Olefin–Acetylene Metal Complexes: Reactions of Olefin–Hexafluorobut-2-yne Complexes of Rhodium(I) with Nitrogen, Phosphorus, Arsenic, and Antimony Donor Ligands

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Reaction of the complex [Rh(tmhd)(C_2H_4)(C_4F_6)] (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate, C_4F_6 = hexafluorobut-2-yne) with 1 mole equivalent of the ligands L [PPh_3, $P(C_6H_{11})_3$, or $AsPh_3$] results in displacement of ethylene to afford [Rh(tmhd)L(C_4F_6)]. Similarly [Rh(tmhd)(olefin)(C_4F_6)] [olefin = cycloheptene (C_7H_{12}) or cyclo-octene (C_8H_{14})] reacts with 1 mole equivalent of PPh_3 to give [Rh(tmhd)(PPh_3)(C_4F_6)], and 1 mole equivalent of $AsPh_3$ reacts with [Rh(tmhd)(C_7H_{14})(C_4F_6)] to give [Rh(tmhd)($AsPh_3$)(C_4F_6)]. The complexes [Rh(tmhd)L(C_4F_6)] react with a further mole equivalent of L to give the 18-electron complexes [Rh(tmhd)L_2(C_4F_6)] and complexes of this type, [Rh(tmhd)L_2(C_4F_6)] (L = PPh_3, $AsPh_3$, $SbPh_3$, $PMePh_2$, or $PEtPh_2$; 2L = $Ph_2PCH_2CH_2PPh_2$), are formed upon treatment of [Rh(tmhd)(C_2H_4)(C_4F_6)] with 2 mole equivalents of L. Similarly reaction of [Rh(acac)(C_2H_4)(C_4F_6)] (acac = pentane-2,4-dionate) with 2 mole equivalents of L (PPh_3, $PMePh_2$, or $SbPh_3$) affords the complexes [Rh(acac)L_2(C_4F_6)]. Treatment of [Rh(tmhd)(C_2H_4)(C_4F_6)] with 1 mole equivalent of $SbPh_3$ gives [Rh(tmhd)($SbPh_3$)$_2$(C_4F_6)]. In contrast to these results, the nitrogen-donor ligands (L' = pyridine, 3-methylpyridine, or 3,5-dimethylpyridine) react with the complex [Rh(tmhd)(C_2H_4)(C_4F_6)] to give the rhodacyclopent-2-ene complexes [Rh{$CH_2CH_2C(CF_3)$=$C(CF_3)$}(tmhd)L'$_2$], the pyridine (py) derivative reacting with PPh_3 to afford [Rh{$CH_2CH_2C(CF_3)$=$C(CF_3)$}(tmhd)(py)(PPh_3)]. Pyridine reacts with [Rh(tmhd)(C_2H_4)(C_2F_4)] to give [Rh(tmhd)(py)$_2$(C_2F_4)]. Hexafluorobut-2-yne reacts with [Rh(tmhd)($AsPh_3$)(C_4F_6)] and [Rh(tmhd)($SbPh_3$)$_2$(C_4F_6)] to afford the rhodacyclopentadienes [Rh{$C(CF_3)$=$C(CF_3)C(CF_3)$=$C(CF_3)$}(tmhd)L] (L = $AsPh_3$ or $SbPh_3$) respectively, and [Rh(tmhd)($AsPh_3$)(C_4F_6)] reacts with tetrafluoroethylene at −95 °C to afford [Rh(tmhd)($AsPh_3$)(C_2F_4)]. The complex [Rh(acac)(PPh_3)$_2$(C_4F_6)] reacts with carbon monoxide to give [Rh(acac)(CO)(PPh_3)]. Variable-temperature ^{19}F n.m.r. data for the complexes [Rh(tmhd)L_2(C_4F_6)] and [Rh(acac)L_2(C_4F_6)] (L = PPh_3, $AsPh_3$, or $SbPh_3$) are interpreted in terms of dissociation of the ligand L.

Examples of complexes which contain a monoene and a monoalkyne co-ordinated to the same metal atom are rare and their chemical behaviour has not been investigated in any detail. We have described some alkenehexafluorobut-2-yne complexes of rhodium(II),[1] and kinetic studies have provided evidence for an intermediate in which alkene and alkyne are simultaneously co-ordinated to cobalt(I) in cobalt-assisted alkene–alkyne co-oligomerization.[2] We now give full details of the reactions of some Group 5 donor ligands with ethylene hexafluorobut-2-yne complexes of rhodium(I), as briefly reported elsewhere.[3,4]

Results and Discussion

Reaction of [Rh(tmhd)(C_2H_4)(C_4F_6)] (1) (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) with 1 mole equivalent of triphenylphosphine in diethyl ether at 25 °C results in displacement of ethylene to afford [Rh(tmhd)(PPh_3)(C_4F_6)] (2a) (Table 1), in high yield. The ^1H n.m.r. spectrum (Table 2) showed two singlets due to two inequivalent tertiary butyl groups in agreement with the illustrated structure. Related reactions, equation (i), afford the complexes [Rh(tmhd)-{$P(C_6H_{11})_3$}(C_4F_6)] (2b) and [Rh(tmhd)($AsPh_3$)(C_4F_6)] (2c)

$$[Rh(tmhd)(olefin)(C_4F_6)] + L \longrightarrow [Rh(tmhd)L(C_4F_6)] + olefin \quad (i)$$

(olefin = C_2H_4, L = PPh_3, tricyclohexylphosphine, or $AsPh_3$; olefin = cycloheptene, L = PPh_3 or $AsPh_3$; olefin = cyclo-octene, L = $AsPh_3$). These complexes (2a)—(2c) can be regarded as derivatives of the simple η^2-alkyne complex [RhCl(PPh_3)$_2$(C_4F_6)] which has been isolated from the reaction of [RhCl(PPh_3)$_3$] with hexafluorobut-2-yne.[5]

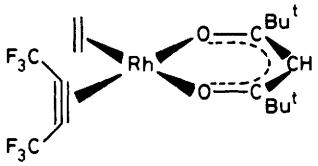
In contrast to these results the reaction of 1 mole equivalent of triphenylantimony with complex (1) gave only the bis(triphenylantimony) complex (3a), unreacted (1) remaining in the reaction mixture. Treatment of (1) with 2 mole equivalents of triphenylantimony gave a pure sample of (3a). The i.r. spectrum of complex (3a) showed two absorptions at 1 829 and 1 790 cm^{-1} which can be attributed to the C≡C stretching frequencies of the co-ordinated acetylene, the presence of two C≡C stretching frequencies being associated with Fermi resonance doubling.[6] These C–C stretching frequencies are much lower than those observed for the complexes (2) (Table 1), and are consistent with an increase in co-ordination number and electron density at the rhodium on going from (2) to (3a).

The ^{19}F n.m.r. spectrum of complex (3a) measured at −58 °C showed two signals at δ 51.62 and 54.10 p.p.m. in agreement with the illustrated static structure with the C–C bond axis of the co-ordinated acetylene lying in the equatorial plane as is usually observed in five-co-ordinate d^8 metal acetylene complexes.[7] Upon warming to room temperature these signals undergo reversible changes and at room temperature they are replaced by one signal which exhibits a small coupling to the ^{103}Rh nucleus. The coalescence temperature for this exchange process is −21 °C. In a [$^2H_1$]chloroform solution of (3a) saturated with triphenylantimony the coalescence temperature is raised to −10 °C suggesting that reversible dissociation of triphenylantimony from (3a) is responsible for the tempera-

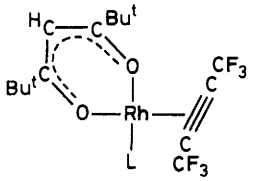
Table 1. Melting points, yields, infrared, and analytical data [a]

Complex	M.p. (θ_c/°C)	Colour	Yield (%)	ν(C≡C)/cm^{-1}	Analysis (%) C	Analysis (%) H
(2a)	166—167	Yellow	90	1 940	55.4 (55.9)	4.8 (4.8)
(2b)	184—186	Yellow	91	1 924	54.2 (54.4)	7.3 (7.2)
(2c)	139—141	Yellow	82	1 934	52.2 (52.5)	4.8 (4.5)
(3a)	144—146 [b]	Orange-red	75	1 829, 1 790	53.3 (53.1)	4.4 (4.3)
(3b)	129—130	Yellow	85	1 815, 1 787	63.0 (63.0)	5.2 (5.1)
(3c)	152—154	Orange	80	1 821, 1 790	57.5 (57.3)	4.9 (4.7)
(3d)	128—129	Yellow	15	1 829, 1 794	59.1 (58.2)	5.4 (5.1)
(3e)	126—127	Yellow	92	1 810, 1 781	57.8 (58.0)	5.7 (5.3)
(3f)	98—99	Yellow	76	1 829, 1 790	58.1 (58.9)	5.7 (5.6)
(4a)	127—128	Yellow	79	1 820, 1 786	61.0 (60.8)	4.5 (4.2)
(4b)	151—152	Orange	78	1 829, 1 791	55.3 (55.3)	4.0 (3.8)
(4c)	98—100 [b]	Red-brown	75	1 832, 1 790	50.7 (50.5)	3.8 (3.5)
(4d)	113—114	Yellow	97	1 815, 1 782	55.0 (55.0)	4.5 (4.4)
(5a) [c]	48—49	Pale green	40		51.2 (51.1)	5.4 (5.3)
(5b) [d]	112—114	Pale yellow-green	65		52.9 (52.6)	5.8 (5.6)
(5c) [e]	131—132	Cream	79		53.8 (53.9)	5.8 (6.0)
(5d) [f]	136—138	Pale yellow	64		58.7 (58.8)	5.5 (5.3)
(7)	122—140 [b]	Cream	77		51.0 (50.8)	5.4 (5.4)

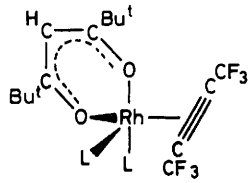
[a] Calculated values are given in parentheses. [b] With decomposition. [c] N, 4.7 (4.4%). [d] L = 3-methylpyridine. N, 4.4 (4.2%). [e] L = 3,5-dimethylpyridine. N, 4.1 (4.1%). [f] N, 1.9 (1.7%).



(1)



(2a) L = PPh_3
(2b) L = $P(C_6H_{11})_3$
(2c) L = $AsPh_3$



(3a) L = $SbPh_3$
(3b) L = PPh_3
(3c) L = $AsPh_3$
(3d) L_2 = $Ph_2PCH_2CH_2PPh_2$
(3e) L = $PMePh_2$
(3f) L = $PEtPh_2$

ture-dependent n.m.r. spectrum rather than rotation of the acetylene about the rhodium–acetylene bond axis.

The mono(triphenylphosphine) complex (2a) is co-ordinatively unsaturated and addition of a further mole equivalent of triphenylphosphine to it gave the bis(triphenylphosphine) complex (3b). Other complexes of this type (3c)—(3f) were obtained by the reactions outlined in equations (ii) (L = PPh_3 or $AsPh_3$) and (iii) (2L = $Ph_2PCH_2CH_2PPh_2$; L = $PMePh_2$ or $PEtPh_2$). The bis(triphenylphosphine) and the bis(triphenylarsine) complexes, (3b) and (3c), also exhibit

$$[Rh(tmhd)L(C_4F_6)] + L \longrightarrow [Rh(tmhd)L_2(C_4F_6)] \quad (ii)$$

$$[Rh(tmhd)(C_2H_4)(C_4F_6)] + 2L \longrightarrow [Rh(tmhd)L_2(C_4F_6)] + C_2H_4 \quad (iii)$$

temperature-dependent ^{19}F n.m.r. spectra (Table 2), which can be attributed to dissociation of the Group 5 donor ligand. Moreover, the absence of phosphorus–fluorine coupling in the room-temperature ^{19}F n.m.r. spectrum of $[Rh(tmhd)(PPh_3)_2(C_4F_6)]$ (3b) provides further evidence for reversible dissociation of triphenylphosphine from this complex in solution; ^{103}Rh–^{19}F coupling is still observed at room temperature. The n.m.r. data for the tertiary phosphine derivatives (3e) and (3f) (Table 2) indicate that they do not undergo dissociation in solution at room temperature on the n.m.r. time-scale. The greater stability of (3e) and (3f) towards ligand dissociation as compared to (3a)—(3c) can be correlated with the presence of less sterically demanding and more basic phosphines in (3e) and (3f). The addition of 2 mole equivalents of tricyclohexylphosphine to (1) gave only the monophosphine complex (2b).

The ability of the complexes (2a) and (2c) to add a further mole equivalent of a two-electron donor ligand is presumably due in part to the presence of the strong π-acceptor ligand hexafluorobut-2-yne [8] which will reduce electron density at the rhodium centre in (2a) and (2c). In contrast the fluoroolefin complexes $[Rh(tmhd)(C_2H_4)(C_2F_3X)]$ (X = F, Cl, Br, or CF_3) react with donor ligands L (PPh_3, $AsPh_3$, or $SbPh_3$) to give the 16-electron complexes $[Rh(tmhd)L(C_2F_3X)]$ only.[9] However, these differences must be marginal since $[Rh(acac)(C_2H_4)(C_2F_4)]$ reacts with triphenylphosphine to afford $[Rh(acac)(PPh_3)_2(C_2F_4)]$ (acac = pentane-2,4-dionate).[10] The formation of the bis(triphenylantimony) complex (3a) in the reaction of 1 mole equivalent of triphenylantimony with (1) can be related to the inability of the weak donor ligand triphenylantimony to satisfy the electronic requirements of the 16-electron species $[Rh(tmhd)(SbPh_3)(C_4F_6)]$. In this context it is noteworthy that hexafluorobut-2-yne has been shown to react with $[RhCl(SbPh_3)_3]$ to afford the five-co-ordinate complex $[RhCl(SbPh_3)_3(C_4F_6)]$.[11]

The presence of a *cis* arrangement of ligands L in the complexes (3) as indicated by their n.m.r. spectra (Table 2) is in contrast with the tetrafluoroethylene complexes $[Rh(acac)L_2(C_2F_4)]$ (L = PPh_3 or PBu^n_3) which contain *trans* tertiary phosphine ligands.[10] In view of this difference we investigated the reactions of $[Rh(acac)(C_2H_4)(C_4F_6)]$ with 2 mole equivalents of a ligand L to give the complexes $[Rh(acac)L_2(C_4F_6)]$ (4), equation (iv) (L = PPh_3, $AsPh_3$, $SbPh_3$, or

Table 2. Hydrogen-1 and fluorine-19 n.m.r. data [a] for the complexes

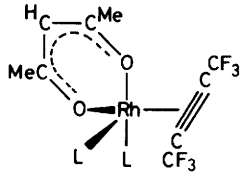
Complex	^{1}H N.m.r.	^{19}F N.m.r.
(2a)	0.78 (s, 9 H, Bu^t), 1.08 (s, 9 H, Bu^t), 5.83 (s, 1 H, γ-CH), 7.54 (m, 15 H, Ph)	53.40 [d, 6 F, CF_3, J(RhF) 2.1]
(2b)	1.13 (s, 18 H, Bu^t), 1.85 (m, 33 H, C_6H_{11}), 5.79 (s, 1 H, γ-CH)	52.34 [d, 6 F, CF_3, J(RhF) 2.1]
(2c)	0.82 (s, 9 H, Bu^t), 1.04 (s, 9 H, Bu^t), 5.76 (s, 1 H, γ-CH), 7.36 (m, 15 H, Ph)	54.03 [d, 6 F, CF_3, J(RhF) 1.6]
(3a)	0.86 (s, 9 H, Bu^t), 1.05 (s, 9 H, Bu^t), 5.64 (s, 1 H, γ-CH), 7.26 (m, 30 H, Ph)	52.97 [d, 6 F, CF_3, J(RhF) 1.5] [b]
(3b)	0.80 (s, 9 H, Bu^t), 0.98 (s, 9 H, Bu^t), 5.71 (s, 1 H, γ-CH), 7.37 (m, 30 H, Ph)	51.66 [d, 6 F, CF_3, J(RhF) 2] [c]
(3c)	0.86 (s, 9 H, Bu^t), 1.00 (s, 9 H, Bu^t), 5.73 (s, 1 H, γ-CH), 7.27 (m, 30 H, Ph)	52.66 [d, 6 F, CF_3, J(RhF) 2] [d]
(3d)	0.70 (s, 9 H, Bu^t), 0.97 (s, 9 H, Bu^t), 1.35 (m, 4 H, CH_2CH_2), 5.30 (s, 1 H, γ-CH), 7.0—7.7 (m, 20 H, Ph)	51.80 [dd, 3 F, CF_3, J(PF) 17.4, J(RhF) 4.5], 53.42 [d, 3 F, CF_3, J(RhF) 3]
(3e)	0.77 (s, 9 H, Bu^t), 1.16 (s, 9 H, Bu^t), 1.54 [d, 3 H, PMe, J(PH) 9], 1.63 [d, 3 H, PMe, J(PH) 9], 5.49 (s, 1 H, γ-CH), 7.25 (m, 20 H, Ph)	51.13 [dd, 3 F, CF_3, J(PF) 16.3, J(RhF) 3.6], 51.91 [d, 3 F, CF_3, J(RhF) 2.2]
(3f)	0.60 (m, 6 H, PCH_2CH_3), 0.92 (s, 9 H, Bu^t), 1.10 (s, 9 H, Bu^t), 2.23 (m, 4 H, PCH_2CH_3), 5.63 (s, 1 H, γ-CH), 7.28 (m, 20 H, Ph)	50.66 [d, 3 F, CF_3, J(PF) 11], 53.01 (s, 3 F, CF_3)
(4a) [e]	1.73 (s, 6 H, Me), 5.33 (s, 1 H, γ-CH), 7.40 (m, 30 H, Ph)	51.72 [d, 6 F, CF_3, J(RhF) 1.6] [f]
(4b)	1.65 (s, 3 H, Me), 1.84 (s, 3 H, Me), 5.31 (s, 1 H, γ-CH), 7.29 (m, 30 H, Ph)	52.50 [d, 6 F, CF_3, J(RhF) 1.8] [g]
(4c)	1.51 (s, 3 H, Me), 1.84 (s, 3 H, Me), 5.20 (s, 1 H, γ-CH), 7.29 (m, 30 H, Ph)	52.57 [d, 6 F, CF_3, J(RhF) 2.0] [h]
(4d)	1.40 [d, 3 H, PMe, J(PH) 12], 1.54 [d, 3 H, PMe, J(PH) 12], 1.56 (s, 3 H, Me), 1.90 (s, 3 H, Me), 5.04 (s, 1 H, γ-CH), 7.26 (m, 20 H, Ph)	51.54 [d, 3 F, CF_3, J(PF) 16.4], 51.96 (s, 3 F, CF_3)
(5a)	0.99 (s, 9 H, Bu^t), 1.10 (s, 9 H, Bu^t), 2.13—3.20 (m, 4 H, CH_2CH_2), 5.44 (s) and 5.51 (s) (1 H, γ-CH), 7.27 (m, 4 H, py), 7.74 (m, 2 H, py), 8.01 (d, 1 H, py), 8.14 (d, 1 H, py), 8.65 (d, 1 H, py), 8.86 (d, 1 H, py)	52.83 (q) and 54.72 (q) [3 F, RhC(CF_3), J(CF_3–CF_3) 14], 57.93 [q, 3 F, RhC(CF_3)=C(CF_3), J(CF_3–CF_3) 14]
(5b)	1.02 (s, 9 H, Bu^t), 1.13 (s, 9 H, Bu^t), 2.23 (s), 2.29 (s), and 2.36 (s) (6 H, Me), 2.32—3.22 (m, 4 H, CH_2CH_2), 5.43 (s) and 5.51 (s) (1 H, γ-CH), 7.12 (m), 7.52 (m), 7.88 (m), and 8.55 (m) (8 H, py)	53.87 (q) and 55.94 (q) [3 F, RhC(CF_3), J(CF_3–CF_3) 15.3], 59.19 [m, 3 F, RhC(CF_3)=C(CF_3), J(CF_3–CF_3) 15.3]
(5c)	1.01 (s, 9 H, Bu^t), 1.12 (s, 9 H, Bu^t), 2.17 (s), 2.24 (s), and 2.31 (s) (12 H, Me), 2.26—3.19 (m, 4 H, CH_2CH_2), 5.39 (s) and 5.49 (s) (1 H, γ-CH), 7.32 (m), 7.63 (m), 7.84 (m), 8.30 (m), and 8.49 (m) (6 H, py)	53.15 (q) and 55.26 (q) [3 F, RhC(CF_3), J(CF_3–CF_3) 12.7], 58.26 [m, 3 F, RhC(CF_3)=C(CF_3), J(CF_3–CF_3) 12.7]
(5d)	1.00 (s, 9 H, Bu^t), 1.10 (s, 9 H, Bu^t), 2.06—3.50 (m, 4 H, CH_2CH_2), 5.38 (s, 1 H, γ-CH), 7.27 (m) and 8.61 (d) (20 H, Ph, py)	53.85 [m, 3 F, RhC(CF_3)], 60.46 [q, 3 F, RhC(CF_3)=C(CF_3), J(CF_3–CF_3) 13.1] [i]
(7)	0.98 (s, 9 H, Bu^t), 1.09 (s, 9 H, Bu^t), 5.38 (s, 1 H, γ-CH), 7.12 (m), 7.58 (m), 8.24 (d), and 8.50 (d) (10 H, py)	64.69, 66.25, 67.75, 69.06 [AB, J(FF) 135, Δν 241 Hz]

[a] Measured in [$^2H_1$]chloroform at 30 °C, coupling constants in Hz. [b] ^{19}F N.m.r. at −58 °C: 51.62 (s, 3 F, CF_3) and 54.10 p.p.m. (s, 3 F, CF_3); coalescence temperature −21 °C and in solution saturated with $SbPh_3$ at −10 °C. [c] ^{19}F N.m.r. at −58 °C: 51.62 [d, 3 F, CF_3, J(PF) 16.8 Hz] and 52.41 p.p.m. (s, 3 F, CF_3); coalescence temperature −19 °C and in solution saturated with PPh_3 at −10 °C. [d] ^{19}F N.m.r. at −58 °C: 51.03 (s, 3 F, CF_3) and 52.48 p.p.m. (s, 3 F, CF_3); coalescence temperature −44 °C and in solution saturated with $AsPh_3$ at −37 °C. [e] Measured in [$^2H_2$]dichloromethane–dichloromethane. [f] ^{19}F N.m.r. at −32 °C: 50.98 [s, 3 F, CF_3, J(PF) not discernible] and 51.72 p.p.m. (s, 3 F, CF_3). [g] ^{19}F N.m.r. spectrum measured in dichloromethane; at −93 °C, 52.01 [d, 3 F, CF_3, J(RhF) 2.7 Hz] and 55.54 [d, 3 F, CF_3, J(RhF) 2.7 Hz]. [h] ^{19}F N.m.r. at −28 °C: 52.12 (s, 3 F, CF_3) and 53.43 p.p.m. (s, 3 F, CF_3). [i] ^{31}P N.m.r.: δ 14.6 [dq, J(RhP) 82, J(FP) 11 Hz].

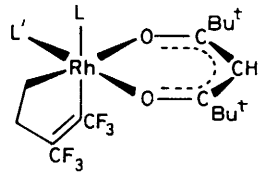
$$[Rh(acac)(C_2H_4)(C_4F_6)] + 2L \longrightarrow [Rh(acac)L_2(C_4F_6)] + C_2H_4 \quad \text{(iv)}$$

$PMePh_2$). The n.m.r. spectra of the triphenyl-phosphine, -arsine, and -antimony complexes (Table 2) indicate that these complexes undergo ligand dissociation in solution. However, the low-temperature ^{19}F n.m.r. spectra of these complexes and the room-temperature ^{19}F n.m.r. spectrum of (4d) are consistent with a *cis* structure.

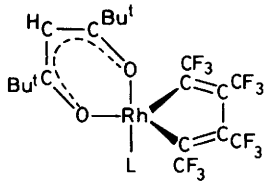
In contrast to the reactions of complex (1) with tertiary-phosphine, -arsine, and -antimony ligands, a different reactivity pattern is observed upon treatment of (1) with pyridine bases, equation (v) (L′ = pyridine, 3-methylpyridine, or 3,5-dimethylpyridine). The bis(pyridine) complex (5a) was



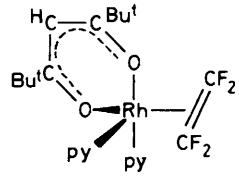
(4a) L = PPh_3
(4b) L = $AsPh_3$
(4c) L = $SbPh_3$
(4d) L = $PMePh_2$



(5a) L = L' = pyridine
(5b) L = L' = 3-methylpyridine
(5c) L = L' = 3,5-dimethylpyridine
(5d) L = PPh_3, L' = pyridine



(6a) L = $AsPh_3$
(6b) L = $SbPh_3$



(7) py = pyridine

also isolated in an analogous reaction of (1) with 1 mole equivalent of pyridine.

$$[Rh(tmhd)(C_2H_4)(C_4F_6)] + 2L' \longrightarrow [Rh\{CH_2CH_2C(CF_3)=C(CF_3)\}(tmhd)L'_2] \quad (v)$$

A single-crystal *X*-ray study has established that this complex contains a rhodacyclopent-2-ene ring formed by cyclization of the co-ordinated ethylene and hexafluorobut-2-yne in (1) at the rhodium centre.[3] Two *cis* pyridine ligands and a 2,2,6,6-tetramethylheptane-3,5-dionate ligand complete the octahedral geometry about the rhodium(III) in (5a). However, in the ^1H n.m.r. spectrum, two singlets of unequal intensity at 5.44 and 5.51 p.p.m. in the region associated with the γ-CH proton of the β-ketoenolate ligand are observed and this together with the complexity of the proton signals due to the co-ordinated pyridines suggest the presence of another isomer in solution. Furthermore, the ^{19}F n.m.r. spectrum (Table 2) showed three quartet signals. The two low-field quartets at 52.83 and 54.72 p.p.m. were poorly resolved and of unequal intensity. However, their combined intensities were equal to the intensity of the other quartet at 57.93 p.p.m. which was well resolved. By analogy with systems containing the moiety $MC(CF_3)=C(CF_3)-$ [12] the two signals at 52.83 and 54.72 p.p.m. can be assigned to the α-CF_3 groups of the two isomers, the chemical shifts of the CF_3 group furthest from the rhodium being identical for the two isomers. The ^{19}F n.m.r. spectrum of complex (5a) in $CDCl_3$ is not altered either by heating the solution to 60 °C or by addition of excess of pyridine. It therefore appears that (5a) is formed as a mixture of isomers. An attempt to separate the isomers by column chromatography on alumina was not successful. The complexes (5b) and (5c) also appear to be formed as a mixture of isomers (Table 2).

In the case of the related rhodacyclopentane complexes $[Rh\{CH_2C(=CH_2)C(=CH_2)CH_2\}(acac)L_2]$ (L = pyridine or PPh_3) a *cis*-bis(pyridine) complex has been characterized by a single-crystal *X*-ray determination, but the corresponding bis(triphenylphosphine) complex has been assigned a *trans* configuration on the basis of ^1H n.m.r. data.[13] In view of this difference the reaction of triphenylphosphine with the bis(pyridine) complex (5a) was investigated. A pale yellow crystalline complex (5d) was isolated, the ^1H n.m.r. spectrum of which exhibited only one resonance for the γ-CH proton of the tmhd ligand. The ^{19}F n.m.r. spectrum showed only two resonances, consistent with the presence of a single isomer. Furthermore the magnitude of $J(PF)$ observed in the $^{31}P-\{^1H\}$ n.m.r. spectrum of complex (5d) suggests that the triphenylphosphine ligand is *trans* to the vinylic carbon. Since the *X*-ray study on the *cis*-bis(pyridine) complex (5a) has established that the pyridine–rhodium bond *trans* to carbon is weaker than the pyridine–rhodium bond *trans* to oxygen,[3] treatment of the *cis* isomer (5a) with triphenylphosphine might be expected to lead to preferential displacement of the pyridine *trans* to carbon.

The collapse of a rhodium–ethylene–hexafluorobut-2-yne complex to the rhodacyclopent-2-ene ring complexes (5a)–(5c) provides good evidence for the intermediacy of metallacyclopent-2-enes in the formation of cyclohexa-1,3-diene derivatives from two acetylenes and one olefin.[1,2,14] However, our attempts to incorporate tetrafluoroethylene into a ring system by treatment of the complexes $[Rh(tmhd)L(C_2F_4)]$ (L = $AsPh_3$ or $SbPh_3$) with hexafluorobut-2-yne have resulted in the formation of the five-co-ordinate rhodacyclopentadiene complexes (6).[15] These reactions presumably proceed *via* initial displacement of co-ordinated tetrafluoroethylene by hexafluorobut-2-yne and in agreement with this pathway we now find that hexafluorobut-2-yne reacts with the complexes (2c) and (3a) to afford the rhodacyclopentadienes (6a) and (6b) respectively. We have previously commented upon the reversibility of the displacement reaction given in equation (vi) and we now find that tetrafluoroethylene will also dis-

$$[Rh(tmhd)(C_2H_4)(C_2F_4)] + C_4F_6 \rightleftharpoons [Rh(tmhd)(C_2H_4)(C_4F_6)] + C_2F_4 \quad (vi)$$

place hexafluorobut-2-yne from (2c) at −95 °C to afford $[Rh(tmhd)(AsPh_3)(C_2F_4)]$. Similarly, the reaction of carbon monoxide with complex (4a) results in displacement of hexafluorobut-2-yne and formation of $[Rh(acac)(CO)(PPh_3)]$.

The reduced tendency of tetrafluoroethylene to enter into cyclization reactions at a rhodium(I) centre, as compared to hexafluorobut-2-yne, is further illustrated by the reaction of pyridine (py) with $[Rh(acac)(C_2H_4)(C_2F_4)]$ which has been shown to give the complex $[Rh(acac)(py)_2(C_2F_4)]$.[10] We similarly find that $[Rh(tmhd)(C_2H_4)(C_2F_4)]$ reacts with pyridine to give $[Rh(tmhd)(py)_2(C_2F_4)]$ (7). In conclusion, however, it should be noted that tetrafluoroethylene does undergo cyclodimerization on reaction with $[Rh(acac)(PMePh_2)_2]$ to give a rhodacyclopentane derivative and that a five-membered rhodacyclic complex results upon reaction of tetrafluoroethylene with the hexafluoroacetone complex $[Rh(acac)(PMePh_2)_2\{OC(CF_3)_2\}]$.[16]

Experimental

Hydrogen-1 and fluorine-19 n.m.r. spectra were measured at 100 and 94.1 MHz respectively on a JEOL JNM-PS-100 spectrometer with CCl_3F (0.0 p.p.m.) as external reference for the ^{19}F n.m.r. spectra. Phosphorus-31 (^1H-decoupled) n.m.r.

spectra were measured at 24.15 MHz on a JEOL JNM-FX60 spectrometer with $P(OH)_4^+$ in D_2O (0.0 p.p.m.) as external reference.[17] N.m.r. data are given in Table 2. Infrared spectra (Table 1) 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 isolated were air-stable. The compounds [Rh(tmhd)$(C_2H_4)(C_4F_6)$],[1] [Rh(tmhd)$(C_7H_{12})(C_4F_6)$] (C_7H_{12} = cycloheptene),[1] [Rh(tmhd)$(C_8H_{14})(C_4F_6)$] (C_8H_{14} = cyclooctene),[1] [Rh(acac)$(C_2H_4)(C_4F_6)$],[1] and [Rh(tmhd)(C_2H_4)-(C_2F_4)][9] were prepared as described in the literature. Yields, melting points, and analytical data for all new compounds are given in Table 1.

Preparation of (Hexafluorobut-2-yne)(2,2,6,6-tetramethylheptane-3,5-dionato)(triphenylphosphine)rhodium(I) (2a).—Triphenylphosphine (0.055 g, 0.21 mmol) was added to a solution of [Rh(tmhd)$(C_2H_4)(C_4F_6)$] (0.10 g, 0.21 mmol) in diethyl ether. After stirring for 4 h, the solvent was removed *in vacuo* to afford yellow *microcrystals* of complex (2a).

The complexes (2b) and (2c) were prepared in a similar manner. Treatment of [Rh(tmhd)$(C_8H_{14})(C_4F_6)$] with 1 mole equivalent of triphenylphosphine for 18 h also gave (2a) (70%) and reaction of [Rh(tmhd)$(C_7H_{12})(C_4F_6)$] with 1 mole equivalent of triphenylarsine for 18 h gave (2c) (70%).

Reaction of Triphenylantimony with [Rh(tmhd)(C_2H_4)-(C_4F_6)].—Triphenylantimony (0.12 g, 0.32 mmol) was added to a solution of [Rh(tmhd)$(C_2H_4)(C_4F_6)$] (0.15 g, 0.32 mmol) in diethyl ether. The yellow solution became orange-red immediately and the solvent was removed *in vacuo*. Careful addition of methanol gave an orange powder which was identified as a mixture of complex (3a) and unreacted [Rh(tmhd)-$(C_2H_4)(C_4F_6)$] by examination of its i.r. spectrum.

Preparation of (Hexafluorobut-2-yne)(2,2,6,6-tetramethylheptane-3,5-dionato)bis(triphenylphosphine)rhodium(I).—Triphenylphosphine (0.45 g, 1.7 mmol) was added to a solution of [Rh(tmhd)$(C_2H_4)(C_4F_6)$] (0.41 g, 0.85 mmol) in diethyl ether. The solution immediately changed colour from yellow to orange and it was stirred for 1 h. Methanol was then added and the solution was slowly evaporated under reduced pressure to give yellow crystals of complex (3b).

The complexes (3a), (3c), (3e), (3f), and (4a)—(4d) were prepared in a similar manner except that (3f) was chromatographed (alumina column, 3 × 20 cm^3). Elution with diethyl ether–methanol (1 : 1) afforded yellow *crystals* of (3f). The complexes (3b) and (3c) were also prepared by reaction of the complexes [Rh(tmhd)L(C_4F_6)] (L = PPh_3 or $AsPh_3$) with 1 mole equivalent of the appropriate ligand L.

Preparation of [1,2-*Bis(diphenylphosphino)ethane*](*hexafluorobut-2-yne*)(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)-*rhodium*(I).—1,2-Bis(diphenylphosphino)ethane (0.13 g, 0.31 mmol) was added to a solution of [Rh(tmhd)$(C_2H_4)(C_4F_6)$] (0.15 g, 0.31 mmol) in diethyl ether. A yellow suspension formed immediately and the mixture was stirred for 15 h to give a clear solution. The solution was filtered and the filtrate was evaporated to a small volume under reduced pressure. Addition of methanol gave a yellow solid which was recrystallized from dichloromethane–light petroleum (b.p. 40—60 °C) to give yellow *crystals* of complex (3d).

Reactions of [Rh(tmhd)$(AsPh_3)(C_4F_6)$].—(*a*) *With tetrafluoroethylene.* An excess of tetrafluoroethylene (1.0 cm^3) was condensed (−196 °C) on to a solution of [Rh(tmhd)$(AsPh_3)$-(C_4F_6)] (0.20 g, 0.27 mmol) in diethyl ether contained in a flask (50 cm^3). The solution was stirred for 1 h at −95 °C and the solvent was removed *in vacuo*. Careful addition of ethanol gave pale yellow crystals of the known complex [Rh(tmhd)$(AsPh_3)(C_2F_4)$] (0.15 g, 80%) identified by its m.p. and i.r. spectrum.[9]

(*b*) *With hexafluorobut-2-yne.* An excess of hexafluorobut-2-yne (1.0 cm^3) was condensed (−196 °C) on to a solution of [Rh(tmhd)$(AsPh_3)(C_4F_6)$] (0.10 g, 0.13 mmol) in diethyl ether contained in a Carius tube. The tube was shaken for 23 h and after removing volatile material the solvent was evaporated to give a dark yellow solid. Recrystallization from diethyl ether–methanol gave [Rh{$C(CF_3)$=$C(CF_3)C(CF_3)$=$C(CF_3)$}(tmhd)-$(AsPh_3)$] (0.09 g, 76%) identified by its m.p. and i.r. spectrum.[15]

Reaction of [Rh(tmhd)$(SbPh_3)_2(C_4F_6)$] *with Hexafluorobut-2-yne.*—As above, an excess of hexafluorobut-2-yne and [Rh(tmhd)$(SbPh_3)_2(C_4F_6)$] (0.30 g, 0.26 mmol) in diethyl ether gave [Rh{$C(CF_3)$=$C(CF_3)C(CF_3)$=$C(CF_3)$}(tmhd)$(SbPh_3)$] (0.22 g, 88%) identified by its m.p. and i.r. spectrum.[15]

Reaction of [Rh(acac)$(PPh_3)_2(C_4F_6)$] *with Carbon Monoxide.*—Carbon monoxide was slowly passed through a solution of [Rh(acac)$(PPh_3)_2(C_4F_6)$] (0.11 g, 0.12 mmol) in benzene for 30 min. The solvent was evaporated and addition of diethyl ether gave [Rh(acac)(CO)(PPh_3)] (0.05 g, 85%) identified by its m.p. and i.r. spectrum.[18]

Reactions of [Rh(tmhd)$(C_2H_4)(C_4F_6)$].—(*a*) *With pyridine.* Pyridine (0.05 g, 0.64 mmol) was added to a solution of [Rh(tmhd)$(C_4H_4)(C_4F_6)$] (0.15 g, 0.31 mmol) in diethyl ether. The solution was stirred for 2 h and was then slowly evaporated *in vacuo* to give a pale yellow-green oil. Careful addition of ethanol gave pale green *crystals* of complex (5a). The same complex was also obtained in a similar reaction using 1 mole equivalent of pyridine.

(*b*) *With 3-methylpyridine.* As above 3-methylpyridine (0.04 g, 0.42 mmol) and [Rh(tmhd)$(C_2H_4)(C_4F_6)$] (0.10 g, 0.21 mmol) in dimethyl ether were stirred together for 2 h. Evaporation of the solvent gave a pale yellow oil which was treated with light petroleum (b.p. 40—60 °C) to give pale yellow-green *crystals* of complex (5b).

(*c*) *With 3,5-dimethylpyridine.* As above 3,5-dimethylpyridine (0.09 g, 0.84 mmol) and [Rh(tmhd)$(C_2H_4)(C_4F_6)$] in diethyl ether were stirred together for 2 h. Evaporation of the solvent gave a pale yellow oil which on careful addition of methanol gave cream *crystals* of complex (5c).

Reaction of Triphenylphosphine with the Complex [Rh{$CH_2CH_2C(CF_3)$=$C(CF_3)$}(tmhd)$(py)_2$].—Triphenylphosphine (0.06 g, 0.23 mmol) and [Rh{$CH_2CH_2C(CF_3)$=$C(CF_3)$}(tmhd)$(py)_2$] (0.15 g, 0.23 mmol) were stirred together for 1 h. Evaporation of the solvent gave an oil which on careful addition of ethanol gave a cream microcrystalline powder. Recrystallization from diethyl ether gave pale yellow *crystals* of complex (5d).

Reaction of Pyridine with [Rh(tmhd)$(C_2H_4)(C_2F_4)$].—Pyridine (0.076 g, 0.96 mmol) and [Rh(tmhd)$(C_2H_4)(C_2F_4)$] (0.20 g, 0.48 mmol) in diethyl ether were stirred together for 1 h. Evaporation of the solvent gave a pale yellow oil which on careful addition of methanol gave complex (7) as a cream microcrystalline powder.

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