Fluorocarbon Complexes of Transition Metals. Part II.[1] Tertiary Arsine Complexes of Rhodium(III) derived from Hexafluorobut-2-yne and 3,3,3-Trifluoropropyne

By **Joel T. Mague,*** **Michael O. Nutt,** and **Edward H. Gause,** Department of Chemistry, Tulane University, New Orleans, Louisiana 70118, U.S.A.

The complexes $RhCl(CO)L_2$ [L = $AsPh_3$, $AsMePh_2$, $AsMe_2Ph$, $AsMe_3$, As(p-$MeC_6H_4)_3$, As(p-$FC_6H_4)_3$, or $AsMe_2$(p-$MeOC_6H_4$)] react with hexafluorobut-2-yne at temperatures between 25 and 100 °C to produce either $RhCl(CO)L_2C_4(CF_3)_4$ or $RhClL_2C_4(CF_3)_4$. In each case the product contains a rhodacyclopentadiene ring. For L = tricyclohexylarsine, little metallocycle is produced but the rhodium(I) complex catalyses the cyclotrimerization of the acetylene. The complexes $RhCl(CO)L_2C_4(CF_3)_4$ decarbonylate smoothly in refluxing benzene and can be recarbonylated by treatment with carbon monoxide under mild conditions. When L = $AsMe_3$ or $AsMe_2$(p-$MeOC_6H_4$) decarbonylation in the presence of moisture leads to the isolation of $RhCl(H_2O)L_2C_4(CF_3)_4$. The chloride ligands are also labile and can be removed by treatment with silver nitrate leading to the complexes $Rh(NO_3)L_2C_4(CF_3)_4$. Reaction of the rhodium(I) complexes with hexafluorobut-2-yne–carbon monoxide mixtures produces $L_2ClRhCOC(CF_3)=C(CF_3)CO$ [L = $AsPh_3$, As(p-$MeC_6H_4)_3$, As(p-$FC_6H_4)_3$, $As(C_6H_{11})_3$]. Reaction of the rhodium(I) complexes with 3,3,3-trifluoropropyne produces the acetylides $RhCl(CO)L_2(C{\equiv}CCF_3)_2$.

THE ability of certain complexes of the Group VIII metals to catalyse the cyclotrimerization of acetylenes is well known.[2] In some instances these reactions lead instead to what are evidently linear or cross-linked polymers sometimes having quite high molecular weights.[2a,c,3] In Part I of this series,[1] we reported that $RhClL_3$ (L = $AsPh_3$, $SbPh_3$) reacted with hexafluorobut-2-yne to produce the rhodacyclopentadiene complexes $RhClL_2C_4(CF_3)_4$. This behaviour contrasts with that observed for $RhCl(PPh_3)_3$ in which $RhCl(PPh_3)_2C_4F_6$ and an intractable polymer were the only products.[3] To gain further insight into the reasons for this difference and to study systematically the effects of changing the steric and electronic properties of ligands bound to rhodium on the interaction of the complexes with acetylenes, we undertook a study of the reactions of some fluorinated acetylenes with the complexes $Rh(CO)ClL_2$ (L = tertiary phosphine or tertiary arsine). We report here on some of the results of this study with the arsine complexes.

EXPERIMENTAL

All solvents were appropriately dried and distilled before use and were stored under an atmosphere of pre-purified nitrogen. Light petroleum has b.p. 30—60°. ^{19}F N.m.r. spectra were obtained on a JEOL C-60HL spectrometer and ^1H n.m.r. spectra with a JEOL MH-100 instrument. ^{19}F Chemical shifts are referred to α,α,α-trifluorotoluene (0·0 p.p.m.) and increase to high field. ^1H Chemical shifts are expressed as τ values. Infrared spectra were obtained on Beckman IR-5A and IR-18A spectrophotometers using Nujol mulls unless otherwise specified. Hexafluorobut-2-yne and 3,3,3-trifluoropropyne were purchased from PCR, Incorporated while hydrated rhodium(III) chloride was obtained from A. D. Mackay, Inc. and triphenylarsine from Strem Chemicals.

The starting rhodium(I) complexes were prepared from $[Rh(CO)_2Cl]_2$ [4] by the method of Vallarino.[5] The standard Grignard procedure was used to prepare tricyclohexylarsine from $AsCl_3$ while $AsMe_3$, $AsMe_2Ph$, and $AsMe_2$(p-$MeOC_6H_4$) were prepared from sodium dimethylarsenide [6] and methyl iodide, bromobenzene, and p-bromoanisole respectively. $AsMePh_2$ was prepared from lithium diphenylarsenide [7] and methyl iodide.

Chlorocarbonylbis(trimethylarsine)tetrakis(trifluoromethyl)-rhodacyclopentadiene, $RhCl(CO)(AsMe_3)_2C_4(CF_3)_4$.—A thick-walled Pyrex tube of *ca.* 40 ml volume was charged with $Rh(CO)Cl(AsMe_3)_2$ (0·2 g, 0·49 mmol) and was evacuated. The tube was cooled in liquid nitrogen and benzene (5 ml) was condensed in. The tube was warmed to dissolve the complex and was then cooled again in liquid nitrogen. Hexafluorobut-2-yne, *ca.* 2 ml, was condensed in and the tube was sealed and heated at 100° for 18 h. After being cooled to room temperature, the tube was further cooled in liquid nitrogen and opened. The unchanged acetylene was

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[1] Part I, J. T. Mague and G. Wilkinson, *Inorg. Chem.*, 1968, **7**, 542.

[2] (*a*) W. Hübel, in 'Organic Syntheses *via* Metal Carbonyls,' vol. I, eds., I. Wender and P. Pino, Wiley–Interscience, New York, 1968; (*b*) P. M. Maitlis, 'The Organic Chemistry of Palladium,' vol. II, Academic Press, New York, 1971; (*c*) J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.

[3] M. J. Mays and G. Wilkinson, *J. Chem. Soc.*, 1965, 6629.

[4] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

[5] L. Vallarino, *J. Chem. Soc.*, 1957, 2287.

[6] R. D. Feltham and W. Silverthorn, *Inorg. Synth.*, 1967, **10**, 159.

[7] A. M. Aguiar, J. T. Mague, H. J. Aguiar, T. G. Archibald, and G. Prejean, *J. Org. Chem.*, 1968, **33**, 1681.

recovered and the yellow benzene solution of the product filtered. The benzene was evaporated under reduced pressure and the solid recrystallized from diethyl ether to give pale yellow prisms (0·23 g, 64%).

The following compounds were prepared in a similar manner.

Chlorocarbonylbis(dimethylphenylarsine)tetrakis(trifluoromethyl)rhodacyclopentadiene, $RhCl(CO)(AsMe_2Ph)_2C_4(CF_3)_4$.—Pale yellow prisms from diethyl ether (0·25 g, 84%).

*Chlorocarbonylbis[dimethyl(*p*-methoxyphenyl)arsine]tetrakis(trifluoromethyl)rhodacyclopentadiene*, $RhCl(CO)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$.—Pale yellow prisms from diethyl ether (0·24 g, 88%).

Chlorobis(methyldiphenylarsine)tetrakis(trifluoromethyl)-rhodacyclopentadiene, $RhCl(AsMePh_2)_2C_4(CF_3)_4$.—The crude product was chromatographed on Florisil (1·5 × 30 cm column). Elution with hexane–diethyl ether (3 : 2 v/v) produced a yellow band from which yellow crystals of the product could be obtained upon evaporation of the ether (0·20 g, 23%).

Chlorobis(triphenylarsine)tetrakis(trifluoromethyl)rhodacyclopentadiene, $RhCl(AsPh_3)_2C_4(CF_3)_4$.—The crude product was chromatographed on silica gel (1 × 60 cm column). Elution with benzene produced a large greenish yellow band followed by a small pinkish tan band. The first fraction afforded the desired complex which was obtained as orange-yellow prisms upon recrystallization from benzene–diethyl ether (0·18 g, 65%).

*Chlorobis[tris(*p*-fluorophenyl)arsine]tetrakis(trifluoromethyl)rhodacyclopentadiene*, $RhCl\{As(p\text{-}FC_6H_4)_3\}_2C_4(CF_3)_4$.—The crude product was chromatographed on silica gel (1 × 60 cm column). Elution with benzene produced a yellow band from which the product was obtained after concentration to *ca.* 5 ml and dilution with light petroleum as orange-yellow crystals (0·37 g, 51%).

*Chlorobis[tris(*p*-tolyl)arsine]tetrakis(trifluoromethyl)rhodacyclopentadiene*, $RhCl\{As(p\text{-}MeC_6H_4)_3\}_2C_4(CF_3)_4$.—The crude product was heated at 80° for 3 h under high vacuum in a sublimation apparatus to remove a small amount of hexakis-(trifluoromethyl)benzene. The residue was then chromatographed on Florisil (1·5 × 30 cm column). Elution with 1 : 1 (v/v) hexane–diethyl ether produced a broad yellow band which was collected and evaporated to dryness *in vacuo*. The solid was taken up in a minimum volume of benzene and crystallization induced by the slow diffusion of light petroleum. The desired product was obtained as large yellow-orange prisms which were separated by hand from a small quantity of light yellow flakes.

*Chlorobis[dimethyl(*p*-methoxyphenyl)arsine]tetrakis(trifluoromethyl)rhodacyclopentadiene*, $RhCl\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$.—The carbonyl complex, $RhCl(CO)[AsMe_2(p\text{-}MeOC_6H_4)]_2C_4(CF_3)_4$ was refluxed in dry benzene (15 ml) under nitrogen for 5 h. Concentration of the resulting bright yellow solution followed by addition of light petroleum and cooling at 0 °C afforded the product as yellow prisms in essentially quantitative yield.

Chlorobis(dimethylphenylarsine)tetrakis(trifluoromethyl)-rhodacyclopentadiene, $RhCl(AsMe_2Ph)_2C_4(CF_3)_4$.—This compound was prepared from the corresponding carbonyl derivative in an analogous manner to the previous complex.

Chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)-rhodacyclopentadiene, $RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4$.—The carbonyl complex, $RhCl(CO)(AsMe_3)_2C_4(CF_3)_4$, was refluxed for 4 h in benzene (15 ml) to give a bright yellow solution. The solution was evaporated under reduced pressure to give an off-white solid which was recrystallized from diethyl ether–light petroleum to give very pale yellow prisms in essentially quantitative yield.

Chlorobis(triphenylarsine)-3,4-bis(trifluoromethyl)rhodacyclopent-3-ene-2,5-dione–Benzene (1/2), $(AsPh_3)_2Cl\overline{RhCOC(CF_3){=}C(CF_3)CO},2C_6H_6$.—A thick-walled Pyrex Carius tube was charged with $RhCl(CO)(AsPh_3)_2$ (0·2 g, 0·26 mmol) which was then evacuated and chilled in liquid nitrogen; dry benzene (5 ml) was then condensed in. The tube was warmed to room temperature to dissolve the solid and then rechilled. An excess of hexafluorobut-2-yne was then condensed in followed by pressurization of the cold tube with CO to *ca.* 400 Torr. The tube was sealed and heated at 100 °C for 2 h following which the tube was again cooled in liquid nitrogen, opened, and the excess of acetylene recovered. The resulting yellow-brown solution was filtered, concentrated to *ca.* 2 ml, and chromatographed on a 1 × 60 cm column of silica gel. Development with benzene gave three bands, yellow-green, pinkish tan, and yellow in that order. Elution with benzene first removed some $RhCl(AsPh_3)_2C_4(CF_3)_4$ followed by the desired compound. The third band proved to be unchanged $RhCl(CO)(AsPh_3)_2$. The middle fraction was evaporated to dryness and the product obtained as pinkish tan needles by recrystallization from benzene–light petroleum (0·12 g, 46%).

The following complexes were produced in a similar manner.

*Chlorobis[tris(*p*-tolyl)arsine]3,4-bis(trifluoromethyl)rhodacyclopent-3-ene-2,5-dione–Benzene* (1/2·5), $\{As(p\text{-}MeC_6H_4)_3\}_2Cl\overline{RhCOC(CF_3){=}C(CF_3)CO},2{\cdot}5C_6H_6$.—The brown solid obtained by evaporating the reaction mixture to dryness was taken up in a minimum volume of benzene and chromatographed on silica gel (1 × 60 cm column). Elution with benzene produced a yellow band followed immediately by a brown-orange one. The yellow fraction consisted mainly of $RhCl[As(p\text{-}MeC_6H_4)_3]_2C_4(CF_3)_4$. The leading portion of the brown-orange band was discarded and the remainder was collected. The volume was reduced to *ca.* 1 ml under reduced pressure and upon the addition of diethyl ether, the product separated as pale orange-brown needles (0·17 g, 34%).

*Chlorobis[tris(*p*-fluorophenyl)arsine]3,4-bis(trifluoromethyl)rhodacyclopent-3-ene-2,5-dione–Benzene* (1/1·5), $\{As(p\text{-}FC_6H_4)_3\}_2Cl\overline{RhCOC(CF_3){=}C(CF_3)CO}, 1{\cdot}5C_6H_6$.—The orange-brown material obtained by evaporating the reaction mixture to dryness was taken up in a minimum volume of chloroform and chromatographed on silica gel (1 × 60 cm column). Elution with 4 : 1 (v/v) hexane–benzene removed a small yellow band. Further elution with 1 : 1 (v/v) hexane–benzene removed a second yellow band, however, neither of these fractions contained enough material for satisfactory characterization. Elution was continued with benzene and an orange band containing the desired product was collected. Upon concentration and addition of light petroleum the product was obtained as pale brown-orange needles (0·11 g, 38%).

Chlorobis(tricyclohexylarsine)-3,4-bis(trifluoromethyl)rhodacyclopent-3-ene-2,5-dione–Benzene (1/0·5), $\{As(C_6H_{11})_3\}_2Cl\overline{RhCOC(CF_3){=}C(CF_3)CO},0{\cdot}5C_6H_6$.—Evaporation of the reaction mixture to dryness gave a brown gum. This was taken up in a minimum volume of benzene and chromatographed on silica gel (1 × 60 cm volume). Elution with a

3 : 1 (v/v) hexane–benzene mixture removed a small yellow band whose infrared spectrum indicated it to be a mixture of $RhCl(CO)\{As(C_6H_{11})_3\}_2$ and an unidentified fluorocarbon complex. Further elution with 2 : 1 (v/v) hexane–benzene produced a wide orange band which was collected and evaporated to dryness. The pale brown solid was recrystallized from benzene–light petroleum to give the product as needles (0·12 g, 26%).

Nitratobis(trimethylarsine)tetrakis(trifluoromethyl)rhodacyclopentadiene, $Rh(NO_3)(AsMe_3)_2C_4(CF_3)_4$.—To a solution of $RhCl(CO)(AsMe_3)_2C_4(CF_3)_4$ (0·19 g, 0·26 mmol) in 1 : 1 (v/v) benzene–ethanol (10 ml) was added $AgNO_3$ (0·044 g, 0·26 mmol). The solution was stirred for 20 min to complete precipitation of the AgCl. The mixture was filtered through a pad of diatomaceous earth and the filtrate was evaporated to dryness. The solid was taken up in benzene and filtered again to remove a small amount of brown residue. Upon concentration and addition of light petroleum, the product was obtained as pale yellow-brown needles (0·12 g, 62%).

Nitratobis(dimethylphenylarsine)tetrakis(trifluoromethyl)-rhodacyclopentadiene, $Rh(NO_3)(AsMe_2Ph)_2C_4(CF_3)_4$.—This compound prepared in an analogous manner to the trimethylarsine complex from $RhCl(CO)(AsMe_2Ph)_2C_4(CF_3)_4$ (0·21 g, 0·24 mmol) and $AgNO_3$ (0·041 g, 0·24 mmol) was obtained as pale yellow-brown needles from benzene–light petroleum (0·09 g, 44%).

Chlorocarbonylbis(methyldiphenylarsine)tetrakis(trifluoromethyl)rhodacyclopentadiene, $RhCl(CO)(AsMePh_2)_2C_4(CF_3)_4$.—A benzene solution of $RhCl(AsMePh_2)_2C_4(CF_3)_4$ was stirred for 2 h under pressure of carbon monoxide (25 p.s.i.) in a Fisher–Porter pressure bottle. The pale yellow solution was then diluted with CO-saturated, light petroleum and cooled at ice temperature to produce pale yellow needles of the product in essentially quantitative yield.

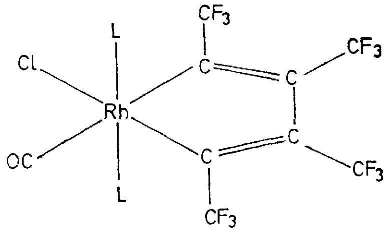
Reaction of $RhCl(CO)\{As(C_6H_{11})_3\}_2$ *with Hexafluorobut-2-yne*.—This reaction was carried out as described for $RhCl(CO)(AsMe_3)_2$ with the tricyclohexylarsine complex (0·32 g, 0·4 mmol). After recovery of unchanged acetylene the contents of the tube were filtered under nitrogen and the yellow solid remaining on the frit was washed with benzene (2 ml). The solid was extracted with hot dichloromethane and crystallized by the addition of diethyl ether and cooling at 0 °C to give yellow microcrystals of $RhCl\{As(C_6H_{11})_3\}_2C_4(CF_3)_4$. The benzene washing was combined with the original filtrate and was evaporated to dryness. The residue was sublimed at 100° under high vacuum to give hexakis(trifluoromethyl)benzene (0·23 g, 0·47 mmol). The remaining brown solid was taken up in a minimum volume of dichloromethane and chromatographed on silica gel (1 × 60 cm column). Elution with hexane produced a small yellow band which was shown from its infrared spectrum to consist of a mixture of $C_6(CF_3)_6$ and an unidentified fluorocarbon complex. Continued elution with benzene removed a yellow band, shown by infrared spectral analysis to be unchanged $RhCl(CO)\{As(C_6H_{11})_3\}_2$, followed by a small green band. The latter did not contain sufficient material for satisfactory characterization. There remained on the column a considerable amount of a dark brown oily substance which was not further studied.

Chlorobis(trifluoropropynyl)carbonylbis(trimethylarsine)-rhodium(III), $RhCl(CO)(AsMe_3)_2(C{\equiv}CCF_3)_2$.—This compound was prepared from $RhCl(CO)(AsMe_3)_2$ (0·2 g, 0·4 mmol) and an excess of 3,3,3-trifluoropropyne in benzene in a sealed tube following the procedure detailed above for the hexafluorobut-2-yne reactions except that the reaction time was only 5 h and the reaction temperature was 75 °C. No acetylene could be recovered. The reddish solution was filtered from suspended solid which evidently is polymerized acetylene and evaporated to give a red oil. The oil was taken up in diethyl ether (2 ml) filtered to remove residual polymer, and light petroleum (15 ml) added to precipitate a reddish brown solid. Attempts at recrystallization produced only oils so the solvent was removed under reduced pressure and the oil was triturated with light petroleum to give a reddish brown powder (0·07 g, 30%).

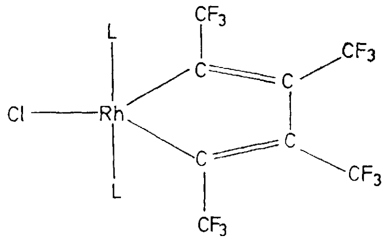
*Chlorobis(trifluoropropynyl)carbonylbis[dimethyl(*p*-methoxyphenyl)arsine]rhodium*(III), $RhCl(CO)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2(C{\equiv}CCF_3)_2$.—This compound, prepared analogously to the trimethylarsine complex from 0·16 g (0·36 mmol) of $Rh(CO)Cl[AsMe_2(p\text{-}MeOC_6H_4)]_2$, was obtained as a brick-red powder by precipitation with light petroleum from diethyl ether (0·04 g, 19%). Again most of the acetylene was polymerized.

Chlorobis(trifluoropropynyl)tris(triphenylstibine)rhodium(III), $RhCl(SbPh_3)_3(C{\equiv}CCF_3)_2$.—This compound, prepared from $RhCl(SbPh_3)_3$ (0·11 g, 0·09 mmol) in the same manner as the previous complex, was obtained as a red-brown powder by precipitation with light petroleum from diethyl ether (0·02 g, 17%).

RESULTS AND DISCUSSION



(1)



(2)

The reaction of an excess of hexafluorobut-2-yne with the complexes $RhCl(CO)L_2$ [L = $AsMe_3$, $AsMe_2Ph$, or $AsMe_2(p\text{-}MeOC_6H_4)$] in benzene at 100 °C for times between 6 and 18 h produces as the only significant product the six-co-ordinate rhodacyclopentadiene complexes (I)—(III) (Table). These compounds are assigned structure (1) on the basis of analytical and spectral data (Table) and by analogy with $RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4$ whose structure has been determined by *X*-ray crystallography.[8] Thus the infrared spectra of compounds

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[8] J. T. Mague, *J. Amer. Chem. Soc.*, 1971, **93**, 3550.

(I)—(III) all exhibit, in addition to ligand absorptions, a sharp band at *ca.* 2100 cm^{-1} which can be assigned to the carbon–oxygen stretching vibration of a terminal carbonyl group, two sharp bands of medium intensity in the 1500—1600 cm^{-1} region, and a complex set of intense bands attributable to carbon–fluorine stretching vibrations in the 1100—1300 cm^{-1} region. The two bands in the 1500—1600 cm^{-1} region are characteristic of the tetrakis(trifluoromethyl)rhodacyclopentadiene moiety and are most likely associated with carbon–carbon stretching vibrations within the five-membered ring. Because of π-delocalization over the four-carbon portion of the ring,[9] which is particularly evident in the case of the five-co-ordinate rhodacyclopentadiene complexes discussed below, it is unlikely that these vibrations can be identified with isolated C=C stretches however, it can be noted that $\nu_{C=C}$ occurs at 1610 cm^{-1} in $RhCl_2C(CF_3)=C(CF_3)H(PPh_3)_2$.[10]

The ^{19}F n.m.r. spectra of compounds (I)—(III) show three complex resonances at *ca.* —7·0, —11·0, and —13·0 p.p.m. whose intensities are in the ratio 2 : 1 : 1. The two low-field resonances can be assigned to the two trifluoromethyl groups nearest the metal which have been rendered non-equivalent by the presence of two dissimilar equatorial substituents. The high-field resonance is assigned to the trifluoromethyl groups remote from the metal. Evidently these are sufficiently far away so as to remain essentially equivalent although the resonance is somewhat broader than in the corresponding five-co-ordinate complexes indicating that they probably have slightly different chemical shifts.

The structural studies of $RhCl(SbPh_3)_2C_4(CF_3)_4$ [11] and $RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4$ [8] show that there are close contacts between fluorine atoms of adjacent trifluoromethyl groups around the periphery of the ring resulting in a ' cogwheel ' arrangement which very likely prevents free rotation of these groups. Thus the broad complex appearance of the ^{19}F resonances is not surprising.

One further point of interest concerning (II) and (III) is their proton spectra. In each case two resonances occur which can be assigned to As–CH_3 indicating two sets of non-equivalent methyl groups bound to arsenic. We suggest that this is a result of a weak interaction between the phenyl groups of the arsines and the rhodacyclopentadiene ring which holds them on either side of the latter thus placing the two methyl groups in each ligand in slightly different environments. Support for this comes from the structural study of $RhCl(SbPh_3)_2C_4(CF_3)_4$ [11] in which one phenyl group of each ligand is directly over the ring. Moreover, the line joining the *ortho*-positions of each phenyl group is nearly parallel to the plane of the rhodacyclopentadiene ring.

The reaction of the complexes $RhCl(CO)L_2$ [L = $AsMePh_2$, $AsPh_3$, $As(p\text{-}FC_6H_4)_3$, or $As(p\text{-}MeC_6H_4)_3$] with an excess of hexafluorobut-2-yne at 100 °C requires longer times (15—18 h) than for the previous systems to produce an appreciable amount of the corresponding rhodacyclopentadienes. Although the rhodacyclopentadienes are still the major products of these reactions, the yields tend to be lower because of the occurrence of side reactions. The infrared spectra of compounds (V)—(VIII) are substantially the same as those of (I)—(III) with the exception that there is no absorption near 2100 cm^{-1} indicating that these complexes do not contain a carbonyl group. The ^{19}F n.m.r. spectra of (V)—(VIII) consist of two complex resonances of equal intensity downfield from α,α,α-trifluorotoluene (Table). On the basis of these and the analytical data, these complexes are assigned structure (2). Confirmation of this assignment comes from the virtual identity of the observed infrared and ^{19}F n.m.r. spectra with those reported for $RhCl(SbPh_3)_2C_4(CF_3)_4$ [1] which has been shown by an *X*-ray crystallographic structure analysis to have structure (2).[11] In that study, the molecule was found to have approximate C_s symmetry if one neglects the differing rotational orientations of the trifluoromethyl groups. Thus the trifluoromethyl groups adjacent to the metal form an equivalent pair as do those remote from the metal in agreement with the observed n.m.r. spectrum. Complex (VI) is identical with that prepared previously from $RhCl(AsPh_3)_3$.[1] Although the differences are small, it appears that the ' ring ' bands in the 1500—1600 cm^{-1} region occur at slightly lower energies in the six-co-ordinate complexes than in the five-co-ordinate species. This suggests some withdrawal of electron density from the ring by the strong π-acid carbon monoxide in the former. One further feature of the infrared spectra of the five- and six-co-ordinate rhodacyclopentadienes which appears to have some characterizational utility is the absorption in the 640—660 cm^{-1} region. For complexes (I)—(III), a single sharp band of medium intensity is observed while in the five-co-ordinate complexes (V)—(VIII) two closely spaced bands occur. We have not been able to unequivocally determine what vibration is responsible for these absorptions but it may be a CF_3 deformation mode since in an analysis of the vibrational spectrum of hexafluorobut-2-yne the strong band at 639 cm^{-1} was assigned to this vibration.[12] In any event, it appears that one can distinguish between six-co-ordinate tetrakis(trifluoromethyl)rhodacyclopentadienes in which two dissimilar equatorial substituents are present and the corresponding five-co-ordinate species on the basis of the number of bands in this region.

The ability of the rhodacyclopentadiene complexes to bind carbon monoxide correlates with the π acid character of the arsine ligands. Thus it is only with the most basic ligands that carbonyl derivatives can be isolated presumably because only these provide sufficient electron density on the metal to permit adequate π back-bonding to the carbonyl group. The methyldiphenylarsine complex exhibits intermediate behaviour in that the initial

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[10] R. D. W. Kemmitt, B. Y. Kimura, and G. W. Littlecott, *J.C.S. Dalton*, 1973, 636.

[11] J. T. Mague, *Inorg. Chem.*, 1970, **9**, 1610.

[12] C. V. Berney, L. R. Cousins, and F. A. Miller, *Spectrochim. Acta*, 1963, **19**, 2019.

TABLE

Analytical and n.m.r.[a,b] and i.r.[c] data for complexes

No.	Complex	Found (%)				Calc. (%)				M.p.‡ (t/°C)	^{19}F	Solvent	^{1}H	Solvent	Assign-ment	
		C	H	Cl	F	C	H	Cl	F							
(I)	$RhCl(CO)(AsMe_3)_2C_4(CF_3)_4$	24·5	2·6	4·45	31·15	24·66	2·48	4·85	31·21	196 (d)	−7·3(m), −10·4(m), −12·0(m)	CH_2Cl_2	8·5(s)	$CDCl_3$	$-CH_3$	2104vs(ν_{CO}), 1577w, 1540m, 1328s, 1232sh, 1225sh, 1218vs, 1194vs, 1165sh, 1153vs, 1135s, 1114s, 1086m, 982w, 649m
(II)	$RhCl(CO)(AsMe_2Ph)_2C_4(CF_3)_4$	34·75	2·55	4·35	27·2	35·17	2·60	4·16	26·70	186 (d)	−6·9(m), −11·9(m), −13·2(m)	CH_2Cl_2	8·2(s), 8·1(s) 2·5(m)	$CDCl_3$	$-CH_3$ $-C_6H_5$	2112vs(ν_{CO}), 1580w, 1534m, 1335s, 1277w, 1261m, 1223vs, 1200vs, 1193sh, 1169vs, 1162vs, 1143vs, 1118vs, 1100s, 649m
(III)	$RhCl(CO)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$	36·3	3·1	3·7	26·15	35·40	2·89	3·88	24·95	141 (d)	−7·0(m), −11·4(m), −14·1(m)	CH_2Cl_2	8·3(s), 8·1(s) 6·1(s) 2·1 (Centre of $A_2'B_2'$ pattern)	$CDCl_3$	$-CH_3$ $-OCH_3$ $-C_6H_4$	2096vs(ν_{CO}), 1574w, 1527w, 1330m, 1221vs, 1199vs, 1185vs, 1160vs, 1148sh, 1112s, 972m, 902w, 645m
IV)	$RhCl(CO)(AsMePh_2)_2C_4(CF_3)_4$	43·15	2·8	3·55	22·1	42·94	2·68	3·62	23·29	219 (d)	−6·5(m), −12·2(m), −14·4(m)	C_6D_6	8·2(s) 2·3(m), 2·6(m), 3·0(m)	C_6D_6	$-CH_3$ $-C_5H_5$	2117vs(ν_{CO}), 1585m, 1537m, 1332s, 1220vs, 1200vs, 1175sh, 1156vs, 1122s, 1114s, 980m, 648m
(V)	$RhCl(AsMePh_2)_2C_4(CF_3)_4$	43·05	2·75	4·3	21·6	42·95	2·76	3·73	23·98	222	−4·5(m), −11·2(m)	CH_2Cl_2	8·0(s) 2·6(m)	$CDCl_3$	$-CH_3$ $-C_6H_5$	1582m, 1539m, 1355m, 1222vs, 1206vs, 1186sh, 1166vs, 1155vs, 1145vs, 1130s, 1121s, 1105m, 980w, 649m, 639m
(VI)	$RhCl(AsPh_3)_2C_4(CF_3)_4$	49·55	2·8	3·75	20·85	49·16	2·81	3·30	21·21	195	−5·1(m), −12·0(m)	CH_2Cl_2	2·4(m)	$CDCl_3$	$-C_6H_5$	1583m, 1541m, 1351m, 1220vs, 1204s, 1170vs, 1160sh, 1129m, 652m, 642m
(VII)	$RhCl\{As(p\text{-}FC_6H_4)_3\}_2C_4(CF_3)_4$	45·85	1·95	3·7	31·1	45·45	2·08	3·05	29·41	265 (d)	−4·8(m), −11·6(m)	CH_2Cl_2	2·7(m)	$CDCl_3$	$-C_6H_4F$	1539m, 1355m, 1240vs, 1220vs, 1201vs, 1162vs, 1125s, 648m, 639m
(VIII)	$RhCl\{As(p\text{-}MeC_6H_4)_3\}_2C_4(CF_3)_4$	51·85	3·45	3·55	18·95	51·81	3·66	3·06	19·67	270 (d)	−5·0(m), −11·8(m)	C_6H_6	7·7(s) 2·7 (Centre of $A_2'B_2'$ pattern)	$CDCl_3$	$-CH_3$ $-C_6H_4$	1585w, 1540m, 1355m, 1222vs, 1200vs, 1193sh, 1168s, 1152vs, 1129s, 1111m, 652m, 645m
(IX)	$RhCl(AsMe_2Ph)_2C_4(CF_3)_4$	35·15	2·75	4·65	25·25	34·87	2·69	4·29	27·58	209	−5·4(m), −10·8(m)	$CHCl_3$	8·3(s) 2·6(m)	$CDCl_3$	$-CH_3$ $-C_6H_5$	1580m, 1538m, 1356s, 1339sh, 1273m, 1260m, 1240sh, 1221vs, 1209vs, 1190s, 1165vs, 1145vs, 1138sh, 1121s, 1104sh, 1089m, 985w, 649m, 639m
(X)	$RhCl\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$	35·6	2·8	4·3	26·65	35·21	2·96	4·00	25·71	135	−5·9(m), −11·7(m)	CH_2Cl_2	8·4(s) 6·3(s) 3·0 (Centre of $A_2'B_2'$ pattern)	$CDCl_3$	$-CH_3$ $-OCH_3$ $-C_6H_4$	1575m, 1537m, 1352m, 1340m, 1219vs, 1194vs, 1182sh, 1162sh, 1153s, 1145s, 1112s, 647sh, 640m
(XI)	$RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4$	23·4	2·45	4·3	30·35	23·33	2·80	4·92	31·64	183 (d)	−5·9(m), −10·1(m)	CH_2Cl_2	8·8(s) 8·3(s)	$CDCl_3$	$-CH_3$ $-OH_2$	3534w(ν_{OH}), 3333m(ν_{OH}) 1590m(δ_{HOH}), 1570m, 1529m, 1342s, 1261vs, 1221vs, 1192vs, 1163vs, 1152sh, 1131vs, 1112vs, 646m

TABLE (*Continued*)

No.	Complex	Found (%)				Calc. (%)				M.p.‡ (t/°C)	^{19}F	Solvent	^{1}H	Solvent	Assign-ment	
		C	H	Cl	F	C	H	Cl	F							
(XII)	$(AsPh_3)_2ClRhCOC(CF_3)=C(CF_3)CO,2C_6H_6$	58·0	3·75	3·25	9·2	58·10	3·86	3·25	10·40	192 (d)	−3·2(s)	C_6D_6	2·7(s) 2·4(m), 2·6(m)	$CDCl_3$	C_6H_6 $-C_6H_5$	1698sh, 1667vs(ν_{CO}), 1260vs, 1248s, 1200s, 1168vs, 815m
(XIII)	$\{As(p\text{-}MeC_6H_4)_3\}_2ClRhCOC(CF_3)=C(CF_3)CO,\text{-}2{\cdot}5C_6H_6$	59·5	4·7	2·3	8·45	60·61	4·61	2·84	9·13	192 (d)	−3·1(s)	C_6H_6	7·7(s) 2·7(s) 2·7 (Centre of $A_2'B_2'$ pattern)	$CDCl_3$	$-CH_3$ C_6H_6 $-C_6H_4$	1694w, 1663vs(ν_{CO}), 1655sh, 1255sh, 1245vs, 1190vs, 1156vs, 688s, 680sh
(XIV)	$\{As(p\text{-}FC_6H_4)_3\}_2ClRhCOC(CF_3)=C(CF_3)CO,\text{-}1{\cdot}5C_6H_6$	50·2	2·45	2·9	17·25	51·30	2·79	2·97	19·09	182 (d)	−2·9(s)	C_6H_6	2·7(m) 2·7(s)	$CDCl_3$	$-C_6H_4F$ C_6H_6	1692w, 1662vs(ν_{CO}), 1653sh, 1400m, 1255sh, 1243vs, 1189vs, 1162vs, 690sh, 687s
(XV)	$\{As(C_6H_{11})_3\}_2ClRhCOC(CF_3)=C(CF_3)CO,\text{-}0{\cdot}5C_6H_6$	50·7	6·95	2·95	9·7	51·74	6·67	3·40	10·91	190 (d)	−3·3(s)	$CDCl_3$	2·7(s) 7·3—9·1(m)	$CDCl_3$	C_6H_6 $-C_6H_{11}$	1702sh, 1697m, 1680m, 1656sh, 1652s, 1292m, 1262m, 1247vs, 1240vs, 1190vs, 1150vs, 683s
(XVI)	$Rh(NO_3)(AsMe_3)_2C_4(CF_3)_4$*	23·65	2·2		30·35	23·06	2·49		31·27	256 (d)	−5·6(m), −9·6(m)	CH_2Cl_2	8·7(s)	$CDCl_3$	$-CH_3$	1583m, 1536sh, 1516vs (1520, CH_2Cl_2), 1505vs (1505, CH_2Cl_2), 1340s 1286m, 1272m, 1242vs, 1220vs, 1200vs, 1171vs, 1150vs, 1142sh, 1122vs, 1004m (1007, CH_2Cl_2), 800w (803, CH_2Cl_2), 651m, 644m
(XVII)	$Rh(NO_3)(AsMe_2Ph)_2C_4(CF_3)_4$†	33·7	2·8		25·0	33·80	2·50		26·80	240	−5·3(m), −10·5(m)	C_6H_6	8·4(s) 2·8(m)	$CDCl_3$	$-CH_3$ $-C_6H_5$	1585m, 1536m, 1518s, 1505vs, 1344s, 1270s, 1254vs, 1221vs, 1208vs, 1200sh, 1192s, 1170vs, 1163sh, 1159s, 1146vs, 1137sh, 1123s, 1013m, 659m, 649m
(XVIII)	$RhCl\{As(C_6H_{11})_3\}_2C_4(CF_3)_4$										−6·2(m), −13·9(m)	$CDCl_3$	7·3—9·1(m)	$CDCl_3$	$-C_6H_{11}$	1585w, 1537m, 1348m, 1219vs, 1199vs, 1170sh, 1155vs, 1146sh, 650sh, 641m
(XIX)	$RhCl(CO)(AsMe_3)_2(C{\equiv}CCF_3)_2$	26·65	3·45	6·7	21·45	26·35	3·06	5·98	19·23		−16·6(s)	CH_2Cl_2	8·4(s) (broad)	$CDCl_3$	$-CH_3$	2138m($\nu_{C\equiv C}$), 2080s($\nu_{C\equiv O}$) 1295sh, 1260sh, 1249vs, 1180sh, 1140sh, 1106vs
(XX)	$RhCl(CO)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2(C{\equiv}CCF_3)_2$	37·75	3·35	5·75	17·8	37·69	3·29	6·03	16·81		−16·0(s)	CH_2Cl_2	8·2(s), 8·0(s) 6·1(s) 2·7 (Centre of $A_2'B_2'$ pattern)	$CDCl_3$	$-CH_3$ $-OCH_3$ $-C_6H_4$	2128m($\nu_{C\equiv C}$), 2070s($\nu_{C\equiv O}$), 1250vs, 1230sh, 1115sh, 1101vs, 1095vs
(XXI)	$RhCl(SbPh_3)_3(C{\equiv}CCF_3)_2$	51·75	3·4	3·0	9·25	52·08	3·28	2·56	7·44		−17·0(s)	CH_2Cl_2	2·6(m)	$CDCl_3$	$-C_6H_5$	2124m($\nu_{C\equiv C}$), 1290m, 1265m, 1242vs, 1200sh, 1185m, 1143sh, 1100vs

* Nitrogen analysis: Found, 1·85; Calc., 1·9%. † Nitrogen analysis: Found, 1·6; Calc., 1·6%. ‡ d = Decomposed.

[a] Shifts in p.p.m. relative to α,α,α-trifluorotoluene, ^{1}H in τ. [b] m: Multiplet, s: singlet. [c] w = Weak; m = medium; s = strong; vs = very strong; sh = shoulder.

reaction product appears to contain a mixture of both (IV) and (V). Upon work-up, however, only compound (V) is recovered. The carbonyl derivative (IV) can be readily prepared, however, by stirring a solution of (V) in benzene under 25 p.s.i. of carbon monoxide. The complex is reasonably stable in the solid state but readily reverts to (V) in solution if an excess of CO is not present. Inspection of the data in the Table confirm that (IV) is analogous to the six-co-ordinate complexes discussed above. Attempts to produce the carbonyl derivative of (VI) failed to yield an isolable product although a colour change from bright to pale yellow occurred on pressurizing the solution with CO which suggests that the desired species was present in solution. However, on venting the CO, the solution reverted to the bright yellow colour and the only (VI) could be isolated.

The carbonyl complexes (I)—(III) can be readily decarbonylated by refluxing in dry benzene under a nitrogen atmosphere. The colour of the solution soon changes from pale yellow to bright yellow and from (II) and (III) can be isolated (IX) and (X) respectively. The infrared spectra of the products no longer show a carbonyl absorption and the single band in the 640—660 cm^{-1} region has been replaced by two closely spaced bands. The ^{19}F n.m.r. spectra consist of two complex resonances of equal intensity thus confirming the identity of these complexes as five-co-ordinate rhodacyclopentadiene derivatives. The ^{1}H n.m.r. spectra of (IX) and (X) differ from those of (II) and (III) in that only one As–CH_3 resonance is observed. This can be interpreted as indicating either an increase in effective symmetry of the complexes from C_1 to C_s or free rotation about the rhodium–arsenic bond. We are inclined to favour the former interpretation since, if anything, the proposed interaction of the phenyl groups with the ring should be enhanced in the five-co-ordinate species. Complexes (II) and (III) can be readily regenerated by passing carbon monoxide through benzene solutions of (IX) and (X).

The behaviour of (I) under the above conditions is somewhat different. Although the final solution is bright yellow, subsequent work-up yields a very pale yellow material which has been identified as the six-co-ordinate aquo-derivative (XI). The infrared spectrum shows bands at 3534, 3333, and 1590 cm^{-1} which can be assigned to the O–H stretching and H–O–H bending vibrations of co-ordinated water. Only one band is observed in the low-energy region at 646 cm^{-1} indicating that the complex is six-co-ordinate. This has been verified by an *X*-ray crystal structure analysis.[8] The solution behaviour of (XI) seems to be rather sensitive to the nature of the solvent. In acetone, the ^{19}F n.m.r. spectrum consists of two complex multiplets of equal intensity which is analogous to those of the five-co-ordinate rhodacyclopentadienes. Addition of increasing amounts of water to the solution up to the point of precipitation of the complex produces no noticeable change in the spectrum. If the complex is dissolved in [^{2}H$_6$]acetone the ^{1}H spectrum consists of singlet resonances at τ 6·3 and 8·2 which can be assigned to free water and the trimethylarsine ligands respectively. Addition of increasing amounts of water to this solution causes the water signal to shift upfield slightly (*ca.* 0·2 p.p.m.) while remaining sharp. Because of the small magnitude of the shift it is not possible to say whether this is indicative of interaction of the water with the metal or is simply a solvent effect. The foregoing observations are consistent with the presence of the equilibrium [equation (1)] with the position of equilibrium lying far to the right.

$$\mathrm{RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4} \rightleftharpoons \mathrm{RhCl(AsMe_3)_2C_4(CF_3)_4 + H_2O} \quad (1)$$

On the other hand, if the ^{1}H n.m.r. spectrum is taken in deuteriochloroform or [^{2}H$_6$]benzene solution one observes in addition to the methyl resonance of the arsine ligand a singlet at τ 8·0—8·3 which disappears upon addition of D_2O while a new resonance due to free water appears at τ 5·2. This indicates that the original resonance is due to co-ordinated water. Addition of water to these solutions causes a slight downfield shift (*ca.* 0·2 p.p.m.) of the high-field resonance but again it is not possible to say whether this shift is indicative of exchange between free and bound water or is simply the result of solvent effects. In these latter spectra, the resonance of free water is also present. While the disappearance of the high-field resonance on addition of D_2O could be taken as evidence of exchange between free and bound water, it is also quite possible that H–D exchange on the bound water molecule has occurred. These experiments do not therefore allow one to conclude whether or not exchange of water is occurring. At this point it is tempting to suggest that equation (1) is established in all three systems with the position of the equilibrium being far to the right in the polar solvent acetone and far to the left in the less-polar media. Unfortunately this is not consistent with the observation that the ^{19}F n.m.r. spectrum of (XI) in deuteriochloroform also shows only two complex resonances of equal intensity unless one assumes that in solution both chloride and water have the same effect on the chemical shifts of the trifluoromethyl groups adjacent to the metal. This last suggestion may not be too unreasonable since the structural study shows both the Rh–Cl and Rh–O distances to be quite long [8] and our molecular orbital calculations indicate the binding of chloride and water to rhodium to be weak.[9] Despite this, the mull spectrum of (XI) shows only a single band at 646 cm^{-1} indicative of a six-co-ordinate species. We are thus left with no definite conclusion as to the nature of (XI) in solution.

While we have not been successful in isolating $\mathrm{RhCl(AsMe_3)_2C_4(CF_3)_4}$ in the pure state, (XI) when heated at 100° *in vacuo* changes from pale yellow to dark yellow which presumably indicates the presence of the desired material. On exposure to air, the colour of the solid rapidly lightens again and the infrared spectrum of the resulting material shows it to be (XI) thus demonstrating the avidity of $\mathrm{RhCl(AsMe_3)_2C_4(CF_3)_4}$ for water.

In the presence of stronger ligands, however, the water is readily displaced. Thus treatment of (XI) with carbon monoxide in benzene under ambient conditions rapidly regenerates (I).

In one experiment, (III) was decarbonylated when refluxed in benzene with no precautions being taken to exclude moisture. Work-up yielded a pale yellow material which from its infrared spectrum was shown to be the corresponding aquo-complex $RhCl(H_2O)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$ ($\nu_{O-H} = 3528, 3263$, $\delta_{HOH} = 1605$sh cm^{-1}). The ^1H n.m.r. spectrum of this complex in deuteriochloroform showed in addition to the expected ligand absorptions a singlet at τ 8·3 which we assign to the water protons. As with (XI) this result suggests that the water is bound in this solvent. When heated at 100° *in vacuo*, the solid darkens and the ^1H n.m.r. spectrum of the resulting material is identical with that observed before heating with the exception that the τ 8·3 resonance is absent. The infrared spectrum of this material shows the absence of water and is identical to that of (X). By contrast with the presumed $RhCl(AsMe_3)_2C_4(CF_3)_4$, the solid material produced by dehydrating $RhCl(H_2O)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4$ does not reaquate when set aside in air.

Further confirmation of relatively weak binding of chloride and water ligands in (XI) which was indicated by the structural[8] and computational[9] studies comes from the observation that (XI) reacts rapidly with silver nitrate in benzene–ethanol to produce the nitrato-complex (XVI). Silver chloride is produced quantitatively and in addition to bands due to the parent rhodacyclopentadiene, the infrared spectrum of (XVI) shows bands attributable to co-ordinated nitrate (Table). Thus, although the observance of the symmetric N–O stretch (ν_2) at 1004 cm^{-1} which is only infrared active in C_{2v} symmetry and the large splitting of the E' mode indicates co-ordination, as has been pointed out previously[13] this alone cannot unequivocally distinguish between uni- and bi-dentate co-ordination. That the nitrate is probably bidentate in (XVI) is suggested by the failure of the complex to add carbon monoxide under mild conditions which shows that there is no vacant or readily accessible co-ordination position. A further indication of bidentate co-ordination of the nitrate is the splitting of the A_1 mode (ν_1 in C_{2v} symmetry). The persistence of this splitting in solution shows that it is not a solid-state effect and similar splittings have been noted in some cobalt complexes containing bidentate nitrate.[13,14] This cannot be taken as proof of the mode of co-ordination, however, since this splitting was also observed in $[Pd(bipy)(NO_3)_2]$ which presumably contains unidentate nitrate.[15] Compound (XVI) can also be produced by the reaction of (I) with silver nitrate in benzene–ethanol. The reaction is rapid which further confirms the lability of the carbonyl group in (I) and also indicates a considerable lability of the chloride in this complex.

An analogous dimethylphenylarsine complex (XVII) can be obtained from (II) and ethanolic silver nitrate. The infrared spectrum (Table) again shows bands suggestive of a bidentate nitrate group with a similar splitting of ν_1. The corresponding triphenylstibine complex $Rh(NO_3)(SbPh_3)_2C_4(CF_3)_4$ (identified by its infrared spectrum) can be prepared in a similar manner from the five-co-ordinate rhodacyclopentadiene derivative, $RhCl(SbPh_3)_2C_4(CF_3)_4$. The complex shows nitrate absorptions at 1510vs, 1503s, 1260s, 1252vs, and 1002m cm^{-1}. In contrast to the previously discussed reactions, precipitation of silver chloride occurred much more slowly and reaction times of several hours were required for completion. This is in accord with our computational results which indicate a significantly greater degree of covalency in the rhodium–chlorine bond in five-co-ordinate rhodacyclopentadienes.[9]

In the reactions of the triarylarsine complexes with hexafluorobut-2-yne one of the minor products produced was characterized by strong absorption in the 1650—1700 cm^{-1} region. This could be separated from the rhodacyclopentadiene complex by chromatography on silica gel and appeared on the column as a pinkish tan or brownish orange band which followed the greenish yellow band of the rhodacyclopentadiene. Because of the small amounts of these complexes which were obtainable in this manner and the tendency to form solvated crystals, characterization was difficult and was only finally accomplished by a full three-dimensional crystallographic structure determination of the material obtained from $RhCl(CO)(AsPh_3)_2$.[16] This proved to be the metallocyclic diketone $(AsPh_3)_2Cl\overline{RhCOC(CF_3)=C(CF_3)CO},2C_6H_6$, (XII). The molecule has crystallographically imposed C_2 symmetry and the ^{19}F n.m.r. spectrum (Table) confirms that this symmetry is effectively maintained in solution. The strong infrared absorption at 1667 cm^{-1} can be assigned to $\nu_{C=O}$ and is comparable to that previously found in $(PPh_3)_2Cl\overline{RhCOC(CH_3)=C(CH_3)CO}$[17] and $(CO)_4\overline{FeCOC(R)=C(R^1)CO}$.[18,19] With the identity of (XII) confirmed, it was then possible to attempt a rational synthesis of the complex which involves the reaction of $RhCl(CO)(AsPh_3)_2$ with an excess of hexafluorobut-2-yne at 100° in the presence of carbon monoxide for 1·5—2 h. In this manner, yields of (XII) were increased from 24% using the optimized conditions (2 h at 100°) with no carbon monoxide present to 46%. The complex evidently slowly decomposes at 100° in the absence of CO as the extended reaction times used to produce (VI) led to much smaller amounts of (XII). This was confirmed by the behaviour of solid (XII) when heated. At *ca.* 80°, the

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clear pinkish tan crystals became opaque presumably through loss of the solvent of crystallization. At 192° effervescence occurred and the solid became yellow. This yellow solid was shown to be $RhCl(CO)(AsPh_3)_2$ by infrared spectral and thin-layer chromatographic analysis. The decomposition of (XII) to hexafluorobut-2-yne and carbon monoxide was confirmed by heating the solid to 200° in a closed system and analysing the volatile products by infrared spectroscopy. The analogous complexes with tris-(*p*-tolyl)arsine, tris-(*p*-fluorophenyl)-arsine, and tricyclohexylarsine (XIII)—(XV) were prepared similarly from the corresponding rhodium(I) complexes. The infrared and n.m.r. spectra of these complexes are all consistent with the proposed formulations. The complexity of the infrared spectrum of (XV) in the carbonyl-stretching region was unexpected but is probably due to the carbonyl groups being rendered non-equivalent through steric interactions with the extremely bulky tricyclohexylarsine ligands. We also attempted to make the methyldiphenylarsine analogue of (XII) but this reaction appears to be much more complex than the others. Chromatography of the crude product afforded a small amount of (V), an orange crystalline material which we have not yet succeeded in identifying, and a tan-coloured material which appears to be a mixture of at least two further species. The ^{19}F n.m.r. spectrum of the tan solid shows several resonances including a singlet at −2·4 p.p.m. while the infrared spectrum shows a strong absorption around 1660 cm^{-1}. These data suggest the presence of $(AsMePh_2)_2Cl\overline{RhCOC(CF_3)=C(CF_3)C}O$ in the reaction products but we have not as yet been able to obtain it in a pure state.

In one series of experiments, the reaction of hexafluorobut-2-yne with $RhCl(CO)L_2$ ($L = AsMe_3$, $AsMe_2Ph$, $AsMePh_2$, or $AsPh_3$) was carried out at 25° for 4 h. Under these conditions when $L = AsMe_3$, (I) was still produced in relatively good yield and there were no significant additional products. In the other three reactions small amounts of (II), (IV), and (VI) respectively were detected in the crude reaction mixtures by infrared and ^{19}F n.m.r. analysis. The yields of these three rhodacyclopentadienes decreased in the order listed with a corresponding increase in the yields of other species. One of these additional products from the reaction where $L = AsPh_3$ was the metallocyclic diketone (XII) and the analogous species with $L = AsMePh_2$ and $AsMe_2Ph$ were also found in the other two reactions. A third product of the reaction when $L = AsPh_3$ could not be obtained pure because of its decomposition upon attempted chromatography. Fractional crystallization enabled its separation from all but a trace of (XII) and some unchanged $RhCl(CO)(AsPh_3)_2$ and it has been tentatively identified as $(AsPh_3)_2Cl\overline{RhCOC(CF_3)=C}CF_3$ on the basis of its infrared and ^{19}F n.m.r. spectra. These show a band of medium intensity at 1760 cm^{-1} assigned to $\nu_{C=O}$ and two resonances of equal intensity at +1·5 (quartet; $J_{F=F} = 7{\cdot}5$ Hz) and −2·5 (doublet of quartets; $J_{F-F} = 7{\cdot}5$, $J_{Rh-F} = 3{\cdot}8$ Hz) p.p.m. No evidence was found in the ^1H n.m.r. spectrum for other than aromatic protons thus indicating the absence of the $-C(CF_3)=C(CF_3)H$ moiety. The spectral data can be compared to $\nu_{C=O} = 1675$ cm^{-1} and ^{19}F resonances at +0·7 and −5·5 p.p.m. (both quartets; $J_{F-F} = 9{\cdot}0$ Hz) in the related ruthenium complex $\{P(OMe)_3\}_2(CO)_2\overline{RuCOC(CF_3)=C}CF_3$.[20]

Although we have been able to prepare $\{As(C_6H_{11})_3\}_2Cl\overline{RhCOC(CF_3)=C(CF_3)C}O$ (XV) without difficulty, the reaction of $RhCl(CO)\{As(C_6H_{11})_3\}_2$ with hexafluorobut-2-yne at 100° for 18 h produces a much more complex mixture of products than do most of the other systems investigated. Most notable is the relatively large amount of hexakis(trifluoromethyl)benzene obtained (1·2 mol/mol of Rh^I). While small amounts of the cyclotrimer of hexafluorobut-2-yne were observed to be formed during the production of (VI)—(VIII), $RhCl(CO)\{As(C_6H_{11})_3\}_3$ is clearly the best catalyst among the complexes studied for effecting this transformation. We are currently studying this aspect of these systems.

As noted in the Experimental section, the only other characterizable products of this reaction were some unchanged $RhCl(CO)\{As(C_6H_{11})_3\}_2$ and a small amount of a yellow solid which we have identified from its infrared and ^{19}F n.m.r. spectra as $RhCl\{As(C_6H_{11})_3\}_2C_4(CF_3)_4$ (XVIII) (Table). Thus one observes only two complex resonances in the ^{19}F n.m.r. spectrum while the infrared spectrum shows the two 'ring' bands at 1585 and 1537 cm^{-1} and two bands in the low-energy region at 650 and 641 cm^{-1}. The complex forms a weak adduct with acetonitrile which can be precipitated from acetonitrile solution as very pale yellow needles by addition of light petroleum. The infrared spectrum of the product shows a nitrile absorption at 2305 cm^{-1} which compares well with the value of 2304 cm^{-1} found in $Cs_2[RhCl_5(NCMe)]$[21] and only one band in the low-energy region at 649 cm^{-1}. Thus the complex appears to be six-co-ordinate in the solid state. In solution the complex is a bright yellow and the ^{19}F n.m.r. spectrum consists of only the two complex resonances of the parent material. The ^1H n.m.r. spectrum in deuteriochloroform shows in addition to ligand absorptions a single resonance at τ 8·00 which is assigned to free acetonitrile. We conclude that in solution the acetonitrile dissociates since the resonance of acetonitrile co-ordinated to Rh^{III} has previously been found to occur at *ca.* τ 7·4.[21] Further support for the weak co-ordination of acetonitrile comes from the observation that upon evaporating the solution to dryness under reduced pressure, (XVIII) is regenerated.

The very low yield of the rhodacyclopentadiene complex and the recovery of unchanged $RhCl(CO)\{As(C_6H_{11})_3\}_2$ serve to emphasize the unique nature of the tricyclohexylarsine system. This is presumably at least partially the result of the unusual steric properties of the tricyclohexylarsine ligand which would be expected to make it difficult for the hexafluorobut-2-yne molecule to

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get close enough to the metal to interact strongly. That this is the case is suggested by the results of a variable-temperature ^{19}F n.m.r. study of the reaction which shows no evidence for significant interaction of hexafluorobut-2-yne with $RhCl(CO)\{As(C_6H_{11})_3\}_2$ up to 50°. This is in marked contrast to studies on some of the systems with less bulky ligands which show evidence for distinct mono-acetylene adducts at temperatures below 0°.[22]

In an effort to more closely determine the stereochemical course of the build-up of the rhodacyclopentadiene ring we attempted the reaction of some of the Rh^I complexes with the unsymmetrical acetylene 3,3,3-trifluoropropyne. Unfortunately these did not appear to produce the desired products but rather what we believe to be the bis(acetylide) complexes (XIX)—(XXI). The elemental analyses and infrared spectra (Table) are consistent with the structures depicted in the Figure, however, the ^{19}F n.m.r. spectra indicated that the materials obtained contained some impurities. This is not surprising since the reaction products were difficult to purify. Thus, while the ^{19}F n.m.r. spectra listed in the Table compare reasonably well with those reported for a variety of trifluoropropynyl platinum complexes[23-25] they should be interpreted with caution. The reaction presumably follows the sequence depicted below by analogy with the

$$RhClL'L_2 + CF_3C{\equiv}CH \longrightarrow RhHCl(C{\equiv}CCF_3)L'L_2 \quad (2)$$

$$RhHCl(C{\equiv}CCF_3)L'L_2 + CF_3C{\equiv}CH \longrightarrow RhCl(C{\equiv}CCF_3)_2L'L_2 + H_2 \quad (3)$$

platinum systems reported previously.[23,24] However, because no rhodacyclopentadienes were obtained these reactions were not studied further.

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