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Comparison of the reactions of some bisphosphines with two related dinuclear rhodium complexes

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Abstract

The reactions of some phosphines and bisphosphines with the dirhodium complexes $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**I**) and $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**II**) have been compared. The complexes $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-}Ph_2P(CH_2)_nPPh_2)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n = 1$–4), which are formed from (**I**) and the appropriate bisphosphine, all have a trans arrangement of the carbonyl and bisphosphine ligands. When left in solution, the complex (**III**, $n = 1$) loses CO to form $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}dppm)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**IV**), but the other complexes are stable. The complex (**II**) was prepared to force a change of stereochemistry on the products of the addition reactions. Treatment of (**II**) with the phosphines $P(p\text{-}MeC_6H_4)_3$ and PPh_2H, and the bisphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–4) gave $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)_2Rh_2(CO)(L)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ in which CO and L adopt a cis configuration on the Rh–Rh bond. UV irradiation of $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(PPh_2H)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**VII**) results in formal insertion of the alkyne into the P–H bond to give $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{\mu_2\text{-}PPh_2C(CF_3)C(CF_3)H\}$ (**VIII**). Unlike (**III**, $n = 1$), $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-}dppm)(\mu_2\text{-}\eta^1{:}\eta^1CF_3C_2CF_3)$ (**IX**, $n = 1$) shows no tendency to lose CO in solution. Some bis(dinuclear) complexes $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}Ph_2P(CH_2)_nPPh_2\})$ (**V**, $n = 2$–4) and $[(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}dppb)$ (**X**) were formed when two equivalents of (**I**) or (**II**) were treated with the bisphosphine. The crystal and molecular structures of (**III**, $n = 2$), (**IV**) and (**IX**, $n = 1$) were determined by X-ray crystallography.

Keywords: Rhodium; Dinuclear complex; Bisphosphine; Di(cyclopentadienyl)methane

1. Introduction

We have shown previously that the dinuclear rhodium complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**I**) readily adds tertiary phosphines including PPh_3, $PMePh_2$, $P(OMe)_3$, and PF_3 [1]. The products of these reactions, $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(PR_3)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$, are inert to further substitution. As an extension of this work, we decided to investigate some reactions of (**I**) with bidentate phosphines. If a unidentate attachment of the ligands was achieved, this would provide scope for developing further chemistry at the 'dangling' end of the bisphosphine. Alternatively, dinuclear bisphosphine-bridged complexes might be formed. There is considerable current interest in complexes of both types (see, for example, Refs. [2,3]). We describe the results of our investigations in this paper. We have also explored some related reactions of phosphines, including bisphosphines, with the new di(cyclopentadienyl)methane complex $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**II**).

2. Experimental

2.1. General procedures

Reactions were generally carried out under an atmosphere of purified nitrogen in oven-dried Schlenk flasks. The progress of the reactions was monitored by infrared spectroscopy and/or analytical thin layer chromatography (Mackery–Nagel, Polygram SIL G/UV$_{254}$). Purification was generally achieved by preparative-scale thin layer chromatography which was carried out on 20 × 20 cm^2 plates with a 1:1 silica gel G-HF$_{254}$ mixture (Type 60, Merck) as adsorbent. All separations were achieved on deactivated plates, obtained by drying at room temperature for 24 h. Microanalyses were performed by the National Analytical Laboratories, Clayton, Australia or the Campbell Microanalytical Labora-

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tory, Department of Chemistry, University of Otago, New Zealand. Melting points were determined on a Buchi or Electrothermal melting point apparatus using analytically pure samples and are uncorrected; sealed capillaries were used for air-sensitive samples.

2.2. *Instrumentation*

Solution infrared spectra (KBr windows) were obtained using a Perkin Elmer PE1640 Fourier transform spectrometer. NMR spectra were measured on Bruker AC 200, AM 300, or DRX 400 spectrometers. Chemical shifts are in parts per million from internal Me_4Si for ^1H, CCl_3F for ^{19}F, and 85% H_3PO_4 for ^{31}P; in all cases, a positive chemical shift denotes a resonance downfield from the reference. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). Electron impact mass spectra were obtained by using VG TRIO or Micromass 70/70-F spectrometers operating at 70 eV and 200 °C inlet temperature. Fast atom bombardment (FAB) mass spectra were recorded on a VG-ZAB-2 mass spectrometer at the University of Adelaide. 3-Nitrobenzyl alcohol was used as the matrix, and dichloromethane or tetrahydrofuran as co-solvent. Xenon atoms were used to bombard the sample to produce positive ions. Caesium iodide clusters were used as calibrants. The photolysis reaction was carried out with an Hanovia medium pressure mercury arc photochemical reactor.

2.3. *Materials*

Acetone was analytical grade reagent; hydrocarbons and dichloromethane were purified by standard procedures [4]. The petroleum ether was the fraction of boiling point range 30–60 °C. All solvents were stored in the dark over activated 4A molecular sieves and were purged with nitrogen prior to use. The complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (**I**) was prepared by a procedure described in the literature [5]. The synthesis of di(cyclopentadienyl)methane was based on the method of Shaltegger et al. [6] modified as described in the thesis by Bryndza [7]. It was converted immediately to the thallium salt $TlC_5H_4CH_2C_5H_4Tl$ by reaction with thallium(I) ethoxide [8]. All tertiary phosphines were purchased from Aldrich Chemical Company and diphenylphosphine and the bisphosphines from Strem Chemicals; the bisphosphines were recrystallized from isopropanol before use.

2.4. *Preparation of $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$*

2.4.1. *Method A*

$[Rh(CO)_2Cl(CF_3C_2CF_3)]_2 \cdot nC_6H_5CH_3$ was prepared from $[Rh(CO)_2Cl]_2$ and hexafluorobut-2-yne in toluene [5]. To a solution of this compound (2.03 g, 2.3 mmol based on $n = 2$) in a 1:7 mixture of acetone and petroleum spirit (60 ml) was added an excess of $TlC_5H_4CH_2C_5H_4Tl$ (1.82 g, 3.3 mmol). The reaction mixture was stirred for 6 h at room temperature. The dark brown reaction solution was filtered through a Celite pad and the residue was washed with dichloromethane (35 ml). After removal of solvents under vacuum, the residue was dissolved in a little dichloromethane and chromatographed with a 1:1 mixture of dichloromethane and petroleum spirit as eluent. A major orange band developed. This product was collected and characterized as $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**II**) (0.140 g, 11%). Anal. Found: C, 37.9; H, 1.8; F, 19.8. $C_{17}H_{10}F_6O_2Rh_2$. Calc.: C, 38.2; H, 1.8; F, 20.1%. Mass spectrum, *m/z*: 566 (13%, M), 538 (24%, M − CO), 510 (70%, M − 2CO), 441 (100%, $[C_{14}H_{10}F_3Rh_2]^+$). IR spectrum (CH_2Cl_2) $\nu(CO)$ at 2032 s, 1990 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.28 and 4.34 (2 × d, $^2J_{H-H} = 14.5$ Hz, 2 × 1H, CH_2), 4.69 (m, 2H, C_5H_4), 5.24 (m, $J_{H-H} = 2$ Hz, 2H, C_5H_4), 5.89 (m, 2H, C_5H_4), 6.09 (m, $J_{H-H} = 2$ Hz, 2H, C_5H_4). ^{19}F NMR ($CDCl_3$): δ −55.5 (t, $^3J_{Rh-F} = 1.1$ Hz, 2 × CF_3).

2.4.2. *Method B*

The complex $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_4$ was prepared from di(cyclopentadienyl)methane and $[Rh(CO)_2Cl]_2$ according to the literature procedure [8]. A solution of this compound (0.082 g, 0.18 mmol) in petroleum spirit (7 ml) was added to a Carius tube, and an excess of hexafluorobut-2-yne (mole ratio about 1:40) was condensed at liquid nitrogen temperature onto the frozen solution. The tube was sealed and placed in a tube furnace at 110 °C for 24 h. The tube was allowed to cool, CO was carefully vented, and unchanged hexafluorobut-2-yne and solvent were removed under vacuum. The crude product was dissolved in a little dichloromethane and purified by preparative TLC with a 1:1 mixture of dichloromethane and petroleum spirit as eluent. Extraction of a major orange band with dichloromethane and removal of solvent gave $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (0.013 g, 13%) which was identified spectroscopically.

2.5. *Reactions of $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)$ (I) with bisphosphines, $Ph_2P(CH_2)_nPPh_2$*

All reactions were done in a similar manner. A detailed description is given for the reaction with $Ph_2P(CH_2)_2PPh_2$, and abbreviated descriptions are presented for other systems.

2.5.1. *$Ph_2P(CH_2)_2PPh_2$, dppe (mole ratio about 1:1)*

A solution of (**I**) (0.099 g) in chloroform (5 ml) was added dropwise to a stirred solution of dppe (0.084 g, mole ratio 1:1.1) in chloroform (5 ml). Within 5 min, the colour of the solution had changed from green to orange. Evaporation of some solvent, and thin layer chromatography of the concentrated solution with a 1:1 mixture of dichloromethane and hexane as eluent separated one major orange band from two minor bands. The major band was extracted with dichloromethane, and the extract was evaporated to dryness. Recrystallization of the residue from pentane gave orange crystals of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-dppe})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n=2$) (0.113 g, 65%) m.p. 135 °C (dec.). Anal. Found: C, 52.9; H, 3.7; F, 12.2. $C_{41}H_{34}F_6OP_2Rh_2$. Calc.: C, 53.2; H, 3.7; F, 12.3%. FAB mass spectrum, *m/z*: 924 (M), 526 (M − dppe), 398 (dppe). IR spectrum (CH_2Cl_2): ν(CO) at 1990 s cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 1.95 (m, 4H, CH_2CH_2), 4.99 (s, 5H, C_5H_5), 5.06 (d, J_{Rh-H} = 1.3 Hz, 5H, C_5H_5), 7.35 (m, 20H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.7 and −55.5 (2 × q, $^5J_{F-F}$ = 11.8 Hz, 2 × CF_3). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$): δ −11.6 (d, $^3J_{P-P}$ = 32.8 Hz, 1P, *free* PPh_2), 40.8 (dd, $^1J_{P-Rh}$ = 180 and $^3J_{P-P}$ = 32.8 Hz, 1P, *coordinated* PPh_2).

2.5.2. *Dppe (mole ratio 2:1)*

A solution of (**I**) (0.055 g) in chloroform (2 ml) was added dropwise to a stirred solution of dppe (0.20 g, mole ratio 2.08:1) in chloroform (5 ml). Orange crystals were deposited, and after 15 min the solution was filtered. The crystals were washed twice with hexane and dried in a vacuum to give $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\mu\text{-}\eta^1{:}\eta^1\text{-dppe})$ (**V**, $n=2$) (0.130 g, 86%) m.p. 195 °C (dec.). Anal. Found: C, 45.8; H, 3.1; F, 15.6. $C_{56}H_{44}F_{12}O_2P_2Rh_4$. Calc.: C, 46.3; H, 3.0; F, 15.7%. FAB mass spectrum, *m/z*: 1450 (M), 924 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$), 896 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ − CO), 566 ($(C_5H_5)Rh(dppe)^+$). IR spectrum (THF): ν(CO) at 1980 s cm^{-1}. No NMR spectra were obtained owing to the poor solubility of the complex in common organic solvents.

2.5.3. *$Ph_2PCH_2PPh_2$, dppm (mole ratio 1:1)*

The reaction mixture yielded orange crystals of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-dppm})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n=1$) (62%) m.p. 160 °C (dec.). Anal. Found: C, 52.6; H, 3.6; F, 12.7; P, 6.8. $C_{40}H_{32}F_6OP_2Rh_2$. Calc.: C, 52.8; H, 3.5; F, 12.5; P, 6.8%. Mass spectrum, *m/z*: 882 (< 1%, M − CO), 714 (< 2%, M − $(C_5H_5)Rh(CO)$), 552 (10%, $[(C_5H_5)Rh(dppm)]^+$), 233 (100%, $[C_{10}H_{10}Rh]^+$). IR spectrum (CH_2Cl_2): ν(CO) at 1990 s cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 3.16 (dd, $^2J_{P-H}$ = 15.0 and $^2J_{P-H}$ = 8.2 Hz, 2H, CH_2), 5.01 (s, 5H, C_5H_5), 5.08 (d, J_{Rh-H} = 1.4 Hz, 5H, C_5H_5), 7.20 (m, 20H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.3 and −55.5 (2 × q, $^5J_{F-F}$ = 12.3 Hz, 2 × CF_3). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$): δ −27.1 (d, $^2J_{P-P}$ = 26.3 Hz, 1P, *free* PPh_2), 38.6 (dd, $^1J_{P-Rh}$ = 180 and $^2J_{P-P}$ = 26.3 Hz, 1P, *coordinated* PPh_2).

Additional peaks were observed in the NMR spectra of aged samples, and these were due to conversion to the decarbonylation product $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-dppm})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**IV**). This complex was isolated by TLC of the aged solutions, with a 2:1 mixture of hexane and dichloromethane as eluent. The product was obtained as orange crystals, m.p. 248 °C. Anal. Found: C, 53.2; H, 3.6; P, 7.8. $C_{39}H_{32}F_6P_2Rh_2$. Calc.: C, 53.1; H, 3.7; P, 7.0%. Mass spectrum, *m/z*: 882 (< 10%, M), 552 (100%, $[(C_5H_5)Rh(dppm)]^+$), 233 (58%, $[C_{10}H_{10}Rh]^+$). IR spectrum (CH_2Cl_2): no ν(CO) absorptions. ^{1}H NMR spectrum ($CDCl_3$): δ 2.80 (m, 1H, CH_2), 3.70 (AX_2 q, $^2J_{P-H}$ = $^2J_{H-H}$ = 11.5 Hz, 1H, CH_2), 5.37 (d, J_{Rh-H} = 1.0 Hz, 10H, C_5H_5), 7.01 (m, 2H, C_6H_5), 6.85 (m, 4H, C_6H_5), 7.22 (m, 4H, C_6H_5), 7.29 (m, 10H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −52.3 (s, CF_3). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$): δ 39.8 (d, $^1J_{Rh-P}$ = 180 Hz, *coordinated* dppe).

The same products were isolated from the reaction between dppm and 2 mol equivalents of (**I**).

2.5.4. *$Ph_2P(CH_2)_3PPh_2$, dppp (mole ratio 1:1)*

Work-up of the reaction solution gave dark red crystals of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-dppp})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n=3$) (60%) m.p. 121 °C (dec.). Anal. Found: C, 53.6; H, 4.2; F, 11.9; P, 6.6. $C_{42}H_{36}F_6OP_2Rh_2$. Calc.: C, 53.8; H, 3.9; F, 12.1; P, 6.6%. FAB mass spectrum, *m/z*: 938 (M), 910 (M − CO), 845 (M − CO − C_5H_5), 580 ($(C_5H_5)Rh(dppp)^+$), 526 (M − dppp), 412 (dppp). IR spectrum (CH_2Cl_2): ν(CO) at 1990 s cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 1.40 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 2.22 (m, 2H, CH_2), 5.00 (s, 5H, C_5H_5), 5.03 (d, J_{Rh-H} = 1.4 Hz, 5H, C_5H_5), 7.30 (m, 20H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.6 and −55.7 (2 × q, $^5J_{F-F}$ = 11.2 Hz, 2 × CF_3). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$): δ −16.9 (s, 1P, *free* PPh_2), 36.0 (d, $^1J_{P-Rh}$ = 180 Hz, 1P, *coordinated* PPh_2).

2.5.5. *Dppp (mole ratio 2:1)*

Work-up of the reaction solution gave red-orange crystals of $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-dppp})$ (**V**, $n=3$) (70%) m.p. 157 °C (dec.). Anal. Found: C, 46.8; H, 3.2; P, 4.5. $C_{57}H_{46}F_{12}O_2P_2Rh_4$. Calc.: C, 46.7; H, 3.2; P, 4.2%. FAB mass spectrum, *m/z*: 1464 (M), 1436 (M − CO), 938, (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ − CO), 526 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$dppp). IR spectrum ($CH_2Cl_2$): ν(CO) at 1985 s cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$): δ 1.45 (m, 2H, CH_2), 2.20 (m, 4H, CH_2), 4.92 (s, 10H, C_5H_5), 5.00 (d, J_{Rh-H} = 1.4 Hz, 10H, C_5H_5), 7.40 (m, 20H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.5 and −55.8 (2 × q, $^5J_{F-F}$ = 11.8 Hz, 2 × CF_3). ^{31}P{^{1}H} NMR spectrum ($CDCl_3$): δ 34.6 (d, $^1J_{P-Rh}$ = 183 Hz, *coordinated* PPh_2).

2.5.6. $Ph_2P(CH_2)_4PPh_2$, dppb (mole ratio 1:1)

Recrystallization of the crude product from hexane at −78 °C gave orange crystals of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-dppb})(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n = 4$) (58%) m.p. 170 °C (dec.). Anal. Found: C, 54.5; H, 4.0. $C_{43}H_{38}F_6OP_2Rh_2$. Calc.: C, 54.2; H, 4.0%. FAB mass spectrum, m/z (this compound is unstable in the matrix and decomposes readily): 952 (M), 924 (M − CO), 526 (M − dppb), 426 (dppb). IR spectrum (CH_2Cl_2): ν(CO) at 1970 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.40 (m, 4H, CH_2), 2.00 (m, 4H, CH_2), 5.04 (s, 5H, C_5H_5), 5.08 (d, $J_{Rh-H} = 1.2$ Hz, 5H, C_5H_5), 7.35 (m, 20H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.5 and −55.7 (2 × q, $^5J_{F-F} = 11.3$ Hz, 2 × CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ −16.0 (s, 1P, *free* PPh_2), 36.7 (d, $^1J_{P-Rh} = 180$ Hz, 1P, *coordinated* PPh_2).

2.5.7. $Ph_2P(CH_2)_4PPh_2$, dppb (mole ratio 2:1)

The reaction gave orange crystals of $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-dppb})$ (**V**, $n = 4$) (83%) m.p. 183 °C (dec.). Anal. Found: C, 46.7; H, 3.0; P, 4.5. $C_{58}H_{48}F_{12}O_2P_2Rh_4$. Calc.: C, 47.1; H, 3.3; P, 4.2%. FAB mass spectrum, m/z: 1478 (M), 1450 (M − CO), 952 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$), 924 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$ − CO), 594 ($(C_5H_5)Rh(dppb)^+$), 526 (M − $(C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$dppb). IR spectrum (THF): ν(CO) at 1995 cm^{-1}. Owing to the low solubility of the compound, NMR spectra could not be obtained.

2.6. Reactions of $(\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (II) with unidentate phosphines

2.6.1. $P(p\text{-}MeC_6H_4)_3$

Tri-*p*-tolylphosphine (0.062 g, 0.200 mmol) was added to a solution of (**II**) (0.093 g, 0.170 mmol) in dichloromethane (50 ml). Over a 15 min period, two equal portions of solid trimethylamine oxide (2 × 0.010 g, 0.272 mmol) were added to the stirred reaction mixture. Stirring was continued for another 5–6 h during which time the colour of the solution changed from orange to red. Removal of solvent under reduced pressure gave an air-stable red solid. This was purified by preparative TLC with a 1:1 mixture of dichloromethane and petroleum spirit as eluent. A major red band developed, and this was extracted with dichloromethane. Removal of solvent gave a red solid which was characterized as $(\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{P(p\text{-}MeC_6H_4)_3\}(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (**VI**) (0.040 g, 22%). Anal. Found: C, 52.7; H, 3.5; F, 13.5; P, 3.5. $C_{37}H_{31}F_6OPRh_2$. Calc.: C, 52.7; H, 3.7; F, 13.5; P, 3.7%. Mass spectrum, m/z: 842 (< 1%, M), 814 (1%, M − CO), 538 (2%, $[C_{15}H_{10}F_6Rh_2]^+$), 441 (21%, $[C_{14}H_{10}F_3Rh_2]^+$). IR spectrum (CH_2Cl_2): ν(CO) at 1984 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 2.34 (s, 9H, CH_3), 3.87 (d, $^2J_{H-H} = 14.6$ Hz, 1H, CH_2), 4.20 (dd, $^2J_{H-H} = 14.5$ Hz and $^4J_{P-H} = 3.7$ Hz, 1H, CH_2), 4.31 (m, 1H, C_5H_4), 5.42 (m, 1H, C_5H_4), 4.67 (m, 2H, C_5H_4), 5.09 (m, 1H, C_5H_4), 5.42 (m, 1H, C_5H_4), 5.86 (d, $J_{Rh-H} = 2.0$ Hz, 2H, C_5H_4), 7.09 (s, 12H, C_6H_4). ^{19}F NMR spectrum ($CDCl_3$): δ −53.1 (qd, $^5J_{F-F} =$ 11.3 Hz and $^3J_{Rh-F} = 3.4$ Hz, 3F, CF_3) and −55.2 (qt, $^5J_{F-F} = 11.3$ Hz, $^3J_{Rh-F} = 3.1$ Hz, and $^4J_{Rh-F} = 3.0$ Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ 38.3 (d, $^1J_{P-Rh} = 179$ Hz, P).

2.6.2. PPh_2H

An excess of diphenylphosphine (0.05 ml, 0.29 mmol) was added to a solution of (**II**) (0.100 g, 0.176 mmol) in dichloromethane (30 ml). Over a 20 min period, three equal portions of solid trimethylamine oxide (3 × 0.005 g, 0.20 mmol) were added to the stirred reaction mixture. Stirring was continued for another 5–6 h during which time the colour of the solution changed from orange to red. Removal of solvent under reduced pressure gave a red solid. This was purified by preparative TLC with a 1:3 mixture of diethyl ether and petroleum spirit as eluent. A major orange-red band developed, and this was extracted with dichloromethane. Removal of solvent gave an orange-red solid which was characterized as $(\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(PPh_2H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (**VII**) (0.030 g, 25%) m.p. 149 °C. Anal. Found: C, 46.1; H, 3.1; F, 16.2; P, 4.3. $C_{28}H_{21}F_6OPRh_2$. Calc.: C, 46.4; H, 2.9; F, 15.7; P, 4.3%. Mass spectrum, m/z: 724 (2%, M), 696 (2%, M − CO). IR spectrum (CH_2Cl_2): ν(CO) at 1982 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 4.13 (d, $^2J_{H-H} = 14.5$ Hz, 1H, CH_2), 4.38 (dm, $^2J_{H-H} =$ 14.5 Hz, 1H, CH_2), 4.64 (s, 1H, C_5H_4), 4.87 (m, 1H, C_5H_4), 5.22 (s, 1H, C_5H_4), 5.36 (m, 3H, C_5H_4), 5.69 (d, $J_{P-H} = 378$ Hz, 1H, P–H), 5.83 (s, 1H, C_5H_4), 5.90 (m, 1H, C_5H_4), 7.33 (m, 8H, C_6H_5), 7.73 (m, 2H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −53.2 (qm, $^5J_{F-F} = 11.3$ Hz, 3F, CF_3) and −55.1 (qm, $^5J_{F-F} =$ 11.3 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ 38.5 (d, $^1J_{P-Rh} = 177$ Hz, P). Monitoring (IR, spot TLC) of a solution of (**VII**) in dichloromethane under nitrogen established that there was no change over 16 h. Another solution of (**VII**) (0.045 g, 0.079 mmol) in tetrahydrofuran was exposed to UV light for 30 min, during which time the solution became blood red in colour. After evaporation of solvent, red crystals were deposited. These were characterized spectroscopically as $(\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{\mu_2\text{-}PPh_2C(CF_3)C(CF_3)H\}$ (**VIII**) (0.035 g, 78%) m.p. 156 °C. Mass spectrum, m/z: 724 (1%, M), 696 (7%, M − CO), 533 (2%, $[C_{23}H_{20}PRh_2]^+$). IR spectrum (CH_2Cl_2): ν(CO) at 2006 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 2.51 (dd, $^2J_{H-H} = 15.0$ and $J_{P-H} = 11.6$ Hz, 1H, CH_2), 3.20 (d, $^2J_{H-H} = 15.0$ Hz, 1H, CH_2), 4.51 (q, $J_{F-H} = 10.6$ Hz, 1H, $C(CF_3)H$), 4.84 (m, 2H, C_5H_4), 5.24 (m, 1H, C_5H_4), 5.77 (m, 2H, C_5H_4), 5.82 (m, 1H, C_5H_4), 5.90 (m, 1H, C_5H_4), 6.04 (m, 1H, C_5H_4), 7.35 (m, 6H,

C_6H_5), 7.83 (m, 4H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −48.3 (m, 3F, CF_3) and −55.4 (pd, $^5J_{F-F}$ = 10.9 Hz, $^3J_{H-F}$ = 10.6 Hz, $^4J_{P-F}$ = 3.9 Hz, 3F, $C(CF_3)H$). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ 12.5 (dq, $^1J_{P-Rh}$ = 147 Hz, $^1J_{P-F}$ = 17.5 Hz, P).

2.7. Reactions of $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (II) with bisphosphines, $Ph_2P(CH_2)_nPPh_2$

All reactions were done in a similar manner. A detailed description is given for the reaction with $Ph_2PCH_2PPh_2$, and abbreviated descriptions are presented for other systems.

2.7.1. $Ph_2PCH_2PPh_2$, dppm (mole ratio about 1:1)

Bis(diphenylphosphino)methane (0.053 g, 0.14 mmol) was added to a solution of (II) (0.064 g, 0.11 mmol) in dichloromethane (15 ml). Over a 15 min period, two equal portions of solid trimethylamine oxide (2 × 0.005 g, 0.124 mmol) were added to the stirred reaction mixture. Stirring was continued for another 5–6 h during which time the colour of the solution changed from orange to red. Removal of solvent under reduced pressure gave an air-stable red solid. This was purified by preparative TLC with a 3:1 mixture of chloroform and petroleum spirit as eluent. A major red band developed, and this was extracted with dichloromethane. Removal of solvent gave a red solid which was characterized as $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-dppm})(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 1$) (0.026 g, 25%). Anal. Found: C, 53.3; H, 3.6; F, 11.7. $C_{41}H_{32}F_6OP_2Rh_2$. Calc.: C, 53.4; H, 3.5; F, 12.4%. Mass spectrum, m/z: 894 (6%, M − CO), 510 (40%, M − CO − dppm). IR spectrum (CH_2Cl_2): ν(CO) at 1976 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 2.60 (dd, $^2J_{H-H}$ = 15.7 Hz, J_{P-H} = 7.9 Hz, 1H, PCH_2P'), 2.89 (AXY spin system, ddd, $^2J_{H-H}$ = 14.6 Hz, $^2J_{P-H}$ = 6.4 Hz, $^2J_{P'-H}$ = 1.8 Hz, 1H, PCH_2P'), 3.84 (d, $^2J_{H-H}$ = 14.6 Hz, 1H, CH_2), 4.25 (dd, $^2J_{H-H}$ = 14.6 Hz and $^4J_{P-H}$ = 3.9 Hz, 1H, CH_2), 4.41 (m, 1H, C_5H_4), 4.59 (m, 1H, C_5H_4), 4.71 (m, 2H, C_5H_4), 5.33 (m, 1H, C_5H_4), 5.40 (m, 1H, C_5H_4), 5.86 (m, J_{H-H} = 2.2 Hz, 2H, C_5H_4), 6.9–7.5 (m, 20H, C_6H_5), 8.25 (m, J_{P-H} = 8.6 Hz, 2H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.8 (qm, $^5J_{F-F}$ = 11.4 Hz, 3F, CF_3), −55.3 (qt, $^5J_{F-F}$ = 11.3 Hz, J_{Rh-F} and J_{P-F} = 4.3 Hz, 3F, CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ −23.2 (ddq, $^2J_{P-P}$ = 23 Hz, $^3J_{P-Rh}$ = 5.7 Hz, J_{P-F} = 2.1 Hz, 1P, *free* PPh_2), 39.0 (dd, $^1J_{P-Rh}$ = 182 Hz, $^2J_{P-P}$ = 23 Hz, 1P, *coordinated* PPh_2).

2.7.2. $Ph_2PCH_2CH_2PPh_2$, dppe (mole ratio about 1:1)

The reaction mixture yielded red crystals of $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-dppe})(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 2$) (21%). Anal. Found: C, 53.6; H, 3.9; F, 12.0; P, 6.2. $C_{42}H_{34}F_6OP_2Rh_2$. Calc.: C, 53.8; H, 3.6; F, 12.2; P, 6.6%. Mass spectrum, m/z: no parent ion observed; 908 (2%, M − CO). IR spectrum (CH_2Cl_2): ν(CO) at 1977 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.25 (m, 4H, PCH_2CH_2P'), 3.90 (d, $^2J_{H-H}$ = 14.8 Hz, 1H, CH_2), 4.27 (m, 2H, 1H of CH_2 and 1H of C_5H_4), 4.62 (m, 1H, C_5H_4), 4.76 (m, 1H, C_5H_4), 4.89 (m, 1H, C_5H_4), 5.36 (m, 1H, C_5H_4), 5.44 (m, 1H, C_5H_4), 5.77 (m, 1H, C_5H_4), 5.81 (m, 1H, C_5H_4), 6.9–7.6 (m, 18H, C_6H_5), 8.02 (m, 2H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −52.4 (m, 3F, CF_3), −55.2 (m, 3F, CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ −10.9 (d, $^2J_{P-P}$ = 32 Hz, 1P, *free* PPh_2), 40.7 (dd, $^1J_{P-Rh}$ = 180 Hz, $^2J_{P-P}$ = 31 Hz, 1P, *coordinated* PPh_2).

2.7.3. $Ph_2P(CH_2)_3PPh_2$, dppp (mole ratio about 1:1)

The reaction mixture yielded red crystals of $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-dppp})(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 3$) (23%) m.p. 134°C. Anal. Found: C, 54.0; H, 4.0; F, 11.6; P, 5.9. $C_{43}H_{36}F_6OP_2Rh_2$. Calc.: C, 54.3; H, 3.8; F, 12.0; P, 6.5%. Mass spectrum, m/z: no parent ion observed; 538 (2%, M − dppp), 510 (9%, M − CO − dppp). IR spectrum (CH_2Cl_2): ν(CO) at 1977 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.37 (m, 2H, $PCH_2CH_2CH_2P'$), 1.9–2.3 (m, 4H, $PCH_2CH_2CH_2P'$), 3.85 (d, $^2J_{H-H}$ = 14.6 Hz, 1H, CH_2), 4.22 (dd, $^2J_{H-H}$ = 14.5 Hz, $^2J_{H-P}$ = 3.7 Hz, 2H, CH_2), 4.44 (m, 1H, C_5H_4), 4.60 (m, 1H, C_5H_4), 4.6–4.7 (m, 2H, C_5H_4), 5.23 (m, 1H, C_5H_4), 5.38 (m, 1H, C_5H_4), 5.85–5.9 (m, 2H, C_5H_4), 7.2–7.45 (m, 18H, C_6H_5), 7.80 (m, 2H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −52.1 (qd, $^2J_{F-F}$ = 11.2 Hz, $^2J_{F-Rh}$ = 3.2 Hz, 3F, CF_3), −55.3 (qdd, $^2J_{F-F}$ = 11.2 Hz, $^2J_{F-P'}$ = 3.2 Hz, $^3J_{F-P}$ = 3.2 Hz, 3F, CF_3). $^{31}P(^1H)$ NMR spectrum ($CDCl_3$): δ −16.7 (s, 1P, *free* PPh_2), 37.8 (d, $^1J_{P-Rh}$ = 180 Hz, 1P, *coordinated* PPh_2).

2.7.4. $Ph_2P(CH_2)_4PPh_2$, dppb (mole ratio about 1:1)

Work-up of the reaction solution gave red-orange crystals of $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-dppb})(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 4$) (18%). Anal. Found: C, 52.9; H, 3.6; F, 11.8. $C_{44}H_{38}F_6OP_2Rh_2$. Calc.: C, 54.8; H, 3.9; F, 11.8%. Mass spectrum, m/z: no parent ion observed; 510 (1%, M − CO − dppb), 426 (12%, dppb). IR spectrum (CH_2Cl_2): ν(CO) at 1977 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.10 (m, 2H, CH_2 of dppb), 1.55 (m, 2H, CH_2 of dppb), 1.90 (m, 4H, CH_2 of dppb), 3.84 (d, J_{H-H} = 14.6 Hz, 1H, CH_2), 4.24 (dd, J_{H-H} = 14.6 Hz, J_{H-P} = 3.7 Hz, 1H, CH_2), 4.42 (m, 1H, C_5H_4), 4.61 (m, 1H, C_5H_4), 4.67 (m, 1H, C_5H_4), 4.70 (m, 1H, C_5H_4), 5.32 (m, 1H, C_5H_4), 5.44 (m, 1H, C_5H_4), 5.87 (m, 1H, C_5H_4), 5.92 (m, 1H, C_5H_4), 7.25 – 7.55 (m, 18H, C_6H_5), 7.95 (m, 2H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −51.9 (qd, J_{F-F} = 11.2 Hz and J_{Rh-F} = 3.2 Hz, 3F, CF_3), −55.4 (qt, J_{F-F} = 11.2 Hz, J_{Rh-F} and J_{P-F} = 3.1 Hz, 3F,

Table 1

Summary of crystal structure data for the complexes $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-}PPh_2(CH_2)_2PPh_2)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (III, $n=2$), $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (IV, $n=1$), and $(\eta^5\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (IX, $n=1$)

	(III, $n=2$)	(IV, $n=1$)	(IX, $n=1$)
Crystal data			
Empirical formula	$C_{41}H_{34}F_6OP_2Rh_2$	$C_{39}H_{32}F_6P_2Rh_2$	$C_{41}H_{32}F_6OP_2Rh_2$
Formula weight	924.4	882.4	922.4
Crystal colour, habit	orange-red, acicular	dark red, prismatic	orange-red, tabular
Crystal dimensions (mm^3)	0.05×0.10×0.30	0.23×0.12×0.19	0.36×0.28×0.20
Crystal system	Monoclinic	Tetragonal	Monoclinic
Lattice type	Primitive	Primitive	Primitive
No reflections for unit cell determination, 2θ range (deg)	30, 10–20	30, 10–30	25, 6–22
Lattice parameters			
a (Å)	11.445(3)	18.620(2)	20.374(5)
b (Å)	15.828(3)	—	10.782(2)
c (Å)	20.322(4)	22.191(4)	18.606(5)
β (deg)	92.15(2)	—	114.94(2)
Volume (Å^3)	3679(2)	7693(2)	3706(2)
Space group	$P2_1/c$ (#14)	$P4_2/n$ (#86)	$P2_1/c$ (#14)
Z value	4	8	4
D_{calc} (g cm^{-3})	1.67	1.52	1.65
F_{000}	1848	3520	1840
μ(Mo Kα) (cm^{-1})	10.48	9.96	10.40
Intensity measurements			
Diffractometer		Nicolet R3m	
Radiation		Mo Kα (λ = 0.71073 Å) graphite monochromated	
Temperature (K)		293	
Scan type		ω	
Scan rate (deg min^{-1})	4.0–15.0 (in ω)	6.0–19.53 (in ω)	6.0–28.0 (in ω)
Scan width (deg)		1.60 (in ω)	
2θ_{max} (deg)	60.0	60.0	55.0
Index range	$-16/h/16$, $-1/k/22$, $-1/l/28$	$-1/h/26$, $-1/k/26$, $-1/l/31$	$-1/h/26$, $-14/k/1$, $-24/l/22$
Reflections collected	12334	13787	10166
Independent	10736 (R_{int} = 0.126)	11229 (R_{int} = 0.102)	8484 (R_{int} = 0.067)
Corrections	Lorentz-polarization, absorption (trans. factors: 0.951–0.892)	Lorentz-polarization absorption (trans. factors: 0.888–0.835)	Lorentz-polarization absorption (trans. factors: 0.838–0.641)
Structure solution and refinement			
Structure solution [9]		SHELXTL/PC	
Refinement [9]		Full-matrix least squares on F^2 for all reflections	
Least squares weights [a]	$[\sigma^2(F_o^2)+(0.0845P)^2]^{-1}$	$[\sigma^2(F_o^2)+(0.0791P)^2+(10.61P)]^{-1}$	$[\sigma^2(F_o^2)+(0.0674P)^2]^{-1}$
No. variables	469	442	469
Residuals: R_1, wR_2 ($I > 2\sigma(I)$)	0.102, 0.175	0.103, 0.193	0.078, 0.144
R indices (all data)	0.311, 0.283	0.307, 0.292	0.191, 0.193
Goodness of fit indicator	0.993	1.013	1.018
Maximum peak in final diff. map (e Å^{-3})	0.67	1.08	1.15
Minimum peak in final diff. map (e Å^{-3})	−0.67	−0.64	−1.31

[a] $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ −15.7 (s, 1P, *free* PPh_2), 38.0 (d, J_{P-Rh} = 179 Hz, 1P, *coordinated* PPh_2).

2.7.5. *$Ph_2P(CH_2)_4PPh_2$, dppb (mole ratio 2:1)*

Work-up of the reaction solution gave red crystals of $[(\eta^5:\eta^5-C_5H_4CH_2C_5H_4)Rh_2(CO)(\mu_2-\eta^1:\eta^1-CF_3C_2CF_3)]_2(\mu-\eta^1:\eta^1$-dppb) (**X**) (18%) m.p. 148 °C. Anal. Found: C, 47.4; H, 3.0; F, 14.8. $C_{60}H_{48}F_{12}O_2P_2Rh_4$. Calc.: C, 47.9; H, 3.2; F, 15.2%. Mass spectrum: no parent ion observed. IR spectrum (CH_2Cl_2): ν(CO) at 1978 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 1.6–2.0 (m, 8H, CH_2 of dppb), 3.82 (d, J_{H-H} = 14.5 Hz, 1H, CH_2), 3.85 (d, J_{H-H} = 14.5 Hz, 1H, CH_2), 4.21(dd, J_{H-H} = 14.6 Hz, J_{P-H} = 3.5 Hz, 2H, CH_2), 4.42 (m, 2H, C_5H_4), 4.59 (m, 2H, C_5H_4), 4.65–4.8 (m, 4H, C_5H_4), 5.24 (m, 2H, C_5H_4), 5.39 (dm, 2H, C_5H_4), 5.8–5.9 (m, 4H, C_5H_4), 7.15–7.45 (m, 16H, C_6H_5), 7.6–7.9 (m, 4H, C_6H_5). ^{19}F NMR spectrum ($CDCl_3$): δ −52.2 (pd, J_{F-F} = 11.3 Hz, 6F, 2 × CF_3), −55.3 (m, J_{F-F} = 11.3 Hz, 6F, 2 × CF_3). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$): δ 36.4 (d, J_{Rh-P} = 179 Hz, 1P, PPh_2), 37.2 (d, J_{Rh-P} = 179 Hz, 1P, PPh_2).

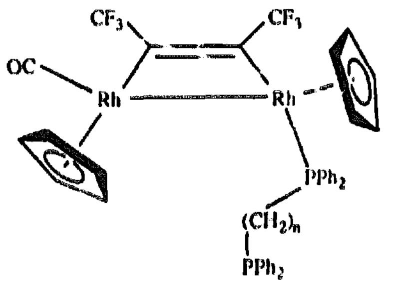
2.8. *Crystallography, $(\eta^5-C_5H_5)_2Rh_2(CO)(\eta^1$-dppe)$(\mu_2-\eta^1:\eta^1-CF_3C_2CF_3)$ (III, $n = 2$), $(\eta^5-C_5H_5)_2Rh_2(\mu_2-\eta^1:\eta^1$-dppm)$(\mu_2-\eta^1:\eta^1-CF_3C_2CF_3)$ (IV), and $(\eta5:\eta5-C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1$-dppm)$(\mu_2-\eta^1:\eta^1-CF_3C_2CF_3)$ (IX, $n = 1$)*

Good-quality crystals used for data collection were obtained as follows: (**III**, $n = 2$) by the slow evaporation of a saturated solution of the complex in hexane; (**IV**) by the slow diffusion of hexane into a saturated solution of the complex in dichloromethane; (**IX**, $n = 1$) by the slow diffusion of pentane into a saturated solution of the complex in dichloromethane. A summary of the crystal data for all three complexes is given in Table 1. Selected bond distances and angles are presented in Tables 2–7.

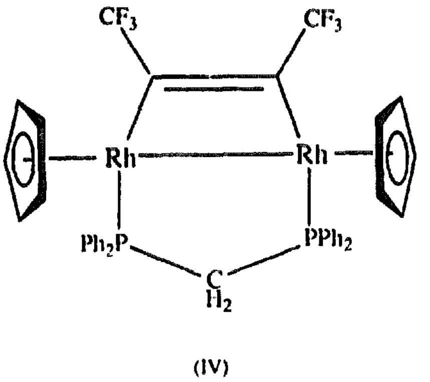
3. Results and discussion

There is a rapid reaction between $(\eta^5-C_5H_5)_2Rh_2(\mu-CO)(\mu_2-\eta^2-CF_3C_2CF_3)$ (**I**) and bis(diphenylphosphino)ethane (dppe) to produce $(\eta^5-C_5H_5)_2Rh_2(CO)(\eta^1$-dppe)$(\mu-\eta^1:\eta^1-CF_3C_2CF_3)$ (**III**, $n = 2$) in good yield (65%). The complex is isolated as air-stable orange crystals, and spectroscopic data are consistent with the structure (**III**). Characteristic features of the spectroscopic results are a terminal carbonyl stretch at 1990 cm^{-1} in the IR spectrum, and resonances for free (δ −11.6, doublet with P–P coupling) and coordinated (δ 40.8, dd with Rh–P and P–P coupling) phosphorus in the $^{31}P\{^1H\}$ NMR spectrum. The FAB mass spectrum shows a parent ion and loss of dppe. Although two geometric arrangements of the CO and phosphine groups are possible in (**III**), it is assumed that the trans isomer is formed because this is known [10] to be the more thermodynamically stable form of the dicarbonyl compound $(\eta^5-C_5H_5)_2Rh_2(CO)_2(\mu-\eta^1:\eta^1-CF_3C_2CF_3)$.

Analogous products were obtained from the related reactions of (**I**) with bis(diphenylphosphino)methane (dppm; 62% yield), bis(diphenylphosphino)propane (dppp; 60%), and bis(diphenylphosphino)butane (dppb; 58%). The complex $(\eta^5-C_5H_5)_2Rh_2(CO)(\eta^1$-dppm)$(\mu-\eta^1:\eta^1-CF_3C_2CF_3)$(**III**, $n = 1$) adds a further example to the small number of dinuclear complexes with unidentate attachment of dppm [11,12]. The electron impact mass spectrum of (**III**, $n = 1$) did not show a molecular ion, and the ion of highest m/z value corresponded to loss of CO from the parent. The high stability of the $[(\eta^5-C_5H_5)Rh(dppm)]$ unit was indicated by the appearance of fragments corresponding to $[(C_5H_5)Rh(dppm)(CF_3C_2CF_3)]^+$ and $[(C_5H_5)Rh(dppm)]^+$ in the mass spectrum. When the complex (**III**, $n = 1$) was left in solution, there was loss of CO to form $(\eta^5-C_5H_5)_2Rh_2(\mu-\eta^1:\eta^1$-dppm)$(\mu-\eta^1:\eta^1-CF_3C_2CF_3)$ (**IV**). No ν(CO) absorption was observed for this complex in the IR spectrum, and the $^{31}P\{^1H\}$ NMR spectrum showed one doublet for the two equivalent coordinated phosphorus atoms (δ 39.8, J_{Rh-P} 180 Hz).



(III)



(IV)

This ready conversion of (**III**, $n = 1$) to (**IV**) is interesting because it involves a significant change in

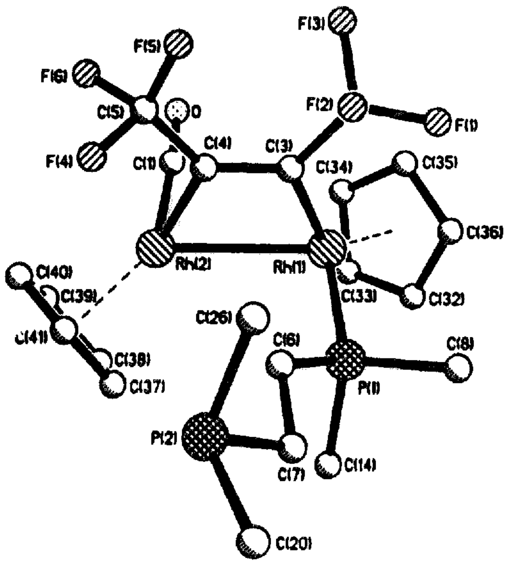


Fig. 1. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)\{\eta^1\text{-}PPh_2(CH_2)_2PPh_2\}(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (III, $n = 2$) with the phenyl groups and hydrogen atoms omitted.

the geometry about the Rh–Rh bond. In (III, $n = 1$) we propose a trans arrangement of the CO and phosphine ligands, but when CO is displaced by the second bisphosphine donor site, the two phosphorus atoms are mutually cis. To establish the overall effects of these structural changes, we determined the molecular structures of (III, $n = 2$) and (IV) from X-ray diffraction data. Although we would have preferred to compare the structures of (III, $n = 1$) and (IV), it was not possible to obtain crystals of the dppm complex (III, $n = 1$) because of its ready conversion in solution to (IV), even under an atmosphere of CO.

The molecular structure of (III, $n = 2$), which is shown in Fig. 1, confirms the trans arrangement of the carbonyl and phosphine ligands. The angles of 81.9(5)° and 94.7(1)° for Rh(1)–Rh(2)–C(1) and Rh(2)–Rh(1)–P(1) respectively are reasonably close to 90°, and the Rh–carbonyl [10,13] and Rh–phosphine [14,15] distances are similar to those observed for related complexes. There are no unexpected parameters for the $\eta^1{:}\eta^1$-attached hexafluorobut-2-yne or η^5-attached cyclopentadienyl ligands [10,13]. Selected bond lengths and angles for the complex are given in Tables 2 and 3.

The free end of the bisphosphine ligand is not close to Rh(2), with a non-bonding distance of 5.92 Å. However, it is clear that there is little barrier to this phosphorus atom approaching the second rhodium. With the related dppm complex, this arrangement would be even more favourable. Thus, the expected pathway for the conversion of (III, $n = 1$) to (IV) is that shown in Fig. 2.

A diagram of the molecular structure of the complex (IV) is presented in Fig. 3, and selected bond distances and angles are given in Tables 4 and 5. Each of the ligands hexafluorobut-2-yne and dppm is $\eta^1{:}\eta^1$-attached to the Rh–Rh bond, and there is a pseudo-mirror plane that passes through the carbon atom C(5) and the mid-point of the Rh(1)–Rh(2) and C(2)–C(3) bonds. The parameters for the dppm ligand are similar to those reported for other complexes containing this ligand bridging a Rh–Rh bond [16–19]. There are no unusual features in the parameters for the coordinated hexafluorobut-2-yne and cyclopentadienyl ligands. We do note an interesting trend in comparing the structures of the three complexes $(\eta^5\text{-}C_5H_5)_2Rh_2LL'(\mu\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ where L = L′ = CO [11], L = CO and L′ =

Table 2
Selected bond lengths (Å) for the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)\{\eta^1\text{-}PPh_2(CH_2)_2PPh_2\}(\mu_2\text{-}\eta^1{:}\eta^1CF_3C_2CF_3)$ (III, $n = 2$) (estimated standard deviations in parentheses)

Metal–metal			
Rh(1)–Rh(2)	2.734(2)		
Hexafluorobut-2-yne			
Rh(1)–C(3)	2.02(1)	Rh(2)–C(4)	2.02(1)
C(2)–C(3)	1.50(2)	C(3)–C(4)	1.30(2)
C(5)–C(4)	1.51(2)		
Bis(diphenylphosphino)ethane ligand			
Rh(1)–P(1)	2.252(4)	C(7)–P(2)	1.85(1)
P(1)–C(14)	1.84(1)	P(1)–C(8)	1.81(1)
P(1)–C(6)	1.81(1)	P(2)–C(20)	1.85(2)
C(6)–C(7)	1.52(2)	P(2)–C(26)	1.82(2)
Cyclopentadienyl rings			
C(37)–C(38)	1.41(2)	C(32)–C(36)	1.37(3)
C(37)–C(41)	1.38(2)	C(32)–C(33)	1.39(3)
C(38)–C(39)	1.38(2)	C(35)–C(36)	1.39(3)
C(39)–C(40)	1.43(2)	C(33)–C(34)	1.39(3)
C(40)–C(41)	1.40(2)	C(34)–C(35)	1.40(3)
Carbonyl ligand			
Rh(2)–C(1)	1.83(2)	C(1)–O	1.13(2)

dppe, and LL′ = dppm. The Rh–Rh distance increases from 2.682(1) through 2.734(2) to 2.745(2) Å for these complexes revealing an influence of the π-acidity of the ligands on the metal–metal distance.

The reactions between (**I**) and the bis(diphenylphosphino)alkanes were also attempted on a 2:1 ratio. With dppm, the only products isolated were (**III**, $n = 1$) and (**IV**). However, all other systems yielded the bis(dinuclear) species $[(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)]_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-}Ph_2P(CH_2)_nPPh_2\}$ (**V**). These complexes precipitated out of the reaction solution, and were isolated in high yields (greater than 85%). In the infrared spectra, a terminal carbonyl stretch was observed near 1980 cm^{-1}, and the FAB mass spectra showed molecular ions. We assume that (**V**, $n = 1$) was not formed for steric reasons.

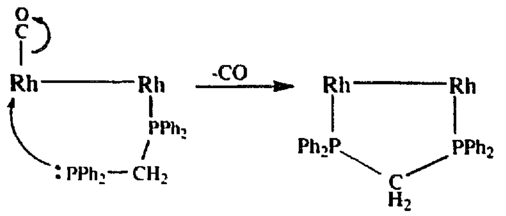


Fig. 2. Expected pathway for the decarbonylation of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(\eta^1\text{-dppm})(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$.

Table 3

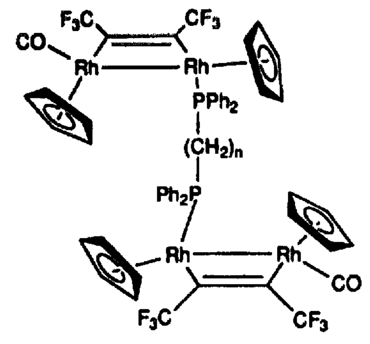
Selected bond angles (deg) for the complex $(\eta\text{-}C_5H_5)_2Rh_2(CO)(\eta^1PPh_2(CH_2)_2PPh_2)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (**III**, $n = 2$) (estimated standard deviations in parentheses)

Around the metals			
Rh(1)–Rh(2)–C(1)	81.9(5)	Rh(1)–Rh(2)–C(4)	68.5(4)
Rh(2)–Rh(1)–C(3)	69.8(4)	Rh(2)–Rh(1)–P(1)	94.7(1)
Carbonyl ligand			
Rh(2)–C(1)–O	175.8(16)	C(4)–Rh(2)–C(1)	84.6(7)
Bis(diphenylphosphino)ethane ligand			
Rh(1)–P(1)–C(14)	114.5(5)	Rh(1)–P(1)–C(8)	111.6(5)
Rh(1)–P(1)–C(6)	118.0(4)	C(14)–P(1)–C(6)	105.7(6)
C(8)–P(1)–C(6)	102.7(7)	C(14)–P(1)–C(8)	102.6(7)
P(1)–C(6)–C(7)	120.5(9)	C(6)–C(7)–P(2)	110.3(9)
C(7)–P(2)–C(20)	100.5(6)	C(7)–P(2)–C(26)	100.0(6)
C(20)–P(2)–C(26)	103.0(7)		
Hexafluorobut-2-yne			
Rh(2)–C(4)–C(3)	112.4(10)	Rh(2)–C(4)–C(5)	120.2(11)
Rh(1)–C(3)–C(4)	109.3(11)	Rh(1)–C(3)–C(2)	122.5(12)
C(5)–C(4)–C(3)	127.3(14)	C(4)–C(3)–C(2)	127.5(14)
Cyclopentadienyl rings			
C(37)–C(38)–C(39)	107.4(15)	C(32)–C(33)–C(34)	104.7(23)
C(38)–C(39)–C(40)	109.3(15)	C(33)–C(34)–C(35)	110.3(23)
C(39)–C(40)–C(41)	105.4(15)	C(34)–C(35)–C(36)	106.2(22)
C(40)–C(41)–C(37)	109.8(16)	C(35)–C(36)–C(32)	108.2(22)
C(41)–C(37)–C(38)	108.0(14)	C(36)–C(32)–C(33)	110.3(20)

Table 4

Selected bond lengths (Å) for the complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}CF_3C_2CF_3)$ (**IV**, $n = 1$) (estimated standard deviations in parentheses)

Metal–metal			
Rh(1)–Rh(2)	2.745(2)		
Hexafluorobut-2-yne			
Rh(1)–C(3)	2.04(1)	Rh(2)–C(2)	2.04(1)
C(2)–C(3)	1.31(2)	C(3)–C(4)	1.51(2)
C(1)–C(2)	1.48(2)		
Bis(diphenylphosphino)methane ligand			
Rh(1)–P(1)	2.206(4)	Rh(2)–P(2)	2.221(4)
P(2)–C(12)	1.83(1)	P(2)–C(6)	1.84(1)
P(1)–C(5)	1.85(1)	P(2)–C(5)	1.78(1)
P(1)–C(18)	1.83(1)	P(1)–C(24)	1.83(1)
Cyclopentadienyl rings			
C(30)–C(31)	1.39(3)	C(30)–C(34)	1.48(3)
C(31)–C(32)	1.37(3)	C(32)–C(33)	1.45(3)
C(33)–C(34)	1.37(3)	C(35)–C(36)	1.26(4)
C(35)–C(39)	1.26(4)	C(36)–C(37)	1.28(3)
C(37)–C(38)	1.36(3)	C(38)–C(39)	1.44(3)



(V)

In order to force complexes of the type (III) to adopt a cis orientation of the CO and bisphosphine groups, we decided to prepare the bis(cyclopentadienyl)methane complex $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_2(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (II). Two synthetic approaches based on our earlier preparations [5,20] of the complex $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ were tried. In one, the reaction of $[Rh(CO)_2Cl]_2$ with hexafluorobut-2-yne gave the solvated complex $[Rh(CO)_2Cl(CF_3C_2CF_3)]_2 \cdot nC_6H_5CH_3$ which was subsequently treated with $TlC_5H_4CH_2C_5H_4Tl$ to form (II); each reaction step was achieved at room temperature. The other involved the initial formation of $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)_4$ from $[Rh(CO)_2Cl]_2$ and $TlC_5H_4CH_2C_5H_4Tl$ and then treatment of this intermediate with hexafluorobut-2-yne at about 110°C. In each case, the yield of (II) was relatively low (10–15%). The complex was fully characterized from spectroscopic data (see Section 2). Two terminal carbonyl absorptions are observed in the IR spectrum at 2032 and 1990 cm^{-1}. These are similar to those observed for the cis isomer of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ [21].

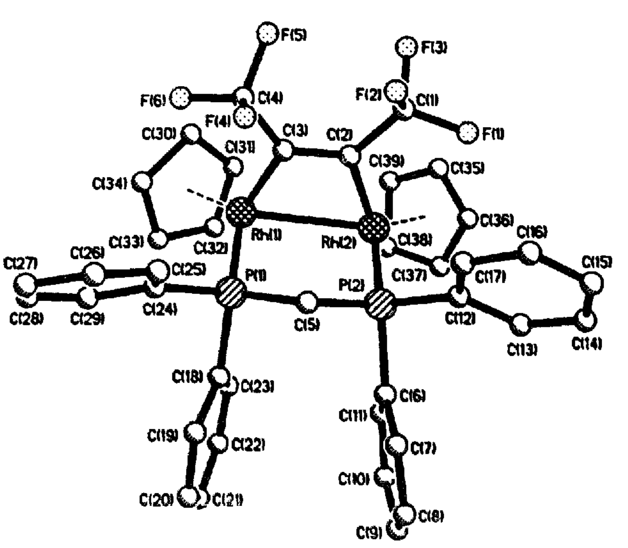


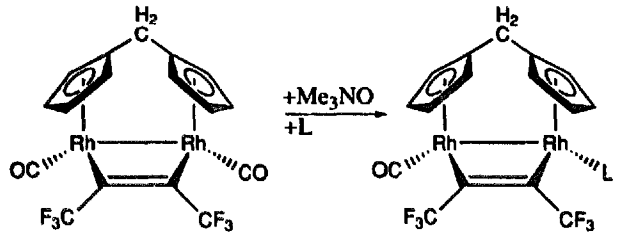
Fig. 3. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1:\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1:\eta^1CF_3C_2CF_3)$ (IV, $n = 1$) with hydrogen atoms omitted.

Although (I) is readily formed from $(\eta5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ by decarbonylation with trimethylamine oxide, an analogous reaction with (II) resulted in decomposition. This is presumably because the intended product $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(\mu\text{-}CO)(\mu_2\text{-}\eta^2\text{-}CF_3C_2CF_3)$ would be highly strained with all ligands in bridging positions. It did prove possible, however, to form substitution derivatives of (II) by treatment with Me_3NO in the presence of added ligand, as shown in Eq. (1). The viability of

Table 5
Selected bond angles (deg) for the complex $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu_2\text{-}\eta^1:\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (IV, $n = 1$) (estimated standard deviations in parentheses)

Around the metals			
Rh(2)–Rh(1)–P(1)	91.2(1)	Rh(1)–Rh(2)–P(2)	93.7(1)
P(1)–Rh(1)–C(3)	88.8(4)	Rh(2)–Rh(1)–C(3)	70.3(4)
P(2)–Rh(2)–C(2)	88.1(4)	Rh(1)–Rh(2)–C(2)	68.5(4)
Bis(diphenylphosphino)methane ligand			
Rh(1)–P(1)–C(5)	113.5(4)	Rh(1)–P(1)–C(18)	116.2(5)
Rh(1)–P(1)–C(24)	116.3(5)	C(5)–P(1)–C(18)	103.9(6)
C(5)–P(1)–C(24)	104.7(6)	C(18)–P(1)–C(24)	100.5(6)
Rh(2)–P(2)–C(5)	113.4(4)	Rh(2)–P(2)–C(6)	121.4(4)
Rh(2)–P(2)–C(12)	113.7(4)	C(5)–P(2)–C(6)	101.7(6)
C(5)–P(2)–C(12)	103.8(6)	C(6)–P(2)–C(12)	100.6(7)
P(1)–C(5)–P(2)	108.0(6)		
Hexafluorobut-2-yne			
Rh(2)–C(2)–C(3)	112.0(10)	Rh(1)–C(3)–C(2)	108.9(11)
Rh(2)–C(2)–C(1)	122.1(10)	Rh(1)–C(3)–C(4)	122.6(11)
C(2)–C(3)–C(4)	128.2(14)	C(1)–C(2)–C(3)	125.7(14)
Cyclopentadienyl rings			
C(30)–C(31)–C(32)	108.0(20)	C(36)–C(35)–C(39)	111.6(33)
C(32)–C(33)–C(34)	106.4(18)	C(35)–C(36)–C(37)	110.3(29)
C(31)–C(30)–C(34)	107.3(18)	C(36)–C(37)–C(38)	109.3(27)
C(31)–C(32)–C(33)	110.6(19)	C(37)–C(38)–C(39)	101.8(22)
C(30)–C(34)–C(33)	107.8(19)	C(35)–C(39)–C(38)	107.0(27)

this approach was established initially by forming $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{P(C_6H_4CH_3)_3\}(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**VI**) in reasonable yield from (**II**) and tri-*p*-tolylphosphine in the presence of Me_3NO. The product was characterized from elemental analyses and spectroscopic data (see Section 2). It is assumed that the terminal carbonyl and phosphine ligands will be forced to be mutually cis in this product.



(1)

The reaction with diphenylphosphine was also investigated because the complex $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$, which is isolated from the reaction of this secondary phosphine with (**I**), readily undergoes an intramolecular proton migration reaction to yield $(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}PPh_2)\{\mu\text{-}C(CF_3)C(CF_3)H\}$ [22]. We were interested to determine if the changed stereochemistry would affect this reaction. Treatment of (**II**) with diphenylphosphine gave the expected product $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(PPh_2H)(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ (**VII**) which was isolated in 25% yield and characterized from elemental analyses and spectroscopic results. Key features of the spectroscopic data are a molecular ion in the mass spectrum, a terminal carbonyl absorption at 1982 cm^{-1} in the IR spectrum, a doublet resonance at δ 5.69 with P–H coupling of 378 Hz in the ^{1}H NMR spectrum, and a doublet resonance at δ 38.5 with Rh–P coupling of 177 Hz in the $^{31}P\{^1H\}$ NMR spectrum. Other results are given in Section 2. Complex (**VII**) proved to be remarkably stable in solution at room temperature. It remained unchanged over 16 h, in contrast to $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)(PPh_2H)(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ which began the proton migration reaction immediately. The extra stability is presumably related to the cis rather than trans arrangement of the CO and PPh_2H ligands. We assume that the transfer is initially to the neighbouring rhodium followed by further migration to the alkyne carbon. Some support for this idea comes from a consideration of the pathway for protonation of the dicarbonyl complex $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)$ [23]. As shown in Fig. 4, this pathway is open in the trans complex but blocked for the cis species.

We attempted to force a transformation of (**VII**) in a number of ways. The most successful was UV irradiation, but this gave an unexpected product $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{\mu\text{-}PPh_2C(CF_3)C(CF_3)H\}$ (**VIII**) in high yield (about 80%). An analytically pure sample of the compound could not be obtained because it decomposed on chromatographic supports, but the complex was characterized from spectroscopic data. Possible structures for the complex are shown in Fig. 5. It is evident that a terminal carbonyl has been retained. The observation of ν(CO) at 2006 cm^{-1} is more consistent with structure (b) in Fig. 5; a lower frequency would be expected for alternative (a) owing to the effects of coordination of the strong phosphorus donor to the Rh–CO unit. NMR data indicate that the hexafluorobut-2-yne ligand has formally inserted into the P–H bond of the coordinated phosphine to produce a phosphinoalkene which is attached to the Rh–Rh bond from the phosphine and alkene functions. The ^{1}H NMR spectrum shows the expected resonances for the bis(cyclopentadienyl)methane ligand and the phenyl

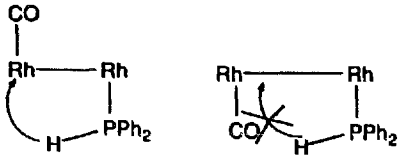


Fig. 4. The expected pathway for intramolecular rearrangements in diphenylphosphanedirhodium complexes.

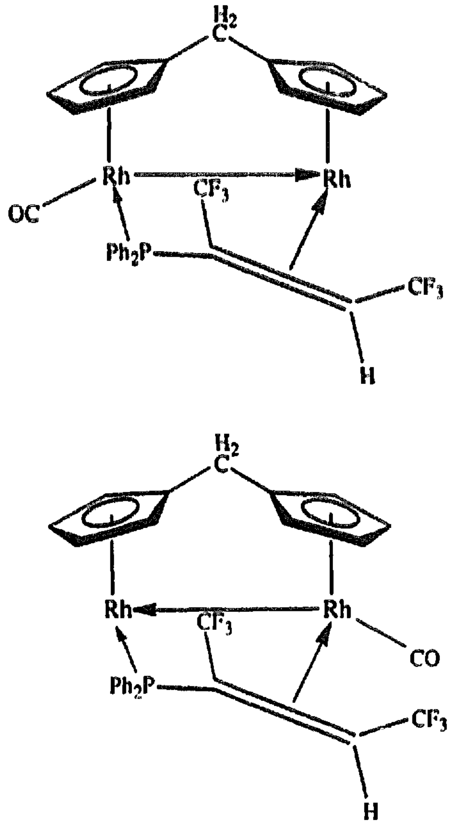


Fig. 5. Two possible structures for $(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)\{\mu_2\text{-}PPh_2C(CF_3)C(CF_3)H\}$ (**VIII**).

groups plus a one hydrogen quartet at δ 4.51 with hydrogen–fluorine coupling of 10.6 Hz. This is assigned to $=C(CF_3)H$. The ^{19}F NMR spectrum contains a multiplet at δ −48.3 and a pentet of doublets at δ −51.4. Analysis of the latter signal reveals fluorine–fluorine, hydrogen–fluorine and rhodium–fluorine couplings of 10.9 Hz, 10.6 Hz and 3.9 Hz respectively. The coordinated phosphine resonance in the $^{31}P\{^1H\}$ NMR spectrum is observed at δ 12.5 with phosphorus–rhodium and phosphorus–fluorine couplings of 147 Hz and 17.5 Hz respectively. This is consistent with formation of the $=C(CF_3)PPh_2$ group and the attachment of phosphorus to one rhodium only.

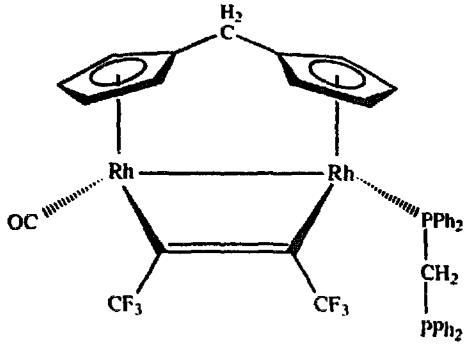
Some other complexes containing this type of ligand have been formed by the insertion of diphenylphosphido groups into metal–alkenyl bonds. Examples include the complexes $(\eta^5\text{-}C_5H_5)_2Rh_2(CNR)\{\mu\text{-}PPh_2C(CF_3)\text{-}C(CF_3)H\}$ [22] and $Mn_2(CO)_7(PEt_3)(\mu\text{-}PPh_2CHCH_2)$ [24]. Since the formation of (**VIII**) by UV irradiation of (**VII**) does not involve decarbonylation, it seems likely that the initial step in this reaction is activation of the P–H bond with formation of bridging phosphido and alkenyl groups. Subsequent insertion of the phosphido group into the rhodium–alkenyl bond would then complete the reaction.

The reaction of (**II**) with bis(diphenylphosphino)methane gave $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-dppm})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 1$) in moderate yield. The terminal carbonyl stretch in the IR spectrum was observed at 1976 cm^{-1}, and the ^{31}P NMR spectrum clearly indicated free (δ −23.2) and coordinated (δ 39.0) phosphorus atoms. The multiplicities of these resonances were interesting. The resonance for the coordinated phosphorus is a doublet of doublets as expected, with phosphorus–phosphorus and phosphorus–rhodium couplings of 23 Hz and 182 Hz respectively. However the 'free' phosphorus resonance is a doublet of doublets of quartets. The phosphorus–phosphorus (23 Hz) and three bond phosphorus–rhodium (5.7 Hz) couplings produce the doublet of doublets, but the quartet splitting (2.1 Hz) must be due to coupling of this phosphorus to the fluorines of a trifluoromethyl group. This is probably through space coupling, since it is unlikely to occur through six bonds. There are also some interesting aspects of the ^1H NMR spectrum. Thus, the resonances for the dppm methylene protons are a doublet of doublets at δ 2.60 and a doublet of doublets of doublets at δ 2.89. The ^{31}P decoupled ^1H NMR spectrum shows the major coupling of approximately 16 Hz for each resonance to be geminal hydrogen–hydrogen coupling. The ^{31}P–^1H 2D correlated spectrum establishes that the proton resonance at δ 2.89 is further coupled to both phosphorus atoms. From a series of ^{31}P–^1H correlated (COSY) spectra optimized at various magnitudes of coupling, it was deduced that the major coupling of 6.4 Hz is due to the interaction of the rhodium-bound phosphorus atom and the smaller coupling of 1.8 Hz is due to coupling from the 'free' phosphorus atom. The COSY spectra also establish that the proton at δ 2.60 couples only to the rhodium-bound phosphorus atom with coupling of 7.9 Hz. Previously, the size of the coupling between two geminal protons has been shown to depend on the H–C–H angle. The negative coupling constants encountered for angles near 109° are reduced in size (become more positive) and approach 0 Hz as the angle is widened to 120°. Similar reasoning may be applied to explain the lack of observable phosphorus–hydrogen coupling between the uncoordinated P and the methylene proton resonating at δ 2.60. It is proposed that this angle is such that the phosphorus–proton coupling is approximately zero. Although the highest peak observed in the mass spectrum of (**IX**, $n = 1$) corresponds to loss of CO from the parent ion, the complex showed no tendency to dissociate CO when left in solution. This contrasts with the behaviour of (**III**, $n = 1$). UV irradiation of a solution of (**IX**, $n = 1$) resulted in extensive decomposition and no products could be extracted from the reaction solution. Presumably the inability to form $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-dppm})(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3\text{-}$

Table 6
Selected bond lengths (Å) for the complex $(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\eta^1\text{-}PPh_2CH_2PPh_2)(\mu_2\text{-}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)$ (**IX**, $n = 1$) (estimated standard deviations in parentheses)

Metal–metal			
Rh(1)–Rh(2)	2.678(1)		
Hexafluorobut-2-yne			
Rh(1)–C(2)	2.01(1)	Rh(2)–C(3)	2.04(1)
C(1)–C(2)	1.52(1)	C(2)–C(3)	1.27(1)
C(3)–C(4)	1.49(1)		
Carbonyl ligand			
Rh(1)–C(5)	1.82(1)	C(5)–O(1)	1.15(1)
Bis(diphenylphosphino)methane ligand			
Rh(2)–P(1)	2.253(3)	P(1)–C(17)	1.84(1)
P(1)–C(23)	1.82(1)	P(1)–C(29)	1.85(1)
P(2)–C(29)	1.86(1)	P(2)–C(30)	1.82(1)
P(2)–C(36)	1.82(1)		

C_2CF_3) can be attributed to the need to have three bridging groups which would be difficult both sterically and electronically.



(IX)

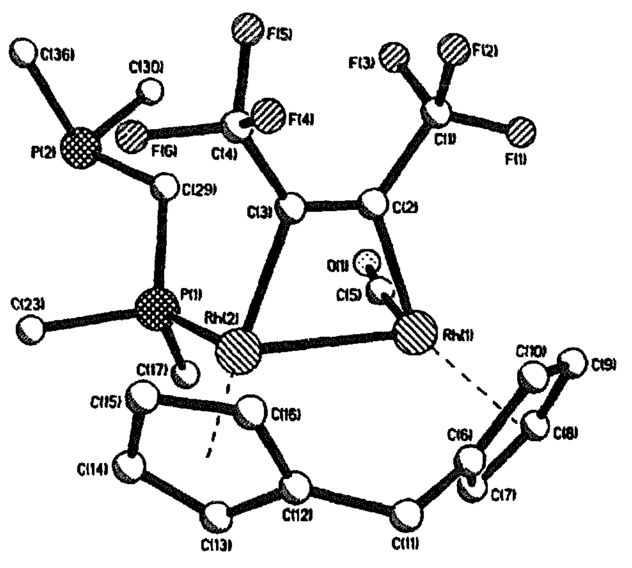


Fig. 6. The molecular structure of (η^5:η^5-$C_5H_4CH_2C_5H_4$)-Rh_2(CO)(η^1-$PPh_2CH_2PPh_2$)($\mu_2\eta^1$:η^1-$CF_3C_2CF_3$) (IX, $n = 1$) with the phenyl groups and hydrogen atoms omitted.

To determine how the bis(cyclopentadienyl)methane affects the geometry of these complexes, the crystal and molecular structure of (**IX**, $n = 1$) was determined by X-ray crystallography. The bond lengths and angles are given in Tables 6 and 7. A diagram of the molecular structure is shown in Fig. 6.

Although the arrangement of the carbonyl and bisphosphine ligands is clearly cis, these ligands do lean away from each other. This is indicated by the angles of 101.9(4)° and 97.78(7)° for Rh(2)–Rh(1)–C(5) and Rh(1)–Rh(2)–P(1) respectively. The rhodium–rhodium bond length is 2.677(1) Å and this is significantly shorter than the corresponding distance (2.734(2) Å) in the related complex (**III**, $n = 2$). The shortening of the rhodium–rhodium distance in complexes where two individual cyclopentadienyl groups are replaced by a single bis(cyclopentadienyl)methane ligand has been observed previously [25]. There are no unusual features within the bond parameters for the various ligands, except that the bis(cyclopentadienyl)methane ligand appears to be disordered over at least two closely related sites, as evidenced in the anisotropic thermal parameters.

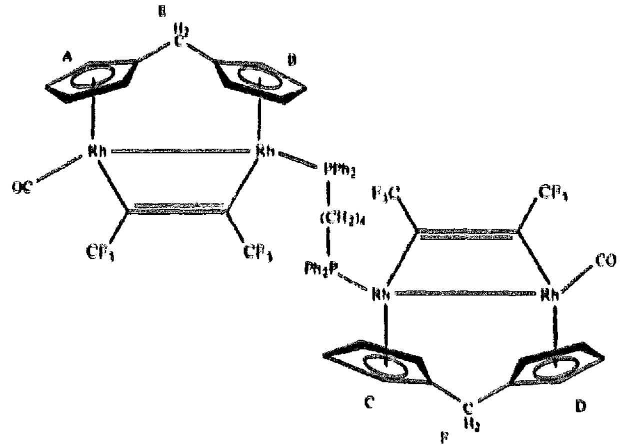
From inspection of the molecular structure of (**IX**, $n = 1$), there does not appear to be a steric barrier to formation of the decarbonylation product (η^5:η^5-$C_5H_4CH_2C_5H_4$)Rh_2(μ_2-η^1:η^1-dppm)(μ_2-η^1:η^1-CF_3-C_2CF_3). However, formation of this product would require prior dissociation of the carbonyl. This contrasts with the conversion of (**III**, $n = 1$) to (**IV**) where there is a 'back-end' approach of the phosphine.

Treatment of (**II**) with other bisphosphines gave related complexes (**III**, $n = 2$–4). These products were isolated in yields of about 20–25%, and all were fully

Table 7
Selected bond angles (deg) for the complex (η^5:η^5-$C_5H_4CH_2C_5H_4$)Rh_2(CO)(η^1-$PPh_2CH_2PPh_2$)(μ_2-η^1:η^1-$CF_3C_2CF_3$) (IX, $n = 1$) (estimated standard deviations in parentheses)

Around the metals			
Rh(2)–Rh(1)–C(2)	69.0(3)	Rh(1)–Rh(2)–C(3)	70.2(3)
Rh(2)–Rh(1)–C(5)	101.9(3)	Rh(1)–Rh(2)–P(1)	97.78(7)
C(2)–Rh(1)–C(5)	90.1(4)	P(1)–Rh(2)–C(3)	93.9(3)
Carbonyl ligand			
Rh(1)–C(5)–O(1)	173.5(10)		
Bis(diphenylphosphino)methane ligand			
Rh(2)–P(1)–C(29)	115.5(3)	Rh(2)–P(1)–C(23)	116.6(3)
Rh(2)–P(1)–C(23)	111.6(3)	C(17)–P(1)–C(23)	101.6(4)
C(17)–P(1)–C(29)	106.6(4)	C(23)–P(1)–C(29)	103.3(4)
C(29)–P(2)–C(30)	101.5(5)	C(29)–P(2)–C(36)	102.0(5)
P(1)–C(29)–P(2)	118.3(5)	C(30)–P(2)–C(36)	101.8(4)
Hexafluorobut-2-yne			
Rh(1)–C(2)–C(3)	113.0(7)	Rh(2)–C(3)–C(2)	107.6(7)
C(1)–C(2)–C(3)	127.0(9)	C(2)–C(3)–C(4)	130.2(10)
Rh(1)–C(2)–C(1)	120.0(8)	Rh(2)–C(3)–C(4)	122.0(8)

characterized from elemental analyses and spectroscopic results (see Section 2). The reaction of $Ph_2P(CH_2)_4PPh_2$ with two equivalents of (II) was also investigated. This gave $[(\eta^5:\eta^5\text{-}C_5H_4CH_2C_5H_4)Rh_2(CO)(\mu_2\text{-}\eta^1:\eta^1\text{-}CF_3C_2CF_3)]_2(\mu_2\text{-}\eta^1:\eta^1\text{-dppb})$ (X) which was isolated in 18% yield. The proposed structure of (X) is supported by spectroscopic results, but there are some unusual observations. In particular, the multinuclear NMR results indicate that either the preferred conformation is unsymmetrical or that two conformers co-exist in solution. The most telling evidence comes from the $^{31}P\{^1H\}$ NMR spectrum which reveals two equally intense doublets at δ 36.4 and 37.2, each with phosphorus–rhodium coupling of 179 Hz. There are also 12 proton resonances for the cyclopentadienyl hydrogens (rather than the eight expected for a symmetrical structure) in the ^1H NMR spectrum. The resonances for the methylene protons (E and F) are also more complex than would apply if the structure was symmetrical. Thus there are doublet resonances at δ 3.82 and 3.85 each of relative intensity 1H, and a further resonance of twice this intensity at δ 4.21. The latter resonance is either a doublet of doublets or two overlapping doublets.



(X)

4. Summary

The dirhodium complexes chosen for this investigation have led to the formation of a range of complexes with unidentate attached bis(diphenylphosphino)alkanes. By manipulating the ligands on an Rh–Rh bond, we have been able to force a change in the stereochemistry of the products. Thus, the addition of bis(diphenylphosphino)alkanes to the bis(cyclopentadienyl) complex (I) results in a trans arrangement of CO and coordinated phosphorus, whereas related additions to the di(cyclopentadienyl)methane complex (II) give products with a cis orientation of CO and P. This does result in a change in reactivity for some of the complexes. For example, the bis(diphenylphosphino)methane complex (III, $n = 1$) readily decarbonylates to form (IV) when left in solution, whereas the related complex (IX, $n = 1$) remains unchanged in solution. The unidentate attachment of the bisphosphine ligands provides a site for the attachment of other metal complexes, and this is explored in the following paper.

5. Supplementary material

Tables of fractional atomic coordinates, anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles and observed and calculated structure factors are available as supplementary material.

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