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SOME TETRAPHENYLCYCLOBUTADIENE COMPLEXES OF RHODIUM

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Summary

$[RhCl(PF_3)_2]_2$ (II) reacts with diphenylacetylene to give the tetraphenylcyclobutadiene complex $[RhCl(C_4Ph_4)]_2$, which on treatment with thallium salts TlR (R = π-C_5H_5, acac, facac), afford good yields of $Rh(\pi\text{-}C_5H_5)(C_4Ph_4)$, $Rh(acac)(C_4Ph_4)$, and $Rh(facac)(C_4Ph_4)$ respectively. The reactions of II with other alkynes are discussed.

Introduction

In recent years a range of cyclobutadiene cobalt complexes have been obtained [1-7] using several different synthetic routes. On the other hand, very few cyclobutadiene complexes of rhodium are known and in contrast to the usefulness of $Co(\pi\text{-}C_5H_5)(CO)_2$ as a precursor, the analogous π-cyclopentadienylrhodium dicarbonyl compound does not afford any cyclobutadiene derivatives when reacted with acetylenes. Thus $Rh(\pi\text{-}C_5H_5)(CO)_2$ and hexafluorobutyne were originally reported to give equal amounts of complexes containing coordinated cyclopentadienone and hexakis(trifluoromethyl)benzene [8,9], while a recent more detailed study by Dickson and Kirsch [10] showed that several other products are also formed, the yields depending on the molar ratio of reactants, temperature, solvent and the reaction time.

Rausch et al. have studied the reaction between $Rh(\pi\text{-}C_5H_5)(CO)_2$ and various acetylenes, but again no cyclobutadiene complexes resulted among a variety of organometallic products [11].

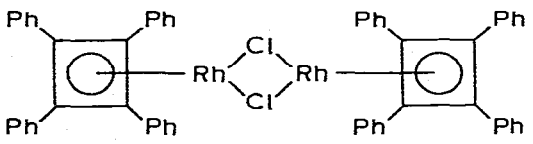
In view of the synthetic difficulties described above, which are often the result of carbonyl insertion reactions, it was felt that a route utilising non-carbonyl-containing rhodium complexes as precursors might be advantageous. The known similarity in the coordinating ability of carbon monoxide and trifluorophosphine [12-14] suggested that the recently synthesised complexes $Rh(\pi\text{-}C_5H_5)(PF_3)_2$, (I), [15,16] and $[RhCl(PF_3)_2]_2$ (II), [15,17,18] might be

suitable starting materials for the synthesis of cyclobutadiene—rhodium complexes*.

Results and discussion

The initial attempt using $Rh(\pi\text{-}C_5H_5)(PF_3)_2$ and diphenylacetylene did not prove successful, the starting materials being recovered unchanged after heating the mixture at 60°C in a sealed tube**.

The reaction of $[RhCl(PF_3)_2]_2$ with diphenylacetylene on the other hand, gave the desired di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) complex (III), which formed as red crystals soluble in aromatic and chlorinated hydrocarbons, but almost completely insoluble in alkanes. The product is formulated as a dimer since it undergoes typical bridge cleavage reactions described below (see Scheme 1) and it is presumably structurally related to the related complexes



(III)

$[MX_2(\pi\text{-}C_4Ph_4)]_2$ (M = Ni, X = Br; M = Pd, X = Cl) [20]. No parent ion was observed in the mass spectrum of III and the most intense peak at m/e = 534 is assigned to hexaphenylbenzene. Attempts to expand the cyclobutadiene ring by heating III with excess diphenyl acetylene proved unsuccessful.

Attempted extension of this cyclobutadiene synthesis to other alkynes of the type RC≡CR′ (R = R′ = CF_3, Me, CO_2Me; R = Ph, R′ = Me_3Si; R = Ph, R′ = H; R = Ph, R′ = Me) did not prove feasible, e.g., II reacted with but-2-yne; PhC≡CMe and $MeO_2CC{\equiv}CCO_2Me$ forming only substituted benzene derivatives. In the case of PhC≡CMe the only isomer obtained was 1,2,4-trimethyl-3,5,6-triphenylbenzene. In these reactions II appears to act mainly as a catalyst for the acetylene trimerisation process. Complete decomposition of starting materials occurred when II reacted with PhC≡CH or $PhC{\equiv}CSiMe_3$.

Hexafluorobutyne reacted with II to give two products. The colourless crystalline product was identified as hexakis(trifluoromethyl)benzene and the other compound, which was a red solid melting at 220°C, could not be satisfactorily recrystallised, but elemental analysis suggested its formulation as $RhCl[C_4(CF_3)_4](PF_3)$ and the IR spectrum showed bands assigned to both C—F and P—F stretching vibrations. The product is tentatively assigned structure IV by analogy with the known structure of a related cobalt complex [19].

A number of other tetraphenylcyclobutadienerhodium derivatives can be obtained from III by bridge cleavage reactions (see Scheme 1). Thus III readily

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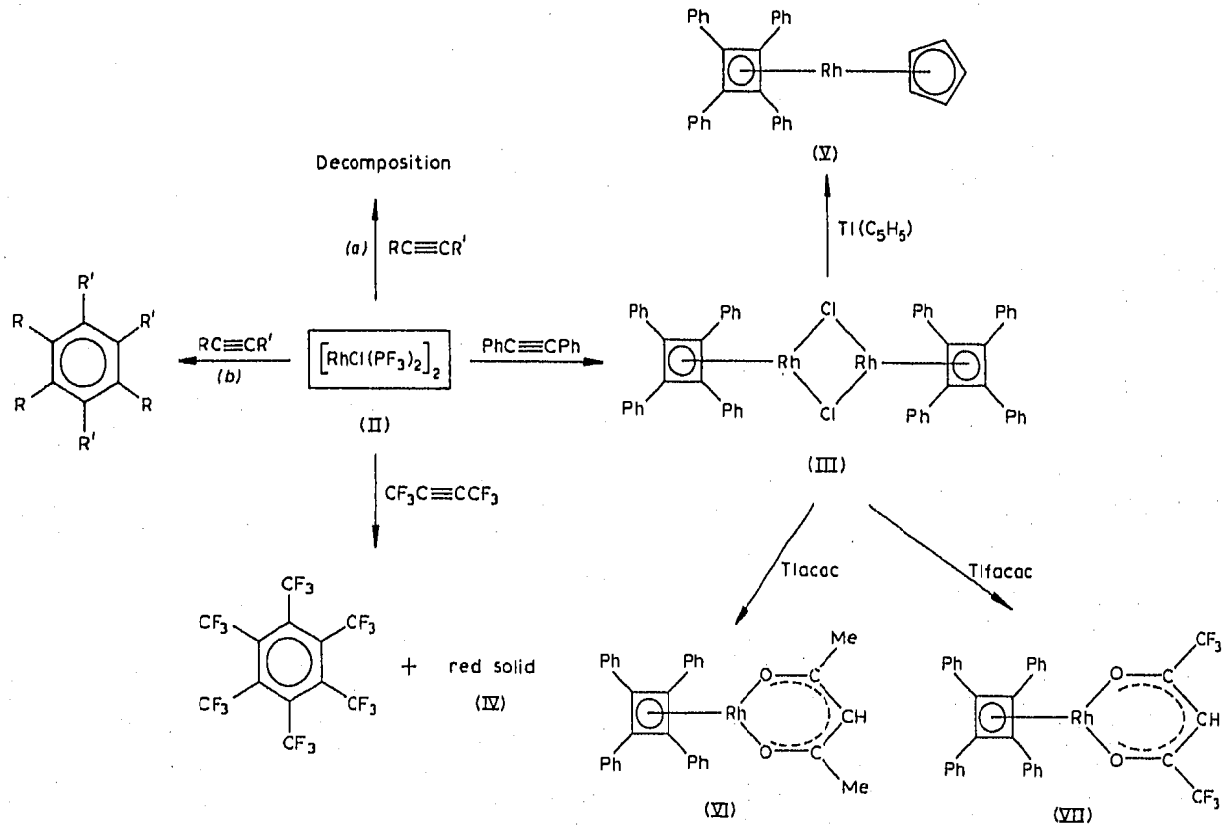
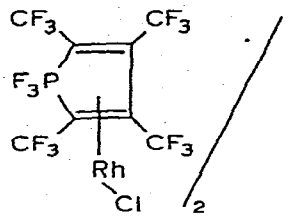
* A preliminary report of part of this work has appeared [26].

** Very recently Sharp et al. [19] found that $Co(\pi\text{-}C_5H_5)(PF_3)_2$ and hexafluorobutyne give a novel heterocyclic cobalt complex in which the PF_3 becomes a member of the ring, but the rhodium analogue does not react.

SCHEME 1. REACTION OF $[RhCl(PF_3)_2]_2$ WITH ALKYNES



[acac = $CH_3COCHCOCH_3$; tacac = $CF_3COCHCOCF_3$] [(a) R = Ph, R' = H, $SiMe_3$; (b) R = R' = CH_3, CO_2Me, R = Ph, R' = CH_3]

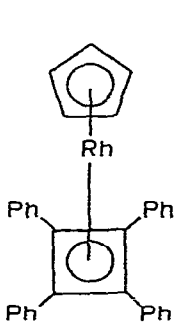


(IV)

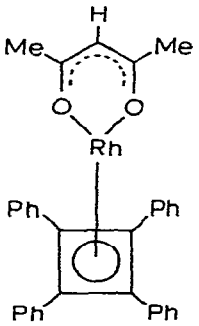
reacted with cyclopentadienylthallium to yield the 'sandwich' compound V, π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I), in 80% yield as cubic yellow air stable crystals. The complex was identified by elemental analysis and its ^{1}H NMR spectrum, which showed the expected multiplet pattern for the phenyl resonances (intensity 20) and a 1/1 doublet (intensity 5) for the cyclopentadienyl protons arising from spin coupling to the ^{103}Rh nucleus (I = ½, 100% abundance) [J(Rh—H) = 1 Hz]. The mass spectrum of V exhibits a parent ion at m/e = 524 and also a weaker peak at m/e = 534, corresponding to hexaphenylbenzene. Molecular ions corresponding to $[C_4Ph_4]^+$ and $[Rh(C_5H_5)(C_2Ph_2)]^+$ were also observed.

After completion of this work an alternative synthesis of V was reported [21], involving displacement of cyclooctadiene from $Rh(\pi\text{-}C_5H_5)(C_8H_{12})$ with an excess of diphenylacetylene under forcing conditions (sealed tube at 180°C). The complex was obtained in extremely low yield (0.3%), the main product being hexaphenylbenzene. The IR, NMR, and mass spectroscopic properties are in good agreement with those reported in the present work. The presence of the cyclobutadiene ring in V was unambiguously established by an X-ray diffraction study. The four-membered ring was found to be planar with mean C—C distance of 1.47 Å [21].

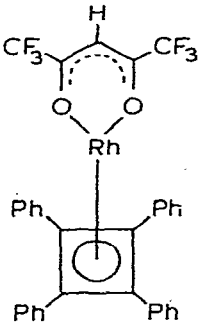
We have been unable to displace the cyclobutadiene ring from V with trifluorophosphine, even at 100°C in a sealed tube. This contrasts with the ease of displacement of ethylene from $Rh(\pi\text{-}C_5H_5)(C_2H_4)_2$ under mild conditions with a variety of fluorophosphines (L) to afford $Rh(\pi\text{-}C_5H_5)L_2$ complexes [16]. Similarly V did not react with CH_3I at 100°C even though the related complexes $M(\pi\text{-}C_5H_5)(CO)_2$ (M = Rh, Ir) and $Rh(\pi\text{-}C_5H_5)(PF_3)_2$ are known to undergo oxidative—addition reactions [22,23].



(V)



(VI)



(VII)

Complex II reacts with thallium acetylacetonate to give air stable red crystals of the acetylacetonato(π-tetraphenylcyclobutadiene)rhodium(I) complex (VI). The ^{1}H NMR spectrum of VI shows the expected three resonances at τ 2.36-2.76 (20H), τ 4.81 (1H), and τ 8.02 (6H) and the strongest peak in the mass spectrum occurs at m/e = 558, corresponding to the parent ion.

In a similar fashion, treatment of II with thallium hexafluoroacetylacetonate gave the red air stable complex hexafluoroacetylacetonato(π-tetraphenylcyclobutadiene)rhodium(I), (VII), which showed a strong parent ion peak at m/e = 666 in the mass spectrum and a singlet in the ^{19}F NMR spectrum.

Experimental

Reactions were carried out and complexes handled either under an atmosphere of dry nitrogen gas, or in vacuo unless otherwise stated. Volatile reactants and products were manipulated in a high vacuum system greased with Apiezon M. Solvents were dried and freshly distilled under dry nitrogen gas before use. IR spectra in the range 4000-400 cm^{-1} were recorded on a Perkin—Elmer model 457 or 125 grating spectrometer. NMR spectra were recorded using a Varian HA100 NMR spectrometer operating at 100 MHz (for ^{1}H NMR) or 94.1 MHz (for ^{19}F NMR). Mass spectra were obtained using either an AEI MS9 or a Hitachi—Perkin—Elmer RMU 6E spectrometer. Trifluorophosphine (Ozark—Mahoning Company) was used after passage through a P_4O_{10} drying tube and purified by trap to trap fractionation on the vacuum line. Di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) was prepared by literature methods [17,18], and the red crystalline material purified by sublimation at room temperature.

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with diphenylacetylene

A mixture of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.257 g, 0.4 mmol) and diphenylacetylene (0.356 g, 2 mmol) was refluxed in hexane (30 ml) for 8 h. The colour of the solution changed from yellow to dark-red. The brown-orange material which precipitated was filtered, washed with hexane, extracted with benzene and recrystallised from benzene/acetone, giving white crystals of hexaphenylbenzene (0.070 g, 20%) [24]. The product was identified by its melting point, infrared spectrum and by the observation of parent ion at m/e = 534 in the mass spectrum. The filtrate was evaporated to dryness and the solid residue was recrystallised from benzene/hexane to afford the red crystalline compound di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) (0.195 g, 50%), m.p. 200°C (dec.) (Found: C, 67.6; H, 4.5. $C_{28}H_{20}ClRh$ calcd.: C, 67.9; H, 4.04%). Infrared spectrum: 3080vw, 3084m, 3034w, 1602m, 1576vw, 1500s, 1450s, 1418(sh), 1405m, 1380(sh) cm^{-1} (HCBD mull): 1180m, 1160m, 1078m, 1030s, 920w, 850w, 760(sh), 700vs, 680s cm^{-1} (Nujol mull). ^{1}H NMR spectrum: τ 2.4 (m), τ 2.8 (m) in the relative area of 2/3 ($CDCl_3$ solution). The compound is air stable both in solid and solution.

Reaction of di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) with cyclopentadienylthallium

Cyclopentadienylthallium (0.054 g, 0.2 mmol) was added to a solution of

di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) (0.050 g, 0.05 mmol) in benzene (10 ml) and the mixture was stirred at room temperature. The initially dark-red solution rapidly became yellow. After stirring for 1 h, the reaction mixture was filtered through a sinter packed with Celite to remove the thallous salts. The solution was then concentrated under vacuum and light petroleum added to yield yellow crystals of π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I) (0.042 g, 80%), m.p. 230-231°C (Found: C, 75.5; H, 4.8. $C_{33}H_{25}Rh$ calcd.: C, 74.85; H, 4.88%). Infrared spectrum: 3080vw, 3060w, 3035vw, 3010vw, 1598m, 1570w, 1492s, 1443s, 1386w, 1355w, 1315m, 1282m, 1180w, 1158m, 1101w, 1070s, 1026s, 998w, 919s, 850w, 802w, 756vs, 697vs, 540s, 511s cm^{-1} (KBr disc). ^1H NMR τ 2.6 (m), τ 2.8 (m), τ 5.06 (d) [J(Rh—H) = 1 Hz] in a ratio 8/12/5. The mass spectrum shows the parent ion, m/e = 524 $[Rh(C_4Ph_4)(C_5H_5)]^+$, and the expected fragmentation pattern.

Reaction of di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) with thalliumacetylacetonate

A mixture of di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) (0.054 g, 0.05 mmol) and thalliumacetylacetonate (0.060 g, 0.2 mmol) in benzene (10 ml) was agitated at room temperature for 30 min and the mixture filtered to remove thallous chloride. Excess thalliumacetylacetonate was precipitated by concentrating the solution, adding hexane and collected by filtration. The filtrate was evaporated and recrystallised from hexane to yield π-tetraphenylcyclobutadienerhodium(I) acetylacetonate (0.049 g, 87%) as shiny red crystals, m.p. 172-3°C (Found: C, 70.8; H, 5.0. $C_{33}H_{27}O_2Rh$ calcd.: C, 70.97; H, 4.83%). Infrared spectrum: 3084vw, 3060m, 3032w, 1614(sh), 1600vs, 1566vs, 1516vs, 1446m, 1380vs, 1350(sh), 1272s, 1236w, 1195m, 1177(sh), 1159w, 1070m, 1027s, 926m, 917m, 828w, 784s, 776s, 768s, 754(sh), 746s, 700vs, 648m, 618m, 600(sh), 589(sh), 579m, 567s, 548m cm^{-1} KBr disc). ^1H NMR: τ 2.36 (m), τ 2.76 (m), τ 4.81 (s), τ 8.02 (s) (relative area of 20/1/6) ($CDCl_3$ solution). The mass spectrum shows a parent ion at m/e = 558 and the expected fragmentation pattern.

Reaction of di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) with hexafluoroacetylacetonatethallium(I)

A mixture of di-μ-chlorobis(π-tetraphenylcyclobutadiene)dirhodium(I) (0.050 g, 0.05 mmol) and hexafluoroacetylacetonatethallium (0.082 g, 0.2 mmol) was stirred in benzene (10 ml) for 30 min at room temperature. After removal of solvent the remaining solid was extracted with light petroleum and recrystallised to give dark-red crystals of π-tetraphenylcyclobutadienerhodium(I) hexafluoroacetylacetonate (0.043 g, 63%), m.p. 149°C (Found: C, 59.0; H, 3.4. $C_{33}H_{21}F_6O_2Rh$ calcd.: C, 59.45; H, 3.15%). Infrared spectrum: 3086vw, 3070m, 3034vw, 1670m, 1615s, 1596s, 1550m, 1520m, 1500m, 1460s, 1445m, 1402m, 1386m, 1342s, 1256vs, 1212vs (br), 1100s, 1068m, 1028m, 948w, 917m, 846w, 824(sh), 800s, 786m, 775m, 740s, 704s, 695vs, 678s, 660(sh), 620m, 580s, 575s, 547m, cm^{-1} (KBr disc). ^1H NMR spectrum: τ 2.4-2.7 (m). (Relative area of 20/1 ($CDCl_3$ solution).) The ^{19}F NMR spectrum contains a singlet at Φ_F = 76.2 ppm. The mass spectrum exhibits a peak at m/e = 666 corresponding to the parent ion and the expected fragmentation pattern.

Reaction of π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I) with trifluorophosphine

No reaction was observed when π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium (0.052 g, 0.1 mmol) was sealed off with an excess of trifluorophosphine and heated at 60°C for 75 h. The starting materials were recovered unchanged.

Reaction of π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I) with diphenylacetylene

The complex did not react with diphenylacetylene in refluxing benzene for 10 h, even on using a ten-fold excess of diphenylacetylene.

Reaction of π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I) with acetylenedicarboxylic acid dimethyl ester

A mixture of the tetraphenylcyclobutadiene complex (0.052 g, 0.1 mmol) and acetylenedicarboxylic acid dimethyl ester (0.130 g, 1 mmol) was refluxed in toluene for 6 h, but no reaction occurred and the starting materials were recovered unchanged.

Reaction of π-cyclopentadienyl-π-tetraphenylcyclobutadienerhodium(I) with methyl iodide

No reaction was observed when an excess of methyl iodide was sealed off with a toluene solution of tetraphenylcyclobutadiene complex and the mixture heated at 100°C for 3 days.

Reaction of π-cyclopentadienylbis(trifluorophosphine)rhodium(I) with hexafluorobutyne

π-Cyclopentadienylbis(trifluorophosphine)rhodium(I) (0.344 g, 1 mmol) was sealed off with an excess of hexafluorobutyne and heated at 60°C for 48 h, but no reaction was observed.

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with dimethylacetylene

Di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.128 g, 0.2 mmol) was sealed off with a three-fold excess of dimethylacetylene in hexane (10 ml) and the mixture was heated at 60°C for 48 h. The ampoule was opened in vacuo and excess dimethylacetylene, solvent and unreacted di-μ-chlorotetrakis(trifluorophosphine)dirhodium were removed. The solid remaining was extracted with hexane, but the only product isolated was hexamethylbenzene (0.075 g, 45%) which was recrystallised from hexane and identified by its ^{1}H NMR (a singlet at τ 7.9), mass spectrum and melting point.

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with hexafluorobutyne

Di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.200 g, 0.3 mmol) was sealed off with hexafluorobutyne (0.326 g, 2 mmol) in a glass ampoule and heated at 60°C for 72 h. The ampoule was opened on to the vacuum line and the volatiles collected at liquid nitrogen temperature; (0.120 g, 0.7 mmol) was identi-

fied as unreacted hexafluorobutyne. The residue was dissolved in acetone and transferred to a Schlenk flask. After removal of acetone the resulting solid was extracted with carbon tetrachloride and recrystallised from ether to afford white crystals of hexakis(trifluoromethyl)benzene (0.065 g, 20%), identified by its ^{19}F NMR spectrum (singlet at Φ_F = 50.89 ppm, mass spectrum and melting point, 209°C (lit. [25], 210-12°C). The residue (0.240 g) which was only soluble in acetone and could not be recrystallised, showed bands in the infrared spectrum corresponding to both C—F and P—F stretching frequencies, but showed no signal in the ^{19}F NMR spectrum. Analysis found: C, 17.46; H, 0.9%; m.p. 220°C (dec.)

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with methylphenylacetylene

Di-μ-chlorotetrakis(trifluorophosphine)dirhodium (0.128 g, 0.2 mmol) was refluxed with methylphenylacetylene (0.185 g, 1.6 mmol) in hexane for 10 h. The colour of the solution changed from yellow to red, but the only product isolated after recrystallisation from benzene/hexane was 1,2,4-triphenyl-3,5,6-trimethylbenzene (0.100 g, 52% of the initial methylphenylacetylene). The product was identified by its ^1H NMR, mass spectrum and m.p., 225°C (lit. [24], 225-227°C).

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with acetylenedicarboxylic acid dimethyl ester

Di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.126 g, 0.2 mmol) was stirred with acetylenedicarboxylic acid dimethyl ester (0.284 g, 2 mmol) in benzene (10 ml) at room temperature for 1 h. The only product obtained was hexa(methylcarboxylate)benzene (0.120 g, 42%), identified by its ^1H NMR, mass spectrum, and melting point, 186-188°C (lit. [24], 187°C).

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with phenylacetylene

Di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.252 g, 0.4 mmol) was refluxed with an excess of phenylacetylene for 2 h. The reaction led to decomposition and no product was obtained.

Reaction of di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) with phenyltrimethylsilylacetylene

In a similar fashion to that described above, di-μ-chlorotetrakis(trifluorophosphine)dirhodium(I) (0.257 g, 0.4 mmol) was treated with an excess of phenyltrimethylsilylacetylene in refluxing benzene for 3 h, but the reaction ended with the decomposition of the starting complex.

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