Olefin–Acetylene Metal Complexes. The Formation of some 1,4-Diene Complexes of Rhodium(I) by the Reactions of Rhodium(I) Olefin–Hexafluorobut-2-yne Complexes with 2,4-Dimethylpenta-2,3-diene, Propene, and Cyclopropane

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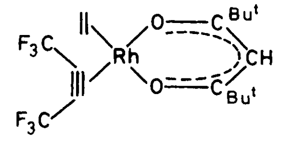
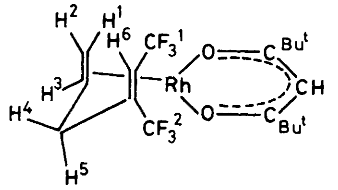
The reactions of the olefin–acetylene metal complexes $[\mathrm{Rh(tmhd)(L)(CF_3C{\equiv}CCF_3)}]$ (L = ethylene, cycloheptene, or cyclo-octene; tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) with cyclopropane afford the 1,4-diene complex $[\mathrm{Rh(tmhd)\{1\text{—}2\text{-}\eta{:}4\text{—}5\text{-}\eta\text{-}CH_2{=}CHCH_2C(CF_3){=}CHCF_3\}}]$ which can also be obtained by the reaction of $[\mathrm{Rh(tmhd)(C_2H_4)(C_4F_6)}]$ with propene at 50 °C. The reactions of tetramethylallene with the complexes $[\mathrm{Rh(O\text{–}O)(L)(C_4F_6)}]$ (O–O = tmhd, L = C_2H_4, cycloheptene, or cyclo-octene; O–O = pentane-2,4-dionate, L = C_2H_4) at room temperature afford the 1,4-diene complexes $[\mathrm{Rh(O\text{–}O)\{1\text{—}2\text{-}\eta{:}4\text{—}5\text{-}\eta\text{-}CH_2{=}CMeC({=}CMe_2)C(CF_3){=}CHCF_3\}}]$. The complexes $[\mathrm{Rh(tmhd)\{1\text{—}2\text{-}\eta{:}4\text{—}5\text{-}\eta\text{-}CH_2{=}CHCH_2C(CF_3){=}CHCF_3\}}]$ and $[\mathrm{Rh(tmhd)\{1\text{—}2\text{-}\eta{:}4\text{—}5\text{-}\eta\text{-}CH_2{=}CMeC({=}CMe_2)C(CF_3){=}CHCF_3\}}]$ react with carbon monoxide to give $[\mathrm{Rh(tmhd)(CO)_2}]$.

Complexes in which an olefin and an acetylene are co-ordinated to the same metal atom are important intermediates in a number of metal-assisted cyclisation reactions.[1-3] We have previously shown that the ethylene ligand in the olefin–acetylene complex $[\mathrm{Rh(tmhd)(CH_2{=}CH_2)(CF_3C{\equiv}CCF_3)}]$ (1) (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate) is labile and can be displaced from the rhodium under mild conditions by the olefins cyclo-octene, cycloheptene, *cis*-but-2-ene, and propene to give new olefin–hexafluorobut-2-yne complexes,[1] and the structures of some of these complexes have been determined by single-crystal *X*-ray studies.[4] To understand more fully the reactions of olefin–acetylene metal complexes, we have examined the reactions of (1) with cyclopropane, propene, and 2,4-dimethylpenta-2,3-diene (tetramethylallene) at slightly higher temperatures. Part of this work has been briefly reported elsewhere.[5]



(1)



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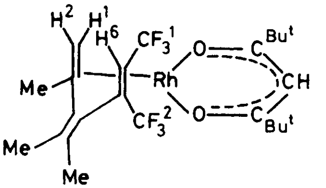


(3)

Results and Discussion

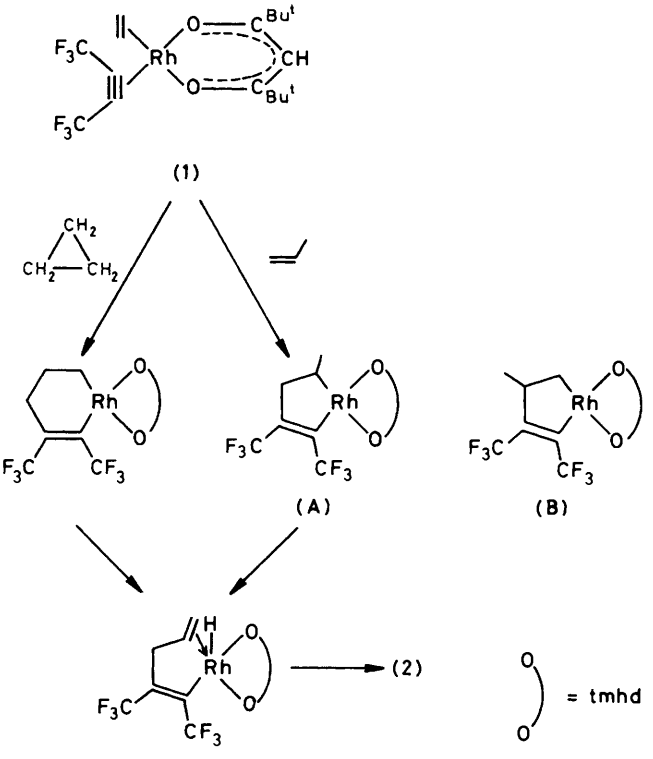
Cyclopropane does not react with $[\mathrm{Rh(tmhd)(C_2H_4)(CF_3C_2CF_3)}]$ (1) at room temperature; however, at 60 °C this reaction mixture gave a red oil, compound (2), and the same red oil was also formed in the reaction of propene with (1) at 50 °C. Elemental analysis, and mass and n.m.r. spectroscopy indicated that one molecule of cyclopropane, or of propene, had replaced the molecule of ethylene present in (1) and confirmation that there was no ethylene present in the complex (2) was provided by its preparation from the complexes $[\mathrm{Rh(tmhd)(L)(CF_3C_2CF_3)}]$ (L = cyclo-octene or norbornene), and cyclopropane at 60 °C.

The ^{1}H and ^{19}F n.m.r. spectra of (2) showed resonances consistent with the illustrated structure arising from an oxygen-bound tmhd ligand and a substituted hexa-1,4-diene ligand formed by attack of cyclopropane or propene upon the co-ordinated hexafluorobut-2-yne ligand present in (1). Thus the ^{1}H n.m.r. spectrum of (2) exhibited six distinct signals for the six protons of the $\mathrm{CH_2{=}CHCH_2C(CF_3){=}C(H)CF_3}$ ligand. The proton resonance at δ 2.51 appeared as a quartet due to geminal coupling to three equivalent fluorines and is assigned to H^6. It appears at relatively high field, consistent with its position as an 'inner' olefinic hydrogen.[6-8] The resonance centred at δ 3.03 is assigned to the other 'inner' olefinic proton, H^1, and appears as a doublet due to *trans* coupling to H^3. The 'outer' proton, H^2, appears at lower field (δ 3.25), as is generally observed [6-8] and exhibits a *cis* coupling to H^3. No coupling between H^1 and H^2 was observed, nor could any rhodium coupling be detected. Small geminal couplings and rhodium coupling to 'inner' and 'outer' protons in similar environments to H^1 and H^2 are sometimes observed.[6-8] The multiplet resonance at δ 4.50 is assigned to H^3. This proton exhibits couplings to H^2, H^4, and H^5 of similar magnitudes, together with a larger *trans* coupling to H^1. The signals at δ 2.04 and 3.62 are assigned to H^4 and H^5 respectively, the high-field signal being assigned to the *exo* proton H^4 since protons in this type of configuration would be expected to experience the greater shielding.[9] Further support for this assignment is provided by the relative magnitudes of the couplings of H^3 to H^4 and H^5 since application of the Karplus equation [10] to these vicinal couplings would suggest that $J(H^3H^5)$ would be slightly greater than $J(H^3H^4)$. The analysis of the ^{1}H n.m.r. spectrum of (2) has been further substantiated by proton–proton decoupling experiments.

Examination of the ^{19}F n.m.r. spectrum of (2) showed the presence of two signals centred at 60.48 and 53.46 p.p.m.

which are assigned to the CF_3 groups of a vinylic system, *cis*-$CH(CF_3{}^1)=C(CF_3{}^2)$, the magnitude of the fluorine–fluorine coupling suggesting that the CF_3 substituents have a relative *cis* configuration.[11]

As illustrated in Scheme 1, the formation of the complex (2) from cyclopropane and (1) can be understood in terms of displacement of ethylene from (1), formation of a rhodacyclohexane species, followed by β-hydride elimination and reductive cleavage of the rhodium–vinyl system $RhC(CF_3{}^1)=C(CF_3{}^2)-$ with retention of configuration at the carbon attached to rhodium. Similarly, the formation of (2) from propene and (1) could proceed *via* a rhodacyclopentene intermediate (A), Scheme 1. There are precedents for most of these proposed steps. We have established that the ethylene ligand in (1) undergoes displacement reactions quite readily,[1] and that rhodium olefin–acetylene complexes can collapse to rhodacyclopentene species.[5] The ability of rhodium(I) species to ring-open cyclopropane and substituted derivatives has also been established.[12] Finally, studies on the decomposition of metallacycles are consistent with a β-elimination process followed by reductive elimination of the unsaturated organo-group with the hydride.[13,14]

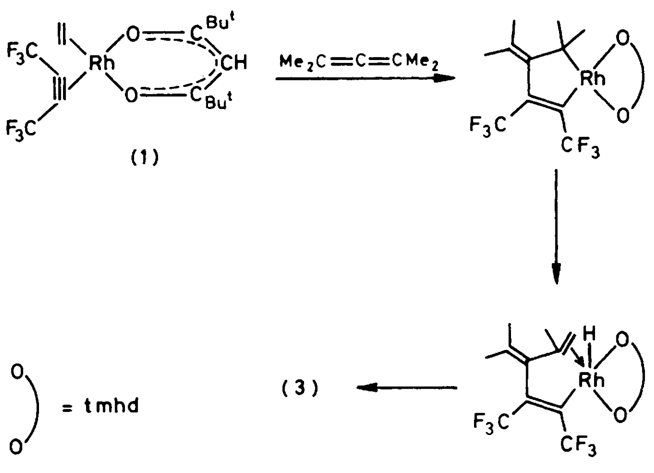


Scheme 1.

It is noteworthy that collapse of a propene–hexafluorobut-2-yne intermediate to rhodacyclopent-2-ene species could occur to give either (A) or an isomer (B), Scheme 1. Theoretical predictions[15] suggest that (B) would be the expected isomer. However, in this instance (A) may be the preferred isomer since steric repulsions between methyl and CF_3 groups are minimized in (A).

The reaction of (1) with tetramethylallene at room temperature gave in 70% yield a yellow-orange complex, (3). In addition to resonances associated with an oxygen bound tmhd ligand, the ^1H n.m.r. spectrum of (3) showed a resonance at δ 2.36 attributable to the ' inner ' proton H^6, which exhibited coupling to three equivalent fluorines and ^{103}Rh, a doublet at δ 2.63 assigned to the ' inner ' proton H^1, a lower field singlet at δ 3.26 due to the ' outer ' proton H^2, and three singlets attributable to three different methyl groups. The ^{19}F n.m.r. spectrum established the presence of a *cis*-$C(CF_3)=C(CF_3)H$ group. All these signals are consistent with the illustrated structure and confirmation of this structure has been provided by an *X*-ray study on a single crystal of (3).[5] The 1,4-diene complex (3) is also formed upon treatment of the complexes $[Rh(tmhd)(alkene)(CF_3C{\equiv}CCF_3)]$ (alkene = cyclo-octene or cycloheptene) with tetramethylallene and a pentane-2,4-dionate (acac) derivative can be isolated from the reaction of $[Rh(acac)(C_2H_4)(CF_3C{\equiv}CCF_3)]$ with tetramethylallene.

β-Hydride elimination from a rhodacyclopent-2-ene intermediate again provides an attractive route to the 1,4-diene complex (3), Scheme 2.



Scheme 2.

Treatment of both of the 1,4-diene complexes (2) and (3) with carbon monoxide results in displacement of the diene to give $[Rh(tmhd)(CO)_2]$.

Experimental

Hydrogen-1 n.m.r. spectra were recorded on a JEOL JNM-PS-100 spectrometer at 100 MHz with $SiMe_4$ (0.00 p.p.m.) as internal reference. Fluorine-19 n.m.r. spectra were obtained on a JEOL-PS-100 spectrometer at 94.1 MHz with CCl_3F (0.0 p.p.m.) as external reference. I.r. 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 $[Rh(tmhd)(alkene)(C_4F_6)]$ (alkene = ethylene, norbornene, or cyclo-octene) and $[Rh(acac)(C_2H_4)(C_4F_6)]$ were prepared as described previously.[1]

Reactions of $[Rh(tmhd)(C_2H_4)(C_4F_6)]$.—(*a*) *With Cyclopropane.* An excess of cyclopropane (1.0 g, 0.024 mmol) was condensed (−196 °C) onto a solution of $[Rh(tmhd)(C_2H_4)(C_4F_6)]$ (0.25 g, 0.53 mmol) in diethyl ether contained in a Carius tube. The tube was sealed, heated at 60 °C for 20 h, cooled, opened, and volatile material removed. Evaporation of the solution *in vacuo* gave $[Rh(tmhd)\{1\text{—}2\text{-}\eta\text{:}4\text{—}5\text{-}\eta\text{-}CH_2=CHCH_2C(CF_3)=CHCF_3\}]$ as a red oil (0.22 g, 85%) (Found: C, 44.0; H, 5.3%; *M* (mass spectrum), 490. $C_{18}H_{25}F_6O_2Rh$

requires C, 44.1; H, 5.1%; *M*, 490]. N.m.r. (q = quartet): ^1H ([$^2H_1$]chloroform), δ 5.84 (s, 1 H, γ-CH), 4.50 [m, 1 H, H^3, $J(H^3H^4)$ = 6, $J(H^3H^2)$ = $J(H^3H^5)$ = 8, $J(H^3H^1)$ = 12], 3.62 [dd, 1 H, H^5, $J(H^5H^4)$ = 13, $J(H^5H^3)$ = 8], 3.25 [d, 1 H, H^2, $J(H^2H^3)$ = 8], 3.03 [d, 1 H, H^1, $J(H^1H^3)$ = 12], 2.51 [q, 1 H, H^6, $J(H^6CF_3{}^1)$ = 11], 2.04 [dd, 1 H, H^4, $J(H^4H^5)$ = 13, $J(H^4H^3)$ = 6 Hz], and 1.13 p.p.m. (s, 18 H, $2CMe_3$); ^{19}F ([$^2H_1$]chloroform), 53.46 [qd, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ = 11, $J(CF_3{}^1H^6)$ = 11] and 60.48 p.p.m. [dq, 3 F, $CF_3{}^2$, $J(CF_3{}^2CF_3{}^1)$ = 11, $J(CF_3{}^1Rh)$ = 1.2 Hz].

(*b*) *With propene.* An excess of propene (1.0 g, 0.024 mmol) was condensed onto a solution of [Rh(tmhd)(C_2H_4)(C_4F_6)] (0.20 g, 0.42 mmol) in diethyl ether contained in a Carius tube. The tube was sealed, heated at 50 °C for 4 d, cooled, opened, and volatile material removed. Evaporation of the solution *in vacuo* gave a red oil (0.19 g, 92%) identified as [Rh(tmhd){1—2-η:4—5-η-CH_2=$CHCH_2C(CF_3)$=$CHCF_3$}] by its ^1H and ^{19}F n.m.r. spectra.

(*c*) *With tetramethylallene.* Tetramethylallene (0.04 g, 0.42 mmol) was added to a solution of [Rh(tmhd)(C_2H_4)(C_4F_6)] (0.20 g, 0.42 mmol) in diethyl ether. The solution was stirred for 22 h at room temperature. The solvent was slowly removed *in vacuo* and careful addition of methanol gave orange *crystals* of [Rh(tmhd){1—2-η:4—5-η-CH_2=CMeC(=CMe_2)C(CF_3)=$CHCF_3$}] (0.16 g, 70%), m.p. 113—114°C (Found: C, 49.1; H, 6.0. $C_{22}H_{31}F_6O_2Rh$ requires C, 48.5; H, 5.7%). N.m.r.: ^1H ([$^2H_1$]chloroform), δ 5.81 (s, 1 H, γ-CH), 3.26 (s, 1 H, H^2), 2.63 [d, 1 H, H^1, $J(H^1Rh)$ = 2.4], 2.36 [dq, 1 H, H^6, $J(H^6CF_3{}^1)$ = 9, $J(H^6Rh)$ = 2.4 Hz], 2.15 (s, 3 H, Me), 1.60 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.11 (s, 9 H, CMe_3), and 1.09 p.p.m. (s, 9 H, CMe_3); ^{19}F ([$^2H_1$]chloroform), 52.52 [q, 3 F, $CF_3{}^2$, $J(CF_3{}^2CF_3{}^1)$ = 9] and 53.86 p.p.m. [dq, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ = 9, $J(CF_3{}^1H^6)$ = 9 Hz].

Similarly, treatment of [Rh(tmhd)(alkene)(C_4F_6)] (alkene = cyclo-octene or cycloheptene) with (*a*) cyclopropane gave respectively 91 and 95% yields of [Rh(tmhd){1—2-η:4—5-η-CH_2=$CHCH_2C(CF_3)$=$CHCF_3$}], and with (*b*) tetramethylallene gave respectively 82 and 80% yields of [Rh(tmhd){1—2-η:4—5-η-CH_2=CMeC(=CMe_2)C(CF_3)=$CHCF_3$}].

Reaction of [Rh(acac)(C_2H_4)(C_4F_6)] *with Tetramethylallene.*—Tetramethylallene (0.05 g, 0.52 mmol) was added to a solution of [Rh(acac)(C_2H_4)(C_4F_6)] (0.20 g, 0.51 mmol) in diethyl ether and the reactants were stirred for 1 d. The solution became orange-red, and evaporation of the solvent followed by careful addition of methanol gave dark yellow *crystals* of [Rh(acac){1—2-η:4—5-η-CH_2=CMeC(=CMe_2)-C(CF_3)=$CHCF_3$}] (0.19 g, 81%), m.p. 130—131 °C (Found: C, 42.7; H, 4.6. $C_{16}H_{19}F_6O_2Rh$ requires C, 41.8, H, 4.2%). N.m.r.: ^1H ([$^2H_1$]chloroform), δ 5.44 (s, 1 H, γ-CH), 3.26 (s, 1 H, H^2), 2.65 [d, 1 H, H^1, $J(H^1Rh)$ = 2.3], 2.40 [dq, 1 H, H^6, $J(H^6CF_3{}^1)$ = 9, $J(H^6Rh)$ = 2.7 Hz], 2.14 (s, 3 H, Me), 1.99 (s, 3 H, Me), 1.96 (s, 3 H, Me), 1.60 (s, 3 H, Me), and 1.55 p.p.m. (s, 3 H, Me); ^{19}F([$^2H_1$]chloroform), 53.22 [q, 3 F, $CF_3{}^2$, $J(CF_3{}^2CF_3{}^1)$ = 9] and 54.51 p.p.m. [dq, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ = 9, $J(CF_3{}^1H^6)$ = 9 Hz].

Reactions with Carbon Monoxide.—(*a*) [Rh(tmhd){1—2-η:4—5-η-CH_2=$CHCH_2C(CF_3)$=$CHCF_3$}]. Carbon monoxide was slowly passed through a solution of the rhodium complex (0.05 g, 0.10 mmol) in diethyl ether for 15 min. Evaporation of the solution gave a red-green solid which was identified as [Rh(tmhd)$(CO)_2$] (0.03 g, 88%) by its m.p. and i.r. spectrum.[16]

(*b*)[Rh(tmhd){1—2-η:4—5-η-CH_2=CMeC(=CMe_2)C(CF_3)=$CHCF_3$}]. As above carbon monoxide and the rhodium complex (0.10 g, 0.18 mmol) gave [Rh(tmhd)$(CO)_2$] (0.05 g, 82%).

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