Olefin–Acetylene Metal Complexes: Olefin–Hexafluorobut-2-yne Complexes of Rhodium(I)

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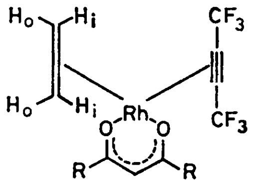
The compounds [Rh(acac)(C_2H_4)$_2$] and [Rh(dpm)(C_2H_4)$_2$] react with hexafluorobut-2-yne at *ca.* −78 °C to give [Rh(acac)(C_2H_4)(C_4F_6)] and [Rh(dpm)(C_2H_4)(C_4F_6)] respectively (acac = pentane-2,4-dionate; dpm = 2,2,6,6-tetramethylheptane-3,5-dionate). Similarly, [Rh(acac)(C_8H_{14})$_2$] reacts with hexafluorobut-2-yne at *ca.* −78 °C to give [Rh(acac)(C_8H_{14})(C_4F_6)] (C_8H_{14} = cyclo-octene). The ethylene ligand in [Rh(dpm)(C_2H_4)(C_4F_6)] exhibits dynamic behaviour in solution with rotation of this ligand, which may be displaced from the rhodium by the olefins L = cyclo-octene, cycloheptene, propene, and *cis*-but-2-ene to give the complexes [Rh(dpm)(L)(C_4F_6)]. Reaction of [Rh(dpm)(C_2H_4)(C_4F_6)] with tetrafluoroethylene gives [Rh(dpm)(C_2H_4)(C_2F_4)] which reacts with hexafluorobut-2-yne at *ca.* −78 °C to reform [Rh(dpm)(C_2H_4)(C_2H_6)]. However, treatment of [Rh(dpm)(C_2H_4)(C_4F_6)] with either carbon monoxide or cyclo-octa-1,5-diene results in the displacement of both C_2H_4 and C_4F_6 from the rhodium. Reactions of [Rh(dpm)(L)(C_4F_6)] (L = C_2H_4, cycloheptene, or cyclo-octene) with hexafluorobut-2-yne at room temperature afford the 1,3-diene complexes [Rh(dpm·C_4F_6)(1,3-diene)] {1,3-diene = 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene; 2,3,4,5-tetrakis(trifluoromethyl)-bicyclo[5.4.0]undeca-2,4-diene; or 2,3,4,5-tetrakis(trifluoromethyl)bicyclo[6.4.0]dodeca-2,4-diene}. The complexes also contain a molecule of hexafluorobut-2-yne which has added 1,4 to the rhodium(I) β-ketoenolate ring. Similar complexes result from the reactions of [Rh(acac)(L)(C_4F_6)] (L = C_2H_4 or cyclo-octene) and hexafluorobut-2-yne. Reactions of hexafluorobut-2-yne with the 4-aminopent-3-en-2-iminato(apemino-) complexes [Rh{HN$\cdots$C(Me)$\cdots$CH$\cdots$C(Me)$\cdots$NH}L$_2$] (L = C_2H_4; L$_2$ = cyclo-octa-1,5-diene), however, afford the hexakis(trifluoromethyl)benzene complex [Rh(apemino·C_4F_6){η^4-$C_6(CF_3)_6$}] which also contains a molecule of C_4F_6 added 1,4 to the rhodium(I) apemino-ring.

ALTHOUGH complexes containing either more than one olefin or more than one acetylene co-ordinated to the same metal atom are well known,[1] this is the first detailed account of mixed complexes which have a mono-olefin and a monoacetylene bonded to the same metal atom. Several examples of complexes having a diene and an acetylene bonded to the same metal atom have been reported,[2-4] and a ruthenium complex, [$Ru_4(CO)_{11}(C_8H_{10})$], containing a co-ordinated cyclo-oct-1-en-5-yne ligand has been described.[5] A crystal-structure determination[6] on this ruthenium complex shows that the acetylenic carbon atoms are bonded to four metal atoms. We now give full details of the preparation of some olefin–acetylene complexes of rhodium(I), as briefly reported elsewhere.[7]

RESULTS AND DISCUSSION

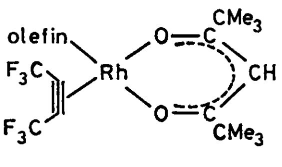
Diethyl ether solutions of [Rh(acac)(C_2H_4)$_2$] (acac = pentane-2,4-dionate) at *ca.* −78 °C react with hexafluorobut-2-yne to give a yellow crystalline complex [Rh(acac)(C_2H_4)(C_4F_6)] (1a). Similarly, treatment of [Rh(dpm)(C_2H_4)$_2$] (dpm = dipivaloylmethanate) with hexafluorobut-2-yne at *ca.* −78 °C gives (1b). The i.r. spectra of (1a) and (1b) show C=O stretching frequencies typical of oxygen-co-ordinated β-ketoenolate systems and both compounds show strong absorptions at 1 976, 1 960 (1a) and 1 976, 1 962 cm^{-1} (1b) due to the C≡C stretching frequency of the co-ordinated acetylene. The presence of two C≡C stretching frequencies is attributed to Fermi resonance doubling.[8] The ^{19}F n.m.r. spectra of (1a) and (1b) exhibit a single resonance at 54.75 and 55.02 p.p.m. respectively. The ^{19}F resonance of (1b) is a doublet, $J(^{103}Rh-^{19}F) = 2$ Hz, but for the complex (1a) this splitting could not be observed. Both the chemical-shift values, and the $J(^{103}Rh-^{19}F)$ value, are in excellent agreement with the value observed for the η^2-bonded hexafluorobut-2-yne in the complex [RhCl(C_4F_6)(PPh$_3$)$_2$].[9]

The complexes (1a) and (1b) are air-stable yellow crystalline solids which are soluble in diethyl ether but can be recrystallised from diethyl ether–methanol at low temperatures. They sublime readily *in vacuo* at *ca.* 50 °C.



(1a) R = Me

(1b) R = CMe$_3$



olefin
(2a) *cis*-cyclo-octene
(2b) cycloheptene
(2c) propene
(2d) *cis*-but-2-ene

Treatment of [Rh(acac)(C_8H_{14})$_2$] (C_8H_{14} = *cis*-cyclo-octene) with hexafluorobut-2-yne at *ca.* 78 °C also gives an olefin–acetylene complex [Rh(acac)(C_8H_{14})(C_4F_6)]. However, the cyclo-octene is not displaced as readily as ethylene from the rhodium(I) by the acetylene. Single-crystal *X*-ray crystallographic studies on the olefin–acetylene complexes (1a) and [Rh(acac)(C_8H_{14})(C_4F_6)] reveal that the olefin and acetylene ligands lie perpendicular to the plane of the rhodium–β-ketoenolate ring.[7] Comparison of the structure of (1a) with that of [Rh(acac)$(C_2H_4)_2$] also reveals that replacement of one C_2H_4 by C_4F_6 causes a considerable weakening in the bonding between Rh and the remaining C_2H_4.[7] This observation is consistent with the predicted π-acceptor properties of C_4F_6 and C_2H_4. Similar trends have been observed in the related systems [Rh(acac)$(C_2H_4)(C_2F_4)$] [10] and [Rh(η-C_5H_5)$(C_2H_4)(C_2F_4)$] [11] and it is apparent that the C_4F_6 and C_2F_4 ligands exhibit similar bond-weakening effects on the remaining ethylene ligand. This weakening of the Rh–C_2H_4 bond observed in (1a) and presumably present in (1b) suggested that these ethylene complexes might be useful precursors for the preparation of other olefin–acetylene complexes. Thus treatment of (1b) with *cis*-cyclo-octene, cycloheptene, propene, and *cis*-but-2-ene does indeed afford the new olefin–acetylene complexes (2). However, attempts to displace the ethylene ligand in (1b) by cyclohexene, bicyclo[2.2.1]-hept-2-ene, or 2,3-dimethylbut-2-ene have not been successful and (1b) is recovered unchanged.

It was anticipated that some of these olefin–acetylene complexes might show dynamic behaviour in solution, due to olefin rotation about the rhodium–olefin bonds, but that on decreasing the temperature of the measurements a slow-exchange limit on the n.m.r. time scale would be reached.[12] From previous studies on bis-(olefin) complexes of rhodium(I) it has been possible to estimate the activation energies for olefin rotation.[13-18] Examination of the ^{1}H n.m.r. spectra of (1b), [Rh-(dpm)$(C_2H_4)(C_4F_6)$], in the temperature range 25 to −50 °C revealed the anticipated temperature-dependent behaviour, the methylene groups of the ethylene ligand appearing equivalent at room temperature and splitting into two doublets centred at τ 5.80 and 7.06 which are assigned to the ' outer ' H_o and ' inner ' H_i protons of (1b) respectively by analogy with related systems. The coalescence temperature for (1b) was found to be −30 °C and application of the relation (1) [19] gave a value for the free energy of activation of 11.4 kcal mol^{-1}.* This

$$\Delta G_{T_c}{}^{\ddagger} = -RT_c \ln(\pi \Delta\nu h / 2^{\frac{1}{2}} \boldsymbol{k} T_c) \qquad (1)$$

value is similar to that observed for the complex [Rh-(acac)$(C_2H_4)_2$] ($\Delta G^{\ddagger}$ = 12.26 kcal mol^{-1}),[18] the lower free energy of activation observed for (1b) being consistent with the presence of the strong π-acceptor hexafluorobut-2-yne which weakens the rhodium–ethylene bond. Similar behaviour has been observed with the two complexes [Rh(η-C_5H_5)$(C_2H_4)_2$] and [Rh(η-C_5H_5)(C_2H_4)-(C_2F_4)] where the barrier to rotation is lowered by *ca.* 1.4 kcal mol^{-1} on replacing C_2H_4 by C_2F_4.[13]

The ^{1}H n.m.r. spectra of the propene and *cis*-but-2-ene complexes are temperature invariant in the range +56 to −50 °C. Furthermore, since only one chemical shift is observed for the methyl group of the propene ligand, it appears that only one isomer of this complex is present. Similarly the ^{1}H n.m.r. spectrum of the *cis*-but-2-ene complex also suggests the presence of a single isomer.

In order to determine whether the methyl groups are in ' inner ' or ' outer ' environments, single-crystal *X*-ray analyses were attempted. Crystals of the propene complex, however, decomposed in the *X*-ray beam but crystals of the *cis*-but-2-ene complex were sufficiently stable for a structure determination to be carried out.[20] The *X*-ray data establish that the methyl groups are directed away from the co-ordinated acetylene as would be expected by steric considerations. A similar geometry would be expected for the propene complex. Studies on propene and *cis*-but-2-ene complexes of the type [PtCl(acac)(olefin)] have shown that the methyl groups are next to an oxygen atom of the pentane-2,4-dionate ligand.[21] The *X*-ray crystallographic study [7] of [Rh(acac)$(C_8H_{14})(C_4F_6)$] also establishes that the cyclo-octene ligand adopts a geometry which has the olefinic protons next to the hexafluorobut-2-yne and the compounds (2b) and (2c) probably adopt a similar structure.

In an attempt to obtain an olefin complex possessing an ' inside ' methyl group the complex [Rh(dpm)-$(C_2H_4)(C_4F_6)$] was treated with ***trans***-but-2-ene. However, this reaction invariably gave the *cis*-but-2-ene complex (2d). The mechanism of this isomerisation has not, as yet, been investigated but it probably proceeds ***via*** an allyl–hydride intermediate.

Previously we have shown that the room-temperature reactions of [Rh(acac)$(C_2H_4)_2$] or [Rh(dpm)$(C_2H_4)_2$] with excess of hexafluorobut-2-yne give the substituted cyclohexa-1,3-diene complexes (3).[22,23] We now find that the reactions of the complexes (1) with excess of hexafluorobut-2-yne at room temperature also give (3). The reactions establish that the formation of these cyclohexadiene derivatives proceeds ***via*** intermediates in which an olefin and an acetylene are simultaneously co-ordinated to rhodium as has been suggested in related studies on rhodium systems [24] and indicated by kinetic studies on cobalt systems.[25] Treatment of the cyclo-octene compounds (2a) and [Rh(acac)$(C_8H_{14})(C_4F_6)$] with excess of hexafluorobut-2-yne at room temperature similarly gives the cyclohexadiene derivatives (4b) and (4a) respectively, and the complex (4c) can also be obtained by the reaction of hexafluorobut-2-yne with the cycloheptene compound (2b). However, the reaction of excess of hexafluorobut-2-yne with (5a) leads to the hexakis(trifluoromethyl)benzene complex (6). It would appear that during this reaction both of the ethylene ligands are displaced by the acetylene from the co-ordination sphere of the rhodium and hence do not take part in the cyclotrimerisation reaction. Displacement of both ethylene ligands from (5a) by hexafluorobut-2-yne would be consistent with studies on compounds of the type (7) which have shown that ethylene ***trans*** to nitrogen is more readily displaced than ethylene ***trans*** to oxygen.[17] In (5a) both ethylenes are ***trans*** to nitrogen. Furthermore in previous work we have shown that treatment of (7; R = H) with excess of hexafluorobut-2-yne also results in displacement of ethylene to give an η^4-hexakis-(trifluoromethyl)benzene complex.[23] Treatment of the

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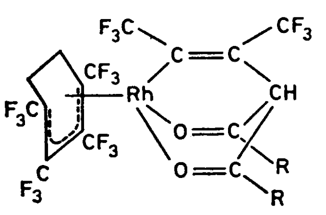
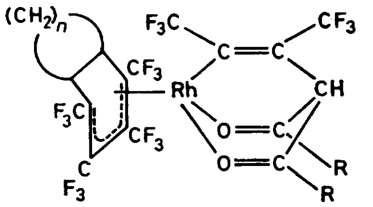
* Throughout this paper: 1 cal = 4.184 J; 1 mmHg ≈ 13.6 × 9.8 Pa.

cyclo-octa-1,5-diene complex (5b) with excess of hexafluorobut-2-yne also gives (6).

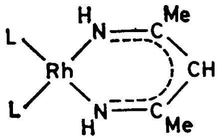
In contrast to the reactions of (1b) with hydrocarbon olefins, tetrafluoroethylene displaces hexafluorobut-2-yne from (1b) to give the complex [Rh(dpm)(C_2H_4)(C_2F_4)]. Treatment of this tetrafluoroethylene complex with hexafluorobut-2-yne regenerates the ethylene–hexafluorobut-2-yne complex (1b). This result is of interest because [Rh(acac)(C_2H_4)(C_2F_4)] and hexafluorobut-2-yne react to give the η^4-cyclohexadiene complex (3a) incorporating ethylene into the cyclohexadiene ring rather than tetrafluoroethylene.[22] The first step in the reaction of C_4F_6 with [Rh(acac)(C_2H_4)(C_2F_4)] is therefore displacement of C_2F_4 by hexafluorobut-2-yne.



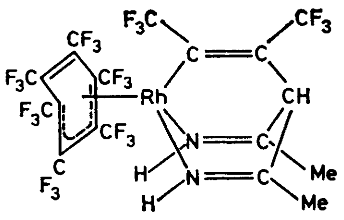
(3a) R = Me
(3b) R = CMe$_3$



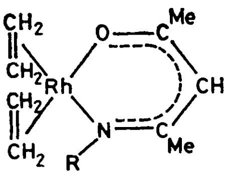
	n	R
(4a)	6	Me
(4b)	6	CMe$_3$
(4c)	5	CMe$_3$



(5a) L = C_2H_4
(5b) L_2 = 1,5-cod



(6)



(7)

Carbon monoxide and cyclo-octa-1,5-diene displace ethylene and hexafluorobut-2-yne from (1b) to give the known compounds [Rh(dpm)(CO)$_2$] and [Rh(dpm)(1,5-cod)] respectively.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a JEOL JNM-PS-100 spectrometer at 100 MHz with SiMe$_4$ (τ 10.00) as internal reference. Fluorine-19 n.m.r. spectra were obtained on a JEOL JNM-PS-100 spectrometer at 94.1 MHz with CCl_3F (0.0 p.p.m.) as external reference. Infrared spectra were obtained as Nujol mulls using CsI plates on a Perkin-Elmer 580 spectrophotometer. Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and degassed before use. The compounds [Rh(acac)(C_2H_4)$_2$],[26] [Rh(dpm)(C_2H_4)$_2$],[22] [Rh(acac)(C_8H_{14})$_2$],[27] [Rh_2Cl_2(C_2H_4)$_4$],[26] [Rh_2Cl_2(cod)$_2$],[28] and 4-aminopent-3-en-2-iminium tetrafluoroborate [29] were prepared as described in the literature.

(Ethylene)(hexafluorobut-2-yne)(pentane-2,4-dionato)-rhodium(I), (1a).—An excess of hexafluorobut-2-yne (1.0 cm^3) was condensed (−196 °C) onto a solution of [Rh(acac)(C_2H_4)$_2$] (0.25 g, 0.97 mmol) in diethyl ether (20 cm^3) contained in a round-bottomed flask (50 cm^3). The flask was allowed to warm to *ca.* −78 °C and the suspension was stirred at this temperature for 2 h to give a clear yellow solution. The solvent was removed *in vacuo*, and the yellow residue was recrystallised from diethyl ether–methanol at −78 °C to give yellow *crystals* of (1a) (85%), m.p. 57—59 °C, sublimes at <40 °C (0.2 mmHg) (Found: C, 33.4; H, 3.0. $C_{11}H_{11}F_6O_2Rh$ requires C, 33.7; H, 2.8%); $\nu_{max.}$ at 1 976s and 1 960s (C≡C), 1 566s, 1 527s, 1 430w, 1 268s, 1 242w, 1 227s, 1 201w, 1 165s, 1 150vs, 1 026m, 995(sh), 984w, 967vw, 936w, 922vw, 900m, 796m,

789m, 728w, 708m, 692m, 664m, 647m, 627m, 601w, 522m, 458m, and 426w cm^{-1}. N.m.r. spectra in $(CD_3)_2CO$: ^1H, τ 4.30 (s, 1 H, CH), 6.33 [d, 4 H, C_2H_4, J(RhH) 2 Hz], and 7.94 (s, 6 H, CH_3); ^{19}F, 54.75 p.p.m. (s, 6 F, CF_3).

(Ethylene)(hexafluorobut-2-yne)(2,2,6,6-tetramethylheptane-3,5-dionato)rhodium(I).—As above, hexafluorobut-2-yne (1.0 cm^3) and [Rh(dpm)$(C_2H_4)_2$] (0.39 g, 1.1 mmol) gave yellow *crystals* of (1b) (93%), m.p. 84—86 °C (decomp.), sublimes at 50—70 °C (0.2 mmHg) (Found: C, 43.1; H, 4.9. $C_{17}H_{23}F_6O_2Rh$ requires C, 42.9; H, 4.9%); $\nu_{max.}$ at 1 976s and 1 962m (sh) (C≡C), 1 548s, 1 538s, 1 521w, 1 505s, 1 426w, 1 374s, 1 356s, 1 266s, 1 259s (sh), 1 240vw, 1 223s, 1 203vw, 1 182w(sh), 1 163m(sh), 1 150vs, 1 145s(sh), 1 136s(sh), 978w, 960w, 938vw, 920vw, 900m, 811m, 786w, 751vw, 724vw, 704w, 662m, 646m, 601vw, 530w, 512w, and 493w cm^{-1}. N.m.r. spectra in $(CD_3)_2CO$: ^1H, τ 3.99 (s, 1 H, CH), 6.33 [d, 4 H, C_2H_4, J(RhH) 2 Hz], and 8.86 (s, 18 H, CH_3); ^{19}F, 55.02 p.p.m. [d, 6 F, CF_3, J(RhF) 2 Hz].

(Cyclo-octene)(hexafluorobut-2-yne)(pentane-2,4-dionato)-rhodium(I).—An excess of hexafluorobut-2-yne (1.0 cm^3) was condensed (−196 °C) onto a solution of [Rh(acac)-$(C_8H_{14})_2$] (0.52 g, 1.2 mmol) in diethyl ether (20 cm^3) contained in a round-bottomed flask (50 cm^3). The flask was allowed to warm to −78 °C and the yellow suspension was stirred at this temperature for 12 h. The resulting mixture was evaporated to dryness at 35 °C in *vacuo* and the yellow residue was recrystallised from diethyl ether–ethanol to give yellow *crystals* of the title compound (91%), m.p. 113—114 °C (decomp.), sublimes at 55—70 °C (0.2 mmHg) (Found: C, 43.3; H, 4.0. $C_{17}H_{21}F_6O_2Rh$ requires C, 43.1; H, 3.6%); $\nu_{max.}$ at 1 958s (C≡C), 1 584s, 1 568s, 1 525s, 1 355m, 1 339w, 1 323m, 1 277s, 1 263vs, 1 241m, 1 227s, 1 197w, 1 170m(sh), 1 159s, 1 149vs, 1 141s, 1 125m(sh), 1 022m, 976w, 967vw, 932w, 919vw, 900m, 857w, 849w, 818vw, 791s, 766w, 723w, 706m, 688w, 673m, 644m, and 623m cm^{-1}. N.m.r. spectra in CD_2Cl_2: ^1H, τ 4.52 (s, 1 H, CH), 6.55 (m, 2 H, CH=CH), 7.97 (s, 6 H, CH_3), and 7.69—8.73 (br, 12 H, CH_2); ^{19}F, 53.79 p.p.m. (s, 6F, CF_3).

(Cyclo-octene)(hexafluorobut-2-yne)(2,2,6,6-tetramethyl-heptane-3,5-dionato)rhodium(I), (2a).—A solution of [Rh-(dpm)$(C_2H_4)(C_4F_6)$] (0.15 g, 0.32 mmol) in diethyl ether was treated with *cis*-cyclo-octene (0.04 g, 0.32 mmol). The yellow solution was stirred for 3 h and then evaporated to dryness in *vacuo*. The yellow solid was recrystallised from diethyl ether–methanol to give yellow *crystals* of (2a) (74%), m.p. 140—142 °C (decomp.) (Found: C, 49.2; H, 6.0. $C_{23}H_{33}F_6O_2Rh$ requires C, 49.5; H, 6.0%); $\nu_{max.}$ at 1 971m(sh) and 1 959s (C≡C), 1 570m, 1 553s, 1 538s, 1 530m(sh), 1 506s, 1 321w, 1 270s, 1 251m(sh), 1 226s, 1 202w, 1 189m, 1 174w(sh), 1 149s, 1 138s, 1 025w(br), 980w, 962w, 933w, 920w, 902m, 806m, 787m, 769m, 750w, 739w, 726w, 706m, 647m(sh), 641m, 522m, 509w, and 497w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 4.20 (s, 1 H, CH), 6.64 (m, 2 H, CH=CH), 7.67 (m, 4 H, CH_2), 8.22—8.76 (br, 8 H, CH_2), 8.83 (s, 9 H, CH_3), and 8.95 (s, 9 H, CH_3); ^{19}F, 52.66 p.p.m. [d, 6F, CF_3, J(RhF) 2 Hz].

(Cycloheptene)(hexafluorobut-2-yne)(2,2,6,6-tetramethyl-heptane-3,5-dionato)rhodium(I), (2b).—As above, [Rh(dpm)-$(C_8H_{14})(C_4F_6)$] (0.15 g, 0.32 mmol) and cycloheptene (0.03 g, 0.32 mmol) gave yellow *crystals* of (2b) (87%), m.p. 121—122 °C (decomp.) (Found: C, 48.3; H, 5.5. $C_{22}H_{31}F_6O_2Rh$ requires C, 48.5; H, 5.7%); $\nu_{max.}$ at 1 974m and 1 959s (C≡C), 1 546, 1 539s(sh), 1 530m(sh), 1 506s, 1 062w, 1 028w(br), 961w, 936w, 902m, 831w, 809m, 788w, 772w, 751w, 727w, 708w, 672m, 643m, 618w(sh), 534w, 516w, 498w, 468w, 454w, 442w, and 431w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 4.19 (s, 1 H, CH), 6.36 (m, 2 H, CH=CH), 7.63 (m, 4 H, CH_2), 7.92—8.68 (br, 6 H, CH_2), 8.82 (s, 9 H, CH_3), and 8.94 (s, 9 H, CH_3); ^{19}F, 53.33 p.p.m. [d, 6 F, CF_3, J(RhF) 2 Hz].

(Hexafluorobut-2-yne)(propene)(2,2,6,6-tetramethylheptane-3,5-dionato)rhodium(I), (2c).—An excess of propene (1.0 cm^3) was condensed (−196 °C) on to a solution of [Rh(dpm)$(C_2H_4)(C_4F_6)$] (0.20 g, 0.42 mmol) in diethyl ether. The reactants were allowed to warm to −44 °C and the solution was stirred for 30 min. The flask was then evacuated and cooled to −196 °C and propene (1.0 cm^3) was again introduced and allowed to react at −44 °C. In this way three aliquots of propene were introduced to the solution. Finally it was evaporated to an orange oil, which on careful addition of methanol gave a yellow solid which was recrystallised from diethyl ether–methanol to give yellow crystals of (2c) (83%), m.p. 61—62 °C (decomp.) (Found: C, 44.3; H, 5.2. $C_{18}H_{25}F_6O_2Rh$ requires C, 44.1; H, 5.1%); $\nu_{max.}$ at 1 973s and 1 960s (C≡C), 1 549s, 1 535s, 1 502s, 1 276s(sh), 1 267s, 1 240m(sh), 1 221s, 1 201w, 1 184m, 1 161s, 1 147s, 1 132s, 1 049w, 996w, 968w, 960w, 930w(br), 900m, 807m, 788w, 771w, 752w, 726w, 706w, 673m, 648m, 532w, 513w, and 496w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 4.17 (s, 1 H, CH), 6.03—6.88 (m, 3 H, CH_2=CH), 8.27 [d, 3 H, CH_3, $J(CH_3$–H) 7 Hz], 8.84 (s, 9 H, CMe_3), and 8.92 (s, 9 H, CMe_3); ^{19}F, 52.68 p.p.m. (s, 6F, CF_3).

(cis-*But-2-ene)(hexafluorobut-2-yne)(2,2,6,6-tetramethyl-heptane-3,5-dionato)rhodium*(I), (2d).—An excess of *cis*-but-2-ene (1.0 cm^3) was condensed (−196 °C) on to a solution of [Rh(dpm)$(C_2H_4)(C_4F_6)$] (0.10 g, 0.21 mmol) in diethyl ether. The flask was allowed to warm to −10 °C and the solution was stirred for 1 h. Evaporation of the solvent gave a yellow solid which was recrystallised from diethyl ether–methanol to give yellow *crystals* of (2d) (71%), m.p. 57—58 °C (Found: C, 45.3; H, 5.4. $C_{19}H_{27}F_6O_2Rh$ requires C, 45.3; H, 5.4%); $\nu_{max.}$ at 1 973s and 1 961s (C≡C), 1 555s, 1 538s, 1 532m(sh), 1 506s, 1 269s, 1 248m, 1 226s, 1 199m, 1 185m, 1 164s(sh), 1 151s, 1 113m(sh), 1 083w(sh), 1 057w, 1 040w, 968w, 937w, 900w, 841w, 806w, 789w, 772w, 751w, 726w, 708w, 672m, 649w, 640w, 531w, 511w, and 497w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^1H, τ 4.20 (s, 1 H, CH), 6.38—6.78 (m, 2 H, CH=CH), 8.27 [d, 6 H, CH_3, $J(CH_3$–H) 6 Hz], 8.85 (s, 9 H, CMe_3), and 8.94 (s, 9 H, CMe_3); ^{19}F, 52.91 p.p.m. [d, 6F, CF_3, J(RhF) 1.6 Hz].

Reactions of Hexafluorobut-2-yne.—(*a*) *With* [Rh(dpm)-$(C_2H_4)(C_4F_6)$]. An excess of hexafluorobut-2-yne (1.0 cm^3) was condensed (−196 °C) onto [Rh(dpm)(C_2H_4)-(C_4F_6)] (0.65 g, 1.4 mmol) dissolved in diethyl ether contained in a Carius tube. The tube was sealed, shaken at room temperature for 2 d, cooled, opened, and volatile material removed. Slow concentration of the solution to *ca.* 2 cm^3 gave yellow crystals of (3b) (0.66 g, 55%) identified by comparison of its m.p. and i.r. spectrum with an authentic sample.[23]

(*b*) *With* [Rh(acac)$(C_2H_4)(C_4F_6)$]. As above, hexafluorobut-2-yne (1.0 cm^3) and [Rh(acac)$(C_2H_4)(C_4F_6)$] (0.39 g, 1.0 mmol) gave yellow crystals of (3a) (0.36 g, 50%) identified by comparison of its m.p. and i.r. spectrum with an authentic sample.[22]

(*c*) *With* [Rh(acac)$(C_8H_{14})(C_4F_6)$]. As above, hexafluorobut-2-yne (1.0 cm^3) and [Rh(acac)$(C_8H_{14})(C_4F_6)$] (0.1 g, 0.21 mmol) after 6 d gave yellow crystals of (4a) (0.11 g, 56%), m.p. 218—222 °C (decomp.) (Found: C, 37.8; H, 2.6. $C_{17}H_{21}F_6O_2Rh$ requires C, 37.6; H, 2.7%); $\nu_{max.}$ at 1 702s (C=O), 1 672vw, 1 593s (C=C), 1 526vw, 1 488m, 1 420m, 1 293s, 1 267w, 1 259w, 1 228vs, 1 208s, 1 194s, 1 170s(sh), 1 161vs, 1 138m, 1 115vs, 1 093m, 1 059vw, 1 034w, 1 027w(sh), 1 014m, 998m, 971m(sh), 967m, 925m, 870w, 841m, 822m, 813w, 773w, 755w(sh), 751w, 743m, 726m, 710w, 688m(sh), 680s, 664s, 656m, 634s, 618w, 588w, 540w, 519m, 507w, and 487m cm^{-1}. N.m.r. spectra in $(CD_3)_2CO$: ^{1}H, τ 3.47 (s, 1 H, CH), 7.25 (s, 6 H, CH_3), 7.47 (m, 2 H, CH–CH), and 8.00—8.55 (br, 12 H, CH_2); ^{19}F, 52.49 [br, 3F, $RhC(CF_3)=$], 55.08 (br, 6F, CF_3), 55.54 (br, 6F, CF_3), and 61.07 p.p.m. [q, 3F, $RhC(CF_3)=CHCF_3$, *J*(FF) 15.5 Hz].

(*d*) *With* $[Rh(dpm)(C_8H_{14})(C_4F_6)]$. As above, hexafluorobut-2-yne (1.0 cm^3) and $[Rh(dpm)(C_8H_{14})(C_4F_6)]$ (0.15 g, 0.27 mmol) gave yellow crystals of (4b) (0.16 g, 67%), m.p. 197—198 °C (decomp.) (Found: C, 42.1; H, 4.1. $C_{31}H_{33}F_{18}O_2Rh$ requires C, 42.2; H, 3.8%); $\nu_{max.}$ at 1 670s (C=O), 1 646w, 1 575m (C=C), 1 309m, 1 274s(sh), 1 248s, 1 229s, 1 212s(sh), 1 196s, 1 172s, 1 156s(br), 1 140s, 1 116s, 1 082m, 1 061m, 1 035m, 1 012m, 1 000m(sh), 965m, 945m, 902w, 869w, 841w, 828w, 821w, 773w, 741w, 724w, 713m, 690m, 679m, 668m, 657m, 610w, 591w, 539w, 519w, 508w, 495w, 456w, and 424w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^{1}H, τ 3.55 (s, 1 H, CH), 7.54 (m, 2 H, CH–CH), 7.88—8.66 (br, 2 H, CH_2), and 8.77 (s, 18 H, CH_3); ^{19}F 52.70 [br, 3F, $RhC(CF_3)=$], 54.44 (br, 6F, CF_3), 54.92 (br, 6F, CF_3), and 56.19 p.p.m. [q, 3F, $RhC(CF_3)=CHCF_3$, *J*(FF) 15.9 Hz].

(*e*) *With* $[Rh(dpm)(C_7H_{12})(C_4F_6)]$. As above, hexafluorobut-2-yne (1.0 cm^3) and $[Rh(dpm)(C_7H_{12})(C_4F_6)]$ (0.15 g, 0.28 mmol) gave yellow crystals of (4c) (0.19 g, 79%), m.p. 234—236 °C (decomp.) (Found: C, 41.8; H, 3.8. $C_{30}H_{31}F_{18}O_2Rh$ requires C, 41.5; H, 3.6%); $\nu_{max.}$ at 1 678s (C=O), 1 649w, 1 580m (C=C), 1 550w, 1 291m, 1 269s, 1 248s, 1 230s, 1 193s, 1 172s, 1 150s, 1 127s, 1 113s, 1 081m, 1 052m, 1 024m, 1 011m, 974w, 958w, 941w, 899w, 850w(sh), 843w, 827w, 811w, 776w, 744w, 728m, 712m, 690w, 681m, 669w, 659m, 651w(sh), 638w, 610w, 592w, 540w, 518w, 479w, 452w, and 426w cm^{-1}. N.m.r. spectra in $CDCl_3$: ^{1}H, τ 3.48 (s, 1 H, CH), 7.35 (m, 2 H, CH–CH), 7.68—8.40 (br, 10 H, CH_2), and 8.76 (s, 18, CH_3); ^{19}F, 53.61 [br, 3F, $RhC(CF_3)=$], 56.07 (br, 12F, CF_3), and 57.54 p.p.m. [q, 3F, $RhC(CF_3)=CHCF_3$, *J*(FF) 15.2 Hz].

(*f*) *With* $[Rh(apemino)(C_2H_4)_2]$. As above, hexafluorobut-2-yne (1.0 cm^3) and (5a) (0.15 g, 0.58 mmol) from acetone–ethanol gave yellow crystals of (6) (0.3 g, 70%), m.p. >320 °C (Found: C, 29.9; H, 1.2. $C_{19}H_9F_{24}N_2Rh$ requires C, 29.7; H, 1.1%); $\nu_{max.}$ at 3 380m and 3 370m (N–H), 1 677s (C=N), 1 634s (C=C), 1 605s (C=C), 1 443s, 1 428s, 1 394s, 1 342s, 1 322s, 1 296m, 1 288m, 1 269s, 1 260s, 1 239m(sh), 1 229s, 1 194vs(br), 1 181s, 1 171s, 1 157s, 1 149s, 1 125s, 1 105m(sh), 1 081w, 1 070w, 1 018w, 937m, 909m, 893w, 866m, 842s(br), 824s, 811s, 799s(sh), 779s, 765w, 752s, 746s, 741m, 717w, 711m(sh), 703s, 695m, 688m, 665vs(br), 642s, 633s, 605m(sh), 561m, 525s, 503s, and 475m cm^{-1}. N.m.r. spectra in $(CD_3)_2CO$: ^{1}H, τ −0.24 (br, 2 H, NH), 4.39 (s, 1 H, CH), and 7.31 (s, 6 H, CH_3); ^{19}F, 50.96 (br, 6F, CF_3), 51.58 [br, 3F, $RhC(CF_3)=$], 53.65 (br, 6F, CF_3), 58.02 (br, 6F, CF_3), and 60.63 p.p.m. [q, 3F, $RhF(CF_3)=CHCF_3$, *J*(FF) 15.6 Hz].

(*g*) *With* [Rh(apemino)(1,5-cod)]. As above, hexafluorobut-2-yne (1.0 cm^3) and (5b) (0.28 g, 0.9 mmol) gave yellow crystals of (6) (0.26 g, 34%), identified by its m.p. and i.r. spectrum.

(4-*Aminopent*-3-*en*-2-*iminato*)*bis*(*ethylene*)*rhodium*(I).—The complex $[Rh_2Cl_2(C_2H_4)_4]$ (0.15 g, 0.38 mmol) suspended in anhydrous methanol was treated with 4-aminopent-3-en-2-iminium tetrafluoroborate (0.14 g, 0.76 mmol) in 0.5 mol dm^{-3} sodium methoxide in methanol (3.5 cm^3). The suspension was stirred for 1 h and evaporated to dryness under reduced pressure. The residue was treated with benzene and evaporation of the extracts and recrystallisation of the residue from dichloromethane–methanol gave yellow *crystals* of $[Rh(apemino)(C_2H_4)_2]$ (0.15 g, 75%), m.p. 124—125 °C (Found: C, 42.2; H, 6.5. $C_9H_{17}N_2Rh$ requires C, 42.2; H, 6.6%); $\nu_{max.}$ at 3 290m (N–H), 1 572m(sh) and 1 556s (C=N), 1 536w, 1 333m, 1 262w, 1 236w, 1 227m, 1 188w, 1 182w, 1 025m, 966m, 938m(br), 783m(sh), 780s, 773s, 669w, 650w, 638w, 606w, 477w, and 468w cm^{-1}. The ^{1}H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 3.0—3.9 (br, 2 H, NH), 5.10 [t, 1 H, CH, *J*(HH) 3 Hz], 7.24 (s, 8 H, C_2H_4), and 7.83 (s, 6 H, CH_3). A similar procedure using $[Rh_2Cl_2(1,5\text{-cod})_2]$ gave yellow crystals of [Rh(apemino)(1,5-cod)] (85%), m.p. 167—168 °C (sublimes *ca.* 164 °C) (Found: C, 50.5; H, 7.1. $C_{13}H_{21}N_2Rh$ requires C, 50.7; H, 6.9%); $\nu_{max.}$ at 3 310m (NH), 1 568m and 1 549s (C=N), 1 329m, 1 303w, 1 234w, 1 216w, 1 196w, 1 172w(br), 1 024w(br), 992w, 954m, 863w, 818w, 795w(br), 768s, 727w, 678w, 667w, 642w, 487w, and 477w cm^{-1}. The ^{1}H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 3.2—3.9 (br, 2 H, NH), 5.22 [t, 1 H, CH, *J*(HH) 2.5 Hz], 6.03 (br, 4 H, =CH), 7.1—8.5 (br, 8 H, CH_2), and 7.90 (s, 6 H, CH_3).

Reaction of $[Rh(dpm)(C_2H_4)(C_4F_6)]$.—(*a*) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (1.0 cm^3) and $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (0.15 g, 0.32 mmol) in diethyl ether were shaken in a Carius tube for 19 h. The solution was evaporated and recrystallisation of the residue from diethyl ether–methanol gave $[Rh(dpm)(C_2H_4)(C_2F_4)]$ (0.10 g, 75%) identified by its m.p. and ^{19}F n.m.r. spectrum.[30]

(*b*) *With cyclo-octa*-1,5-*diene.* Cyclo-octa-1,5-diene (0.012 g, 0.11 mmol) and $[Rh(dpm)(C_2H_4)(C_4F_6)]$ in diethyl ether at room temperature gave, after 2 h, [Rh(dpm)(1,5-cod)] (0.04 g, 92%) identified by its m.p. and ^{1}H n.m.r. spectrum.[22]

(*c*) *With carbon monoxide.* Passage of carbon monoxide through a stirred solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (0.3 g, 0.63 mmol) in diethyl ether for 5 min gave $[Rh(dpm)(CO)_2]$ (0.16 g, 73%) identified by its m.p. and i.r. spectrum.[31]

Reaction of $[Rh(dpm)(C_2H_4)(C_2F_4)]$ *with Hexafluorobut*-2-*yne at* −78 °C.—An excess of hexafluorobut-2-yne (1.0 cm^3) and $[Rh(dpm)(C_2H_4)(C_2F_4)]$ (0.20 g, 0.48 mmol) in diethyl ether were stirred for 2 h at −78 °C. Removal of volatile products gave $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (0.20 g, 88%) identified by its m.p. and i.r. spectrum.

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