m, 1363m, 1327m, 1296sh, 1270s, 1257sh, 1245—1095s,br, 1085m, 1055sh, 1040s, 1031s, 1016,s 987m, 974m, 963m, 948s, 929w, 921w, 909m, 882m, 831s, 827sh, 816s, 802ms, 777sh, 770m, 724s, and 669s cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) of the mixture showed resonances due to (Va) at τ 4·27 (dd, 1H, H^4, $J_{4,5}$ 8·0, $J_{5,6}$ 6·0 Hz), 4·79 (s, 5H, C$_5$H$_5$, 5·30 s, 1H, H^2), 7·15 (s, 1H, H^1), 7·73 (dd, 1H, H^5, $J_{5,6}$ 14·0, $J_{4,5}$ 8·0 Hz), 8·23 [d, 3H, Me, *J*(RhH) 1·5 Hz], and 8·41 [ddq, 1H, H^6, $J_{5,6}$ 14·0, $J_{4,6}$ 6·0, *J*(H^{6}CF$_3$) 1·0 Hz]. The ^{19}F n.m.r. spectrum (acetone) of the mixture showed resonances due to (Va) at 74·2 [q, 3F, CF$_3$, *J*(FF) 9·0, *J*(CF$_3$H^6) 1·0 Hz] and 76·3 [q, 3F, CF$_3$, *J*(FF) 9·0 Hz]; resonances (^{1}H) due to (Vb) occurred at τ 4·79 (s, 5H, C$_5$H$_5$), 4·94 [ddd, 1H, H^3, $J_{1,3}$ 12·0, $J_{2,3}$ 7·5, *J*(RhH) 2·5 Hz], 5·34 (d, 1H, H^2, $J_{2,3}$ 7·5 Hz), 7·21 (d, 1H, H^1, $J_{1,3}$ 12·0 Hz), 7·86 (s, 3H, Me), 7·91 (d, 1H, H^5, $J_{5,6}$ 14·0 Hz), and 8·13 (d, 1H, H^6, $J_{5,6}$ 14·0 Hz); ^{19}F resonances at 74·4 p.p.m. [q, 3F, CF$_3$, *J*(FF) 9·5 Hz] and 76·6 [q, 3F,CF$_3$, *J*(FF) 9·5 Hz].

*Reaction of η-Cyclopentadienyl(*trans*-penta-1,3-diene)-rhodium with Hexafluoroacetone.*—Similarly, a solution of η-cyclopentadienyl(*trans*-pentadiene)rhodium [19,20] (0·50 g, 2·1 mmol) and hexafluoroacetone (0·75 g, 4·5 mmol) in hexane (12 ml) was sealed *in vacuo* in a Carius tube (100 ml) and heated (60 °C) for 12 h. A substantial deposit of large crystals formed, and recrystallisation (0 °C) from acetone–hexane gave orange *needles* of (VI) (0·30 g, 35%), m.p. 179—181 °C (Found: C, 38·7; H, 3·2; F, 28·6. $C_{13}H_{13}F_6ORh$ requires C, 38·8; H, 3·2; F, 28·4%), $\nu_{max.}$ (Nujol) 1410w, 1330w, 1290sh, 1275s, 1219s, 1182s, 1167s, 1140s, 1121sh, 1110sh, 1036m,br, 1008m, 937m, 855w, 808m,br, 726m, and 673w cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 4·32 (ddd, 1H, H^4, $J_{4,5}$ 9·0, $J_{3,4}$ 7·0, $J_{4,6}$ 6·0 Hz), 5·80 (s, 5H, C$_5$H$_5$), 4·90 [ddd, 1H, H^3, $J_{1,3}$ 11·0, $J_{3,4}$ 7·0, *J*(RhH) 2·0 Hz], 6·10 [dq, 1H, H^1, $J_{1,3}$ 11·0, *J*(H^{1}Me) 6·5 Hz], 7·74 (dd, 1H, H^5, $J_{5,6}$ 15·0, $J_{4,5}$ 9·0 Hz), 8·04 [d, 3H, Me, *J*(H^{1}Me) 6·5 Hz], and 8·40 (dd, 1H, H^6, $J_{5,6}$ 15·0, $J_{4,6}$ 6·0 Hz). The ^{19}F n.m.r. spectrum (CH$_2$Cl$_2$) showed resonances at 74·2 p.p.m. [q, 3F, CF$_3$, *J*(FF) 9·5 Hz] and 76·5 [q, 3F, CF$_3$, *J*(FF) 9·5 Hz].

Reaction of η-Cyclopentadienyl(2,3-dimethylbuta-1,3-diene)-rhodium with Hexafluoroacetone.—Similarly, reaction (60 °C/2 days) of η-cyclopentadienyl(2,3-dimethylbuta-1,3-diene)-rhodium [19,21] (0·35 g, 1·4 mmol) in hexane (12 ml) followed by removal of volatile material *in vacuo* and chromatography on alumina gave on elution with acetone an orange solid. Recrystallisation (0 °C) from hexane gave orange *crystals* of (VII) (0·32 g, 39%), m.p. 131—133 °C (Found: C, 35·0; H, 2·6; F, 39·4. $C_{17}H_{15}F_{12}O_2Rh$ requires C, 35·1; H, 2·6; F, 39·2%), $\nu_{max.}$ (Nujol) 3135s (OH), 1414w, 1339w, 1331w, 1323—1072s,br, 1067w, 1040s, 1023m, 999w, 983m, 967m, 956s, 908w, 846sh, 941ms, 936m, 820ms, 785w, 743ms, 721ms, and 675ms cm^{-1}. The mass spectrum (base *m/e* 428) showed peaks at 582 (*P*, 15%) and 563 (*P* − F, 5%). The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at τ 1·71 (s, 1H, OH, exchanged with D$_2$O), 3·83 [m, 1H, H^7 or H^{10}, *J*(HH) 2·0 Hz], 4·06 [m, 1H, H^7 or H^{10}, *J*(HH) 2·0 Hz], 4·69 (m, 1H, H^8, $J_{8,9}$ 2·0 Hz), 5·14 (s, 1H, H^2), 6·51 (ddd, 1H, H^9, $J_{7,9} = J_{8,9} = J_{9,10}$ 2·0 Hz), 7·11 (s, 1H, H^1), 7·80 (s, 3H, Me$^{(2)}$), 7·84 (d, 1H, H^5, $J_{5,6}$ 14·0 Hz), 8·06 [d, 3H, Me$^{(1)}$, *J*(RhH) 1·5 Hz], and 8·15 (d, 1H, H^6, $J_{5,6}$ 14·0 Hz). The ^{19}F n.m.r. spectrum (CHCl$_3$) showed resonances at 74·3 p.p.m. [q, 3F, C(CF$_3$)OH, *J*(FF) 11·0 Hz], 75·2 [q, 3F, RhOC(CF$_3$), *J*(FF) 10·0 Hz], 77·0 [q, 3F, C(CF$_3$)OH, *J*(FF) 11·0 Hz], and 78·2 [q, 3F, RhOC(CF$_3$), *J*(FF) 10·0 Hz].

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Reaction of η-Cyclopentadienyl[hexamethyl(Dewar)benzene]-rhodium with Hexafluoroacetone.—A Carius tube (100 ml) containing a solution of [Rh(η-C_5H_5)(C_6Me_6)] [22] (0·35 g, 1·1 mmol) and hexafluoroacetone (0·67 g, 4·0 mmol) in hexane (12 ml) was set aside at room temperature for one day. Volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with methylene chloride–hexane and recrystallisation (0 °C) from the same solvent system afforded yellow *crystals* of (VIII) (0·22 g, 31%), m.p. 128—130 °C (Found: C, 41·6; H, 3·8; F, 33·9. $C_{23}H_{23}F_{12}O_2Rh$ requires C, 41·7; H, 3·5; F, 34·4%), $\nu_{max.}$ (Nujol) 3545s (OH), 3510sh (OH), 3111w, 1333m, 1320—1130s,br, 1116s, 1091s, 1058s, 1024m, 1007m, 981s, 953s, 938s, 864m, 845s, 809s, 743s, and 719s cm^{-1}. The mass spectrum (base *m/e* 662) showed peaks at *m/e* 662 (*P*, 100%), 645 (*P* − OH, 6%), 643 (*P* − F, 4%), 593 (*P* − CF_3, 41%), and 496 (*P* − C_3F_6O, 7%). The ^1H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·72 (s, 1H, H^1), 4·95 (s, 2H, $H^{2,3}$), 6·56 (br,s, 2H, OH, exchanged with D_2O), 8·39 (s, 12H, =CMe), and 9·22 (s, 6H, =CMe). The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 74·1 p.p.m. [q, 6F, CF_3, *J*(FF) 11·0 Hz], and 76·0 [q, 6F, CF_3, *J*(FF) 11·0 Hz].

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