

# Complexes containing the unit $\text{Rh}_2\text{P}^{\wedge}\text{PM}$ ( $\text{M} = \text{Cr}$ or $\text{Mn}$ , $\text{P}^{\wedge}\text{P} = \text{bis}(\text{diphenylphosphino})$ alkane); the independence of the metal centres

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## Abstract

Treatment of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**I**) with  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  or  $\text{Cr}(\text{CO})_5(\text{thf})$  gives the hetero-trinuclear products  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{:}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 1\text{--}4$ ) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{:}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{Cr}(\text{CO})_5$  (**IV**,  $n = 1\text{--}4$ ) in good yields. In these products, the configuration of the CO and bisphosphine units on the Rh–Rh bond is trans. Related reactions between  $(\eta^5\text{:}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**V**) and the same solvated manganese and chromium complexes give  $(\eta^5\text{:}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{:}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**VI**,  $n = 1, 2$  or  $4$ ) and  $(\eta^5\text{:}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{:}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\text{CrCO})_5$  (**VIII**). The complexes (**VI**) and (**VIII**) have a mutually cis arrangement of CO and the bisphosphine on the Rh–Rh bond. Attempts to induce the complexes (**IV**), (**V**), (**VI**), and (**VIII**) to form clusters by loss of CO and the bisphosphine on the Rh–M bond formation were not successful. Treatment with trimethylamine oxide or sunlight irradiation generally resulted in loss of the hetero-metal and formation of the dirhodium phosphine oxide complexes (**III**,  $n = 2$  or  $4$ ) and (**VII**,  $n = 2, 3$ ).

**Keywords:** Dirhodium; Manganese; Chromium; Hetero-trinuclear; Bisphosphine

## 1. Introduction

Previously [1], we described the formation and characterization of the complexes  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**I**). In these complexes, the bisphosphine is unidentate attached to one rhodium only. When left in solution, (**I**,  $n = 1$ ) loses CO to give  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$ , but solutions of the other complexes are stable over long periods of time. Some bis(dinuclear) complexes  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)]_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}$  were also described in that paper. These were formed by the addition of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  to (**I**). This indicates that it

should be possible to add other metal complexes to the free phosphorus atom in (**I**) and hence form a range of hetero-polynuclear complexes containing the unit  $[\text{Rh}\text{--}\text{Rh}\text{--}\text{P}(\text{CH}_2)_n\text{--}\text{P}\text{--}\text{M}]$ . We have achieved this type of reaction where  $\text{M} = \text{Mn}$  or  $\text{Cr}$ , and the results of the investigation are described in this paper. Attempts to modify these complexes by removal of CO did not achieve the intended aim of cluster formation.

## 2. Experimental

The general procedures and instrumentation were described elsewhere [1]. Tetrahydrofuran (thf) was stored over Na–K alloy and distilled before use. Literature procedures were used to prepare the complexes  $(\eta^1\text{-dppm})\text{Fe}(\text{CO})_4$  [2] and *cis*, *mer*- $\text{MnBr}(\text{CO})_2(\eta^2\text{-dppm})(\eta^1\text{dppm})$  [3]. An Hanovia photochemical reactor was used for the photolysis reactions.

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2.1. Reactions of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**I**) with  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$

For each reaction,  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  was freshly prepared by UV irradiation of a solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$  (0.90 ml) in thf (100 ml) at 0°C. Irradiation was continued until infrared analysis of the solution revealed complete conversion to the solvate [4]. This gave a solution of concentration  $0.055\text{ mol dm}^{-3}$ , and an appropriate aliquot was taken.

#### 2.1.1. $n = 1$

A solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  (2.0 ml, 0.11 mmol) in thf was added by syringe to a stirred solution of (**I**,  $n = 1$ ) (95 mg, 0.10 mmol) in thf (10 ml). After 1 h, solvent was removed under reduced pressure. Preparative TLC of the crude product with a 1:1 mixture of dichloromethane and petroleum spirit separated a major red band from some decomposition material in the baseline. The major red band was extracted with dichloromethane, and a red powder was obtained upon removal of the solvent. The red solid was characterized spectroscopically as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_1\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 1$ ) (88 mg, 80%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1987 s, 1926 s, 1856  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.72 (s, 3H,  $\text{CH}_3$ ), 2.80 (m, 2H,  $\text{CH}_2\text{-P}$ ), 3.60–3.85 (br m, 4H,  $\text{C}_5\text{H}_4$ ), 4.92 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 6.80–7.20 (br m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -50.4 (qm,  $J_{\text{F-F}} = 12.3\text{ Hz}$ , 3F,  $\text{CF}_3$ ), -55.3 (qm,  $J_{\text{F-F}} = 12.3\text{ Hz}$ , 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  38.5 (dd,  $J_{\text{Rh-P}} = 182\text{ Hz}$ ,  $J_{\text{P-P}} = 37\text{ Hz}$ , 1P,  $P\text{-Rh}$ ), 88.6 (d,  $J_{\text{P-P}} = 37\text{ Hz}$ , 1P,  $P\text{-Mn}$ ).

#### 2.1.2. $n = 2$

A solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  (2.5 ml, 0.14 mmol) in thf was added to a solution of (**I**,  $n = 2$ ) (100 mg, 0.11 mmol) in thf (10 ml). Preparative TLC with a 1:1 mixture of diethyl ether and petroleum spirit as eluant developed a major red band which was collected and characterized spectroscopically as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 2$ ) (88 mg, 87%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1988 s, 1924 s, 1857  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.73 (s, 3H,  $\text{CH}_3$ ), 2.00–2.30 (m, 4H,  $2 \times \text{CH}_2$ ), 3.91 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.03 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.86 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.14 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.28–7.65 (br m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.8 (m, 3F,  $\text{CF}_3$ ), -55.4 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  38.9 (dd,  $J_{\text{Rh-P}} = 180\text{ Hz}$ ,  $J_{\text{P-P}} = 26\text{ Hz}$ , 1P,  $P\text{-Rh}$ ), 89.1 (d,  $J_{\text{P-P}} = 26\text{ Hz}$ , 1P,  $P\text{-Mn}$ ). FAB mass spectrum (DMF, 3NBA), positive ion: no parent ion observed, 1086

(22%,  $\text{M} - \text{CO}$ ), 1058 (32%,  $\text{M} - 2\text{CO}$ ), 1030 (16%,  $\text{M} - 3\text{CO}$ ).

#### 2.1.3. $n = 3$

A solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  (1.8 ml, 0.10 mmol) in thf was added to a solution of (**I**,  $n = 3$ ) (73 mg, 0.078 mmol). Preparative TLC with a 1:1 mixture of diethyl ether and petroleum spirit as eluant produced one major red band which was collected and characterised as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{-CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 3$ ) (63 mg, 77%). Anal. Found: C, 53.0; H, 4.3.  $\text{C}_{50}\text{H}_{43}\text{F}_6\text{MnO}_3\text{P}_2\text{Rh}_2$ . Calc.: C, 53.2; H, 3.8%.

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1987 s, 1924 s, 1856  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.71 (s, 3H,  $\text{CH}_3$ ), 2.20–2.40 (br m, 6H,  $\text{CH}_2$ ), 3.60–4.00 (br m, 4H,  $\text{C}_5\text{H}_4$ ), 5.00 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.03 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.25–7.44 (br m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.0 (m, 3F,  $\text{CF}_3$ ), -55.2 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  38.9 (d,  $J_{\text{Rh-P}} = 186\text{ Hz}$ , 1P,  $P\text{-Rh}$ ), 84.1 (s, 1P,  $P\text{-Mn}$ ). FAB mass spectrum (DMF, 3NBA), positive ion: 1128 (3%,  $\text{M}$ ), 1100 (2%,  $\text{M} - \text{CO}$ ).

#### 2.1.4. $n = 4$

A solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  (1.7 ml, 0.093 mmol) in thf was added to a solution of (**I**,  $n = 4$ ) (81 mg, 0.085 mmol). Preparative TLC with a 1:1 mixture of dichloromethane and petroleum spirit as eluant produced one major band which was collected and characterized as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{-CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 4$ ) (81 mg, 83%). Anal. Found: C, 53.2; H, 3.8.  $\text{C}_{51}\text{H}_{45}\text{F}_6\text{MnO}_3\text{P}_2\text{Rh}_2$ . Calc.: C, 53.6; H, 3.9%.

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1987 s, 1924 s, 1856  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.30–1.45 (br m, 4H,  $\text{CH}_2$ ), 1.55 (m, 2H,  $\text{CH}_2$ ), 1.80 (s, 3H,  $\text{CH}_3$ ), 2.20 (m, 2H,  $\text{CH}_2$ ), 3.97 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.09 (m, 2H,  $\text{C}_5\text{H}_4$ ), 5.02 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.06 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.30–7.55 (br m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.4 (m, 3F,  $\text{CF}_3$ ), -55.6 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  36.5 (d,  $J_{\text{Rh-P}} = 178\text{ Hz}$ , 1P,  $P\text{-Rh}$ ), 84.6 (s, 1P,  $P\text{-Mn}$ ). FAB mass spectrum (DMF, 3NBA), positive ion: 1142 (5%,  $\text{M}$ ), 1114 (5%,  $\text{M} - \text{CO}$ ).

2.2. Some attempted decarbonylation reactions; treatment of the complexes (**II**) with  $\text{Me}_3\text{NO}$ , and irradiation with sunlight

#### 2.2.1. **II**, $n = 1$

A solution of (**II**,  $n = 1$ ) (38 mg) in a 9:1 mixture of hexane and dichloromethane (30 ml) was exposed to sunlight over a 5 day period. After concentration of the solution, preparative TLC with a 1:2 mixture of diethyl ether and petroleum spirit as eluant separated a major

red band from a minor red band and considerable decomposition material in the base band. The major red band was extracted with dichloromethane and the product identified ( $R_f$  value, and IR and  $^{31}\text{P}$  NMR spectra [1]) as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  (20 mg, 66%). The material in the minor red band was identified ( $R_f$  value, IR spectrum) as unchanged starting material (8 mg, 21%). No manganese-containing species were isolated.

### 2.2.2. II, $n = 2$

After similar irradiation of a solution of (II,  $n = 2$ ) (41 mg), a small amount (5–10 mg) of a brown residue had formed on the sides of the reaction flask. It consisted of a mixture of products, none of which were identified. Preparative TLC of the remaining solution with a 1:1 mixture of dichloromethane and petroleum spirit as eluant separated a major red band from a minor red band, three very minor bands and decomposition material in the base band. The major red band was extracted with dichloromethane and identified ( $R_f$  value, IR spectrum) as unchanged starting material (II,  $n = 2$ ) (15 mg, 37%). The minor red band was identified spectroscopically as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2\}$  (III,  $n = 2$ ) (less than 5 mg).

IR spectrum:  $\nu(\text{CO})$  1988  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.90 (m, 4H,  $2 \times \text{CH}_2$ ), 5.04 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.09 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.15–7.55 (br m, 20 H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.7 (m, 3F,  $\text{CF}_3$ ), -55.6 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  33.0 (d,  $J_{\text{P-P}} = 31$  Hz, 1P,  $\text{P}=\text{O}$ ), 37.9 (dd,  $J_{\text{Rh-P}} = 179$  Hz,  $J_{\text{P-P}} = 31$  Hz, 1P,  $\text{Rh-P}$ ). Mass spectrum,  $m/z$ : no parent ion observed, 526 (2%,  $\text{M} - \text{dppeO}$ ), 414 (5%,  $\text{dppeO}$ ).

Another solution of (II,  $n = 2$ ) (40 mg) in acetone (30 ml) was treated with an equimolar amount of trimethylamine oxide added in two equal portions at 15 min intervals. The reaction mixture was stirred for 7 h and then filtered through Celite. Evaporation of some solvent followed by preparative TLC with a 2:1 mixture of dichloromethane and petroleum spirit as eluant separated unchanged starting material (II,  $n = 2$ ) (8 mg, 20%) and (III,  $n = 2$ ) (9 mg, 27%) from several minor bands and decomposition material in the base band.

### 2.2.3. II, $n = 4$

The complex (II,  $n = 4$ ) (51 mg) was treated with trimethylamine oxide as described above for (II,  $n = 2$ ). Subsequent workup by preparative TLC with a 1:3 mixture of diethyl ether and petroleum spirit as eluant produced two major red bands, four minor bands which were rejected, and considerable decomposition material in the base band. The first red band was identified ( $R_f$  value, IR spectrum) as unchanged starting material (II,

$n = 4$ ) (10 mg, 20%). The second red band was characterized spectroscopically as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{P}(\text{O})\text{Ph}_2\}$  (III,  $n = 4$ ) (11 mg, 25%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1987  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.50 (m, 4H,  $\text{CH}_2$ ), 1.98 (m, 4H,  $\text{CH}_2$ ), 5.05 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.09 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.20–7.60 (br m, 20 H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.7 (m, 3F,  $\text{CF}_3$ ), -55.8 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  32.5 (s, 1P,  $\text{P}=\text{O}$ ), 37.5 (d,  $J_{\text{Rh-P}} = 180$  Hz, 1P,  $\text{Rh-P}$ ). Mass spectrum,  $m/z$ : no parent ion observed, 498 (5%,  $\text{M} - \text{CO} - \text{dppbO}$ ), 442 (11%,  $\text{dppbO}$ ).

### 2.3. Reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$ (I) with $\text{Cr}(\text{CO})_5(\text{thf})$

Before each reaction, the solvate  $\text{Cr}(\text{CO})_5(\text{thf})$  was freshly prepared by UV irradiation of a solution of  $\text{Cr}(\text{CO})_6$  in thf at 0°C. Irradiation was monitored by infrared spectroscopy and continued until conversion to the solvate was complete (ca. 1.5 h).

#### 2.3.1. $n = 2$

A solution of  $\text{Cr}(\text{CO})_5(\text{thf})$  (1.7 ml, 0.079 mmol) in thf was added by syringe to a solution of (I,  $n = 2$ ) (60 mg, 0.065 mmol) in thf (10 ml). The mixture was allowed to stir for 1.5 h after which time the solvent was removed under reduced pressure. Preparative TLC of the product with a 1:1 mixture of dichloromethane and petroleum spirit as eluant produced a major orange-red band which was extracted with dichloromethane. Removal of solvent gave a red powder which was characterized as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}\text{Cr}(\text{CO})_5$  (IV,  $n = 2$ ) (62 mg, 85%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2063 w, 1988 m, 1938 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.55 (m, 2H,  $\text{CH}_2$ ), 1.81 (m, 2H,  $\text{CH}_2$ ), 4.82 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.13 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.10–7.55 (m, 20 H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.8 (qm,  $J_{\text{F-F}} = 12$  Hz, 3F,  $\text{CF}_3$ ), -55.5 (qm,  $J_{\text{F-F}} = 12$  Hz, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  36.7 (dd,  $J_{\text{Rh-P}} = 182$  Hz,  $J_{\text{P-P}} = 19$  Hz, 1P,  $\text{P-Rh}$ ), 51.9 (d,  $J_{\text{P-P}} = 19$  Hz, 1P,  $\text{P-Cr}$ ). FAB mass spectrum (DMF, 3NBA) positive ion: 1116 (4%, M), 1088 (5%,  $\text{M} - \text{CO}$ ), 1060 (7%,  $\text{M} - 2\text{CO}$ ).

#### 2.3.2. $n = 4$

Using the same experimental conditions, (I,  $n = 4$ ) (79 mg, 0.083 mmol) was treated with  $\text{Cr}(\text{CO})_5(\text{thf})$  (1.8 ml, 0.089 mmol). Workup by preparative TLC with a 1:1 mixture of dichloromethane and petroleum spirit as eluant produced one major orange-red band which was extracted with dichloromethane and characterized

as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2\}\text{Cr}(\text{CO})_5$  (**IV**,  $n = 4$ ) (83 mg, 87%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2062 w, 1988 m, 1938  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.60–2.60 (br m, 8H,  $\text{CH}_2$ ), 5.02 (s, 5H,  $\text{C}_5\text{H}_5$ ), 5.07 (s, 5H,  $\text{C}_5\text{H}_5$ ), 7.27–7.00 (m, 20H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -51.4 (qm,  $J_{\text{F-F}} = 10$  Hz, 3F,  $\text{CF}_3$ ), -55.6 (m, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  36.0 (d,  $J_{\text{Rh-P}} = 180$  Hz, 1P,  $P\text{-Rh}$ ), 46.3 (s, 1P,  $P\text{-Cr}$ ). FAB mass spectrum ( $\text{CHCl}_3$ , 3NBA), positive ion: 1145 (40%, M), 1117 (13%, M - CO), 1088 (11%, M - 2CO), 1060 (11%, M - 3CO), 1032 (7%, M - 4CO), 1004 (22%, M - 5CO), 976 (24%, M - 6CO).

#### 2.4. Some attempted decarbonylation reactions; treatment of the complexes (**IV**) with $\text{Me}_3\text{NO}$ , and irradiation with sunlight

The reactions were performed as described in Section 2.2.

##### 2.4.1. **IV**, $n = 2$

Treatment of (**IV**,  $n = 2$ ) (55 mg) with trimethylamine oxide and workup by preparative TLC with a 1:2 mixture of chloroform and petroleum spirit as eluant separated two major red bands from three very minor bands and considerable decomposition material in the base band. The first major red band was identified ( $R_f$  value and IR spectrum) as unchanged starting material (**IV**,  $n = 2$ ) (6 mg, 11%). The second red band was characterized spectroscopically as the phosphine oxide complex (**III**,  $n = 2$ ) (10 mg, 22%). None of the remaining minor bands was present in sufficient quantity for characterization.

Another solution of (**IV**,  $n = 2$ ) (52 mg) was exposed to sunlight over a 7 day period. After this time the solution was separated from a brown solid which had formed on the walls of the reaction vessel. Workup by preparative TLC with a 1:2 mixture of chloroform and petroleum spirit as eluant separated one major red band from a minor red band, three very minor bands and decomposition material in the base band. The major red band was identified ( $R_f$  value, IR spectrum) as unchanged starting material (**IV**,  $n = 2$ ) (10 mg, 19%). The minor red band was identified ( $R_f$  value, IR spectrum) as (**III**,  $n = 2$ ) (less than 5 mg). None of the remaining bands was present in sufficient quantity for characterization.

##### 2.4.2. **IV**, $n = 4$

After treatment of (**IV**,  $n = 4$ ) (51 mg) with trimethylamine oxide, workup by preparative TLC with a 1:3 mixture of diethyl ether and petroleum spirit as eluant separated two major red bands from two very minor bands and considerable decomposition material in the base band. The first major red band was identified

( $R_f$  value, IR spectrum) as unchanged starting material (**IV**,  $n = 4$ ) (10 mg, 20%). The second red band was identified spectroscopically as (**III**,  $n = 4$ ) (11 mg, 26%).

#### 2.5. Reactions of $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$ (**V**) with $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{thf})$

##### 2.5.1. $n = 1$

A freshly prepared solution of  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{-Mn}(\text{CO})_2(\text{thf})$  (2.0 ml, 0.081 mmol) in thf was added by syringe to a stirred solution of (**V**,  $n = 1$ ) (60 mg, 0.065 mmol) in thf (15 ml). After 1 h, some solvent was removed under reduced pressure. Preparative TLC of the remaining solution with a 1:1 mixture of dichloromethane and petroleum spirit as eluant resulted in one major red band. This was extracted with dichloromethane and the solvent removed to yield a red powder which was characterized as  $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{-CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2\}(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**VI**,  $n = 1$ ) (53 mg, 73%). Anal. Found: C, 53.2; H, 3.6.  $\text{C}_{49}\text{H}_{39}\text{F}_6\text{MnO}_3\text{P}_2\text{Rh}_2$ . Calc.: C, 52.9; H, 3.5%.

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1975 m, 1925 m, 1859  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.61 (s, 3H,  $\text{CH}_3$ ), 3.00 (m, 1H,  $\text{CHH}'$  of dppm), 3.25 (m, 1H,  $\text{CHH}'$  of dppm), 3.62–3.82 (m, 5H,  $\text{C}_5\text{H}_4\text{-Mn}$  (4H) and  $\text{CHH}'$  (1H)), 4.14 (m, 2H,  $\text{C}_5\text{H}_4$  (1H) and  $\text{CHH}'$  (1H)), 4.39 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.63 (m, 2H,  $\text{C}_5\text{H}_4$ ), 5.16 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.45 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.88–5.90 (m, 2H,  $\text{C}_5\text{H}_4$ ), 6.90–7.20 (m, 18H,  $\text{C}_6\text{H}_5$ ), 7.95 (m, 2H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -50.8 (m,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ), -55.2 (m,  $J_{\text{F-F}} = 10$  Hz, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  43.1 (dd,  $J_{\text{Rh-P}} = 181$  Hz,  $J_{\text{P-P}} = 39$  Hz, 1P,  $P\text{-Rh}$ ), 90.3 (d,  $J_{\text{P-P}} = 39$  Hz, 1P,  $P\text{-Mn}$ ).

##### 2.5.2. $n = 2$

$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  (1.5 ml, 0.079 mmol) was added to a solution of (**V**,  $n = 2$ ) (61 mg, 0.065 mmol). Preparative TLC with a 1:2 mixture of diethyl ether and petroleum spirit as eluant resulted in one major red band which was collected and characterized as  $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{-C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**VI**,  $n = 2$ ) (58 mg, 79%). Anal. Found: C, 53.3; H, 3.6.  $\text{C}_{50}\text{H}_{41}\text{F}_6\text{MnO}_3\text{P}_2\text{Rh}_2$ . Calc.: C, 53.3; H, 3.6%.

IR spectrum:  $\nu(\text{CO})$  1978 m, 1923 m, 1855  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.71 (s, 3H,  $\text{CH}_3$ ), 2.00–2.10 (br m, 4H,  $\text{CH}_2$  of dppe), 3.78–3.84 (m, 2H,  $\text{CH}_2$ ), 3.90 (br s, 1H,  $\text{C}_5\text{H}_4$ ), 3.96 (br s, 1H,  $\text{C}_5\text{H}_4$ ), 4.04 (br s, 1H,  $\text{C}_5\text{H}_4$ ), 4.12–4.21 (m, 2H,  $\text{C}_5\text{H}_4$ ), 4.50–4.62 (m, 3H,  $\text{C}_5\text{H}_4$ ), 5.38 (br s, 1H,  $\text{C}_5\text{H}_4$ ), 5.80–5.90 (m, 3H,  $\text{C}_5\text{H}_4$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -54.9 (br m, 3F,  $\text{CF}_3$ ), -52.3 (br m, 3F,  $\text{CF}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  38.9 (dd,  $J_{\text{Rh-P}} = 181$  Hz,  $J_{\text{P-P}} = 30$  Hz, 1P, P–Rh), 89.9 (d,  $J_{\text{P-P}} = 30$  Hz, 1P, P–Mn).

### 2.5.3. $n = 4$

$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (thf) (1.6 ml, 0.072 mmol) was added to a solution of (V) (60 mg, 0.062 mmol). Preparative TLC with a 2:1 mixture of diethyl ether and petroleum spirit as eluant separated a major red band from a minor red band. The major band was extracted with diethyl ether and characterized as  $(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1:\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1:\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (VI,  $n = 4$ ) (57 mg, 80%). IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1976 m, 1924 m, 1858  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.76 (s, 3H,  $\text{CH}_3$ ), 1.90–2.30 (m, 8H,  $\text{CH}_2$  of dppb), 3.82–3.95 (m, 3H, unassigned), 4.05–4.09 (m, 2H, unassigned), 4.21–4.26 (m, 1H, unassigned), 4.40 (s, 1H,  $\text{C}_5\text{H}_4$ ), 4.61–4.69 (m, 3H,  $\text{C}_5\text{H}_4$ ), 5.31 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.44 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.87–5.91 (m, 2H,  $\text{C}_5\text{H}_4$ ), 7.10–7.55 (br m, 18H,  $\text{C}_6\text{H}_5$ ), 7.90 (m, 2H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -51.8 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ), -55.2 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  37.4 (d,  $J_{\text{Rh-P}} = 179$  Hz, 1P, P–Rh), 84.4 (s, 1P, P–Mn).

### 2.6. Some attempted decarbonylation reactions; treatment of the complexes (VI) with $\text{Me}_3\text{NO}$ , and irradiation with sunlight

The reactions were performed as described in Section 2.2. Workup gave the following complexes.

(VI,  $n = 2$ ) +  $\text{Me}_3\text{NO}$ : unchanged (VI,  $n = 2$ ) (43%), and  $(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1:\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$  (VII,  $n = 2$ ) (17%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1977  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.60 (m, 4H,  $\text{CH}_2$  of dppe), 3.81 (d,  $J_{\text{H-H}} = 14.6$  Hz, 1H,  $\text{CH}_2$ ), 4.21 (dd,  $J_{\text{H-H}} = 14.8$  Hz,  $J_{\text{P-H}} = 3.9$  Hz, 1H,  $\text{CH}_2$ ), 4.44 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.60 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.67 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.74 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.27 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.40 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.84 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.88 (m, 1H,  $\text{C}_5\text{H}_4$ ), 7.10–7.65 (m, 18 H,  $\text{C}_6\text{H}_5$ ), 7.87 (m, 2H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -52.1 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ), -54.9 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  33.2 (d,  $J_{\text{P-P}} = 39$  Hz, 1P, P=O), 39.0 (dd,  $J_{\text{Rh-P}} = 180$  Hz,  $J_{\text{P-P}} = 39$  Hz, 1P, P–Rh). Mass spectrum,  $m/z$ : no parent ion observed; 924 (3%, M – CO), 510 (12%, M – CO – dppeO).

(VI,  $n = 4$ ), sunlight: unchanged (VI,  $n = 4$ ) (36%), (VII,  $n = 4$ ) (less than 5 mg).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1977  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  34.1 (s, 1P, P=O), 39.4 (d,  $J_{\text{Rh-P}} = 180$  Hz, 1P, Rh–P). Mass spectrum: no parent ion observed,  $m/z$  at 538 (2%, M – dpppO), 510 (10%, M – dpppO – CO).

### 2.7. Reaction of $(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1:\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\eta^1\text{-PPh}_2(\text{CH}_2)_3\text{PPh}_2)$ (V) with $\text{Cr}(\text{CO})_5(\text{thf})$

A freshly prepared solution of  $\text{Cr}(\text{CO})_5(\text{thf})$  (1.8 ml, 0.083 mmol) in thf was added to a stirred solution of (V) (68 mg, 0.072 mmol) in thf (20 ml). After 1 h, some solvent was removed under reduced pressure. Preparative TLC of the remaining solution with a 1:1 mixture of dichloromethane and petroleum spirit as eluant separated one major red band from decomposition material in the baseline. The red band was extracted with dichloromethane, and the solvent removed to yield an orange-red powder which was characterized as  $(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1:\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1:\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\text{Cr}(\text{CO})_5$  (VIII) (63 mg, 77%).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2062 w, 1977 m, 1937  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  1.50–2.05 (br m, 4H,  $\text{CH}_2$  of dppp), 2.23 (m, 2H,  $\text{CH}_2$  of dppp), 3.85 (d,  $J_{\text{H-H}} = 14.5$  Hz, 1H,  $\text{CH}_2$ ), 4.22 (dd,  $J_{\text{H-H}} = 14.8$  Hz,  $J_{\text{P-H}} = 3.6$  Hz, 1H,  $\text{CH}_2$ ), 4.46 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.59 (m, 1H,  $\text{C}_5\text{H}_4$ ), 4.68 (m, 2H,  $\text{C}_5\text{H}_4$ ), 5.21 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.36 (m, 1H,  $\text{C}_5\text{H}_4$ ), 5.87 (m, 2H,  $\text{C}_5\text{H}_4$ ), 7.05–7.45 (m, 18 H,  $\text{C}_6\text{H}_5$ ), 7.72 (m, 2H,  $\text{C}_6\text{H}_5$ ).  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  -52.3 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ), -55.3 (qm,  $J_{\text{F-F}} = 11$  Hz, 3F,  $\text{CF}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  38.0 (d,  $J_{\text{Rh-P}} = 180$  Hz, 1P, P–Rh), 45.9 (s, 1P, P–Cr).

### 2.8. The attempted decarbonylation of (VIII)

The reactions were performed as described in Section 2.2. Workup gave the following complexes.

(VIII) +  $\text{Me}_3\text{NO}$ : unchanged (VIII) (40%) and (VII,  $n = 3$ ) (23%). Spectroscopic characterization of (VII,  $n = 3$ ).

IR spectrum ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1977  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  34.1 (s, 1P, P=O), 39.4 (d,  $J_{\text{Rh-P}} = 180$  Hz, 1P, Rh–P). Mass spectrum,  $m/z$ : no parent ion observed, 538 (2%, M – dpppO), 510 (10%, M – CO – dpppO).

(VIII)/sunlight: unchanged (VIII) (59%).

### 2.9. Reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$ with $(\eta^1\text{-dppm})\text{Fe}(\text{CO})_4$

A thf solution of  $(\eta^1\text{-dppm})\text{Fe}(\text{CO})_4$  (105 mg, 0.190 mmol) was treated with solid  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  (100 mg, 0.190 mmol). The mixture was stirred at room temperature for 1 h. The solvent was then evaporated under reduced pressure and the residue subjected to TLC. Using a 1:2 mixture of dichloromethane and petroleum spirit as eluant, three bands were separated. The first yellow band yielded the complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^1:\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (19 mg, 18%). The third band was extracted with diethyl

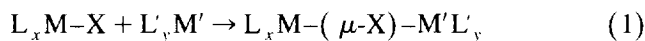
ether and characterized spectroscopically as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppm})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (50 mg, 30%). A major proportion of the mixture remained as an inextractable base band.

### 2.10. Reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$ with *cis, mer*- $\text{MnBr}(\text{CO})_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})$

*cis, mer*- $\text{MnBr}(\text{CO})_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})$  (84 mg, 0.088 mmol) as a solution in toluene (6 ml), was added dropwise to a solution of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  (49 mg, 0.093 mmol) also in toluene (15 ml). Over a 2 h period, the solution colour was observed to change from green to yellow-brown. The reaction was left to continue for 72 h, after which time the reaction was still incomplete. After solvent evaporation under reduced pressure, TLC of the residue with a 2:1 mixture of petroleum spirit and dichloromethane as eluant separated five bands from decomposition material in the base band. The first (green) and second (yellow) bands were identified spectroscopically as unchanged starting material,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  (7 mg) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (17 mg, 40%) respectively. The third band was minor and was not characterized. Band four (orange) was characterized ( $R_f$  value, IR spectrum) as  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-dppm})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (10 mg, 33%), and the fifth band yielded a trace amount of purple crystals, identified spectroscopically [4] as  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$ .

### 3. Results and discussion

The proposed synthesis of new hetero-trinuclear complexes was based on the established [5] bridge-assisted approach shown in Eq. (1).



The 'free' end of the unidentate attached bisphosphine in the complexes  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**I**,  $n = 1-4$ ) was the target for the attachment of metal complexes  $\text{L}'_y\text{M}'$ . To test the viability of the reaction, two readily prepared solvated complexes were added to solutions of (**I**). These were the manganese complex  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  and the chromium complex  $\text{Cr}(\text{CO})_5(\text{thf})$ . Each is readily prepared by UV photolysis of the parent carbonyl in thf.

The additions of the manganese complex to (**I**,  $n = 1-4$ ) were done in thf at room temperature. Workup of the reaction solutions by preparative TLC gave the products  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**II**,  $n = 1-4$ ) in 75–85% yields. They were isolated as air

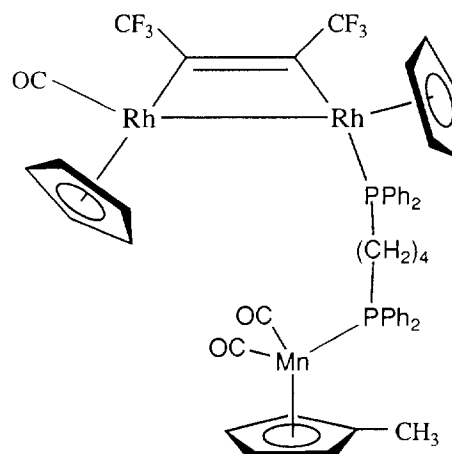


Fig. 1. Complex (**II**,  $n = 4$ ).

stable red solids. A diagrammatic representation of the structure of the bis(diphenylphosphino)butane complex (**II**,  $n = 4$ ) is shown in Fig. 1. In the infrared spectrum of this complex, three strong carbonyl absorptions were observed at 1987, 1926 and 1856  $\text{cm}^{-1}$ . The highest frequency band is assigned to the single carbonyl attached to rhodium, and is not shifted from that in the starting complex (**I**,  $n = 4$ ). The remaining carbonyl absorptions are assigned to the two carbonyls attached to manganese. Again, these are not shifted significantly from the carbonyl absorptions at 1921 and 1848  $\text{cm}^{-1}$  for the solvated reactant  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$ . The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra (see Section 2) are consistent with the proposed structure. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum contains two signals of equal intensity, a doublet at  $\delta$  36.5 and a singlet at  $\delta$  84.6. The coupling of 178 Hz in the doublet indicates that this resonance can be assigned to the phosphorus atom directly attached to rhodium [6]. The other resonance is therefore assigned to the phosphorus attached to manganese. This resonance has shifted about 100 ppm from that for the free phosphorus in the starting complex (**I**,  $n = 4$ ). The chemical shift is similar to that at  $\delta$  85.5 for the complex  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$  [7]. Similar spectroscopic results were obtained for the related complexes (**II**,  $n = 1-3$ ).

The complexes (**II**,  $n = 1-4$ ) behave essentially as equimolar mixtures of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  and  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$  sharing a common bis(diphenylphosphino)alkane unit. In an attempt to induce an intramolecular rearrangement reaction, a solution of one of the complexes (**IV**,  $n = 2$ ) was exposed to sunlight for several days. We have found previously that sunlight irradiation is a mild and effective way of inducing decarbonylation in some complexes containing the  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)$  moiety [8]. With (**IV**,  $n = 2$ ), there was about 40% recovery after 5 days. A number of decom-

position products were evident, but the only one that could be isolated and characterized was the phosphine oxide complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{-P}(\text{O})\text{Ph}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**III**,  $n = 2$ ). The spectroscopic properties of this complex were similar to those for (**I**,  $n = 2$ ) except that the chemical shift of the oxidized phosphorus atom was shifted to  $\delta$  33.0 in the  $^{31}\text{P}$  NMR spectrum. From a similar irradiation of the complex (**IV**,  $n = 1$ ), the major product isolated (66% yield) was  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2\text{-}(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\}$ . This is presumably formed by initial dissociation of  $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2]$  from (**IV**,  $n = 1$ ) to give (**I**,  $n = 1$ ) which is known [1] to undergo facile decarbonylation in solution.

The use of trimethylamine oxide offers an alternative approach to decarbonylation reactions with some metal carbonyl systems [9]. For example, we have used it effectively in the conversion of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  to  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  [10]. The effect of treating the complexes (**IV**,  $n = 2$  and 4) with trimethylamine oxide was investigated. The only species isolated from these reactions were the starting complexes (20% recovery after 7 h) and the phosphine oxide complexes (**III**,  $n = 2$  and 4) which were isolated in about 25% yield. It seems probable that oxygen is transferred directly from nitrogen to phosphorus in these reactions. Other workers have observed the oxidation by trimethylamine oxide of phosphorus atoms within complexes [11,12]. To test this idea further, a mixture of (**I**,  $n = 4$ ) and trimethylamine oxide in acetone was stirred for 6 h. The only product isolated was (**III**,  $n = 4$ ).

In order to bind a species with a different ligand conformation to the dangling phosphorus atom in the complexes (**I**), (**I**,  $n = 2$  and 4) were treated with  $\text{Cr}(\text{CO})_5(\text{thf})$ . This gave the new heteronuclear complexes  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}\text{Cr}(\text{CO})_5$  (**IV**,  $n = 2$  and 4). The proposed structure for (**IV**,  $n = 2$ ) is shown in Fig. 2. In the infrared spectrum of this complex, three terminal carbonyl absorptions were observed at 2063, 1988 and  $1938\text{ cm}^{-1}$ . The infrared spectrum of the starting complex (**I**,  $n = 2$ ) has  $\nu(\text{CO})$  at  $1990\text{ cm}^{-1}$ , while that of the complex  $\text{Cr}(\text{CO})_5\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}$  exhibits three carbonyl absorptions at 2063(w), 1984(m) and  $1942(\text{s})\text{ cm}^{-1}$  [11]. Thus the two absorptions at 2063 and  $1938\text{ cm}^{-1}$  for (**IV**,  $n = 2$ ) are assigned to Cr–CO stretching frequencies, while the remaining absorption at  $1988\text{ cm}^{-1}$  is a combination of Rh–CO and Cr–CO frequencies. In the  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of this complex, a doublet of doublets is observed at  $\delta$  36.7 and a doublet at  $\delta$  51.9. The higher field resonance has couplings of 182 Hz (Rh–P) and 19 Hz (P–P') and is assigned to the phosphorus attached to rhodium. The other phosphorus chemical shift is similar to that at  $\delta$  50.7 for  $\text{Cr}(\text{CO})_5\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}$  [11] and is

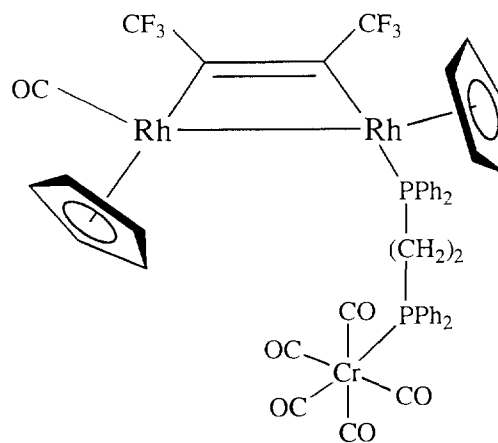


Fig. 2. Complex (**IV**,  $n = 2$ ).

assigned to the phosphorus attached to chromium. The spectroscopic results for the related complex (**IV**,  $n = 4$ ) are similar (see Section 2). As with the Rh<sub>2</sub>–Mn complexes (**II**), attempts to decarbonylate these complexes by sunlight irradiation or treatment with trimethylamine oxide gave the phosphine oxide products (**III**,  $n = 2$  and 4).

In the investigations described above, it is possible that decarbonylation of Rh and/or M (M = Mn or Cr) does occur, but that the geometry of the resultant intermediate is unsuitable for subsequent metal–metal bond formation to yield an Rh<sub>2</sub>M cluster. To determine whether stereochemistry has an effect on these reactions, we extended the study to the bis(cyclopentadienyl)methane complexes  $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_4)\text{-Rh}_2(\text{CO})(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (**V**). Owing to the restrictions imposed by the coordination of the bis(cyclopentadienyl)methane ligand, the CO and bisphosphine ligands must adopt a cis configuration on the Rh–Rh bond. Thus, as shown in Fig. 3, any metal species attached to the free end of the bisphosphine ligand has direct access to the Rh–CO site.

We prepared the following heteronuclear complexes by treatment of (**V**) with  $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{thf})$  or  $\text{Cr}(\text{CO})_5(\text{thf})$ ;  $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$  (**VI**,  $n = 1, 2$  or 4) and  $(\eta^5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1\text{:}\eta^1\text{-CF}_3\text{C}_2\text{CF}_3)\{\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\}\text{Cr}(\text{CO})_5$  (**VII**). The isolated yields were generally about 75–80%. Except for the greater complexity in the  $^1\text{H}$  NMR spectra due to the non-equivalence of the ring protons, the spectroscopic properties of these complexes were similar to those for (**II**) and (**IV**). The proposed structure for (**VII**) is shown in Fig. 4. Once again, our aim of cluster formation by decarbonylation of these complexes was not achieved. If anything, these complexes were even more stable under decarbonylation conditions than the corresponding bis(cyclopentadienyl) complexes (**II**) and (**IV**). In

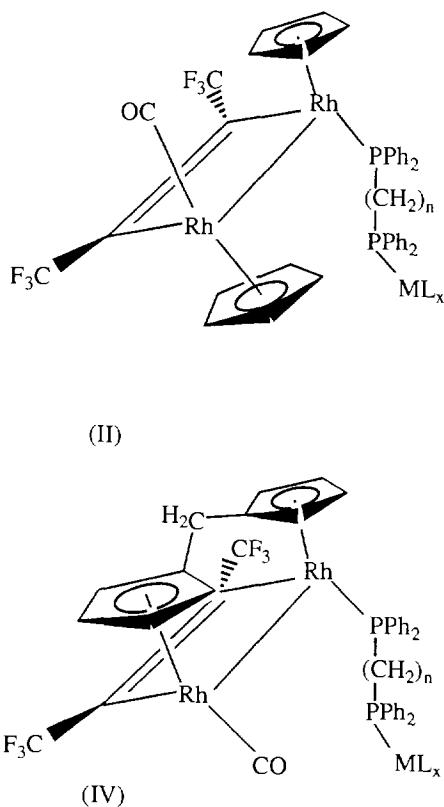


Fig. 3. Comparison of the geometries of the complexes (II) and (IV).

the reactions with trimethylamine oxide, the main product isolated was the phosphine oxide complex  $(\eta^5: \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_4\text{H}_4)\text{Rh}_2(\text{CO})\{\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2\}(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (VIII,  $n = 3,4$ ).

We explored another approach to the formation of heteronuclear complexes containing the  $\text{Rh}_2\text{P}(\text{CH}_2)_n\text{PM}$  unit. Treatment of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  with  $\text{Fe}(\text{CO})_4(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  did not give the target compound  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\mu\text{-}\eta^1: \eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Fe}(\text{CO})_4$ .

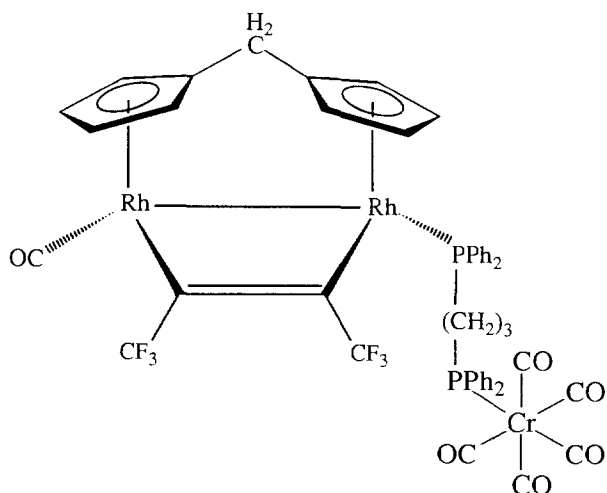


Fig. 4. Complex (VII).

Instead, the dirhodium reactant abstracted CO and the bisphosphine from the iron complex to form  $(\eta^5\text{-C}_5\text{-H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$ . No iron-containing products were identified. This contrasts with the results of previous studies of the reactions of  $\text{Fe}(\text{CO})_4(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  [13] or  $\text{PtX}_2(\text{cod})$  [14] which yielded  $\text{Fe}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{M}$  complexes in high yield.

A similar reaction between  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})(\mu\text{-}\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)$  and *cis, mer*- $\text{MnBr}(\text{CO})_2(\eta^2\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  was conducted over a longer time. This manganese complex has been used previously in a reaction with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  to form a  $\text{Mn}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\text{Rh}$  product [15]. The main products isolated from this system were  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)$  (40%) and  $(\eta^5\text{-C}_5\text{-H}_5)_2\text{Rh}_2(\mu\text{-}\eta^1: \eta^1\text{-CF}_3\text{C}_2\text{CF}_3)(\eta^1: \eta^1\text{-Ph}_2\text{PCH}_2\text{PPh}_2)$  (33%). No manganese-containing products were isolated.

#### 4. Summary

We have shown that the complexes (I) can be used in the systematic synthesis of hetero-trinuclear complexes containing Rh<sub>2</sub> and Mn or Cr fragments linked via a  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  bridge. Attempts to decarbonylate these complexes and hence form clusters lead instead to dissociation of the Mn or Cr unit and oxidation of one end of the bisphosphine ligand. Replacement of the independent cyclopentadienyl groups in (I) by a single bis(cyclopentadienyl)methane ligand changed the stereochemistry but not the reactivity patterns. To achieve cluster formation from systems of this type, it will be necessary to add different metal species that incorporate more labile ligands.

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