BIS(DIPHENYLPHOSPHINO)METHANE TRIMETHYLPHOS-PHINE ALKYL AND η⁵-CYCLOPENTADIENYL COMPOUNDS OF RHODIUM(I); ³¹P{¹H} TWO DIMENSIONAL δ/J RESOLVED AND OVERHAUSER EFFECT NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Abstract—Neutral mononuclear tertiary phosphine rhodium(I) complexes of the formula RhX(PMe₃)(dppm), X = Cl, CH₂SiMe₃, CH₂CMe₃, CH₂CMe₂Ph, η^{5} -C₅H₅, dppm = *bis*(diphenylphosphino)methane, RhCl(PPh₃)(dppm), RhX(dppm)₂, X = Cl, Me and Rh(η^{5} -C₅H₅)(dppm) have been synthesised. In Rh(η^{5} -C₅H₅)(PMe₃)(dppm), the dppm ligand is unidentate according to ³¹P{¹H} NMR and X-ray data.

The ${}^{31}P{}^{1}H{}$ NMR spectral parameters of RhX(PR₃)(dppm) have been determined by a combination of two dimensional δ/J resolved spectroscopy and heteronuclear nuclear Overhauser effect difference spectroscopy (NOEDS) in conjunction with iterative analysis of the one dimensional spectra.

INTRODUCTION

Although there is a variety¹⁻⁴ of mono- and bi-nuclear rhodium *bis*(diphenylphosphino)methane(dppm) complexes, neutral mononuclear species are rare. The neutral η^3 -2-methylallyl *bis*(diphenylphosphino)methane rhodium(I)² exists as a dimer in solution, but is said to be monomeric, based on mass spectral evidence, in the solid state. Here we describe the synthesis and characterisation of several neutral mononuclear rhodium *bis*(diphenylphosphino)methane complexes.

The interaction of excess dppm with [Rh(PMe₃)₄]Cl gives RhCl(PMe₃)(dppm) and with RhCl(PPh₃)₃ gives RhCl(PPh₃)(dppm) or RhCl(dppm)₂³, depending on the conditions. In toluene solution, RhCl(PMe₃)(dppm) Me₃SiCH₂Li, Me₃CCH₂MgBr, with reacts PhMe₂CCH₂MgCl and C₅H₅Na to give, respectively, Rh(CH₂SiMe₃)(PMe₃)(dppm), Ph(CH₂CMe₃)(PMe₃)-(dppm), $Rh(CH_2CMe_2Ph)(PMe_3)(dppm)$ and $Rh(\eta^3 C_{5}H_{5}$ (PMe₃)(dppm). In toluene solution, RhCl(dppm)₂ reacts with MeLi and C₅H₅Na to give RhMe(dppm)₂ and Rh(η^{5} -C₅H₅)(dppm), respectively; the latter compound is also obtained by refluxing $Rh(\eta^5-C_5H_5)(PMe_3)(dppm)$ in toluene.

The ³¹P proton decoupled spectra of these complexes can be complicated, due to the presence of both J_{PP} and J_{RhP} coupling. Since J_{PP} can be as large as 500 Hz in these systems, assignment with the aid of selective homonuclear double resonance experiments can be difficult or impossible to achieve by ordinary r.f. decoupling, due to the high power levels required. A more general approach is to obtain J-resolved 2D spectra, using the pulse sequence $90^{\circ} - \tau_1 - 180^{\circ} - \tau_1$ -acquire (τ_2) with a suitable set of values for τ_1 , followed by successive Fourier transformations with respect to τ_2 (to achieve $\delta \pm J$ dispersion) and to τ_1 (to achieve J dispersion only). A rotation of 45° of the resulting data matrix gives a 2D spectrum which (in the weak coupling limit) can be projected onto one axis (the " δ " axis) to give the effect of a broadband homonuclear decoupled spectrum and onto the other axis (the "J" axis) to show only the homonuclear couplings.⁵ A valuable feature of this approach is its ability to separate the homo- and heteronuclear coupling and to simplify the analysis of the chemical shifts associated with the different phosphorus sites. Although such a separation of variables depends on the spin system being weakly coupled, a substantial degree of strong coupling can in fact be tolerated, and its effects when present can be readily recognised and calculated.⁵

The application of this 2D technique to the complex RhCl(PMe₃)(dppm) enabled the spectrum to be readily analysed for the phosphorus chemical shifts, the ${}^{31}P{}^{-31}P$ and the ${}^{31}P{}^{-103}Rh$ couplings. These could be transferred by analogy to the other complexes in this series, as the starting point in an iterative analysis of the conventional one dimensional spectra.⁵

RESULTS AND DISCUSSION

(1) Bis (diphenylphosphino)methane(trimethylphosphine) -chlororhodium(I)

The complex $[Rh(PMe_3)_4]Cl^6$ reacts with excess dppm in refluxing toluene to give the air-sensitive orange crystalline complex RhCl(PMe_3)(dppm) in high yield (95%); it is monomeric in benzene.

Application of the two-dimensional δ/J resolved NMR method enabled the ${}^{32}P{}^{2}H$ spectrum of this compound (Fig. 1) to be readily analysed for the approximate values of the coupling constants and phosphorus chemical shifts.⁵ These were then used as the starting point for an iterative analysis of the ${}^{31}P{}^{1}H$ one dimensional spectrum. The values obtained for the homonuclear ${}^{31}P{}^{-31}P$ coupling constants, the heteronuclear ${}^{31}P{}^{-103}Rh$ coupling constants and the ${}^{31}P$ chemical shifts are shown in Table 1. Good agreement between the calculated and the observed spectrum (Fig. 2a, b) could be obtained only by setting the relative values of J_{PP}^{trans} and J_{PP}^{cis} to be opposite in sign.

Although the large $(J_{PP} = 407.7 \text{ Hz})$ coupling can be assumed to correspond to a *trans* interaction, there,

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Fig. 1. Two dimensional ³¹P{¹H} δ/J resolved spectrum of *ca.* 10 mM solution of RhCl(PMe₃)dppm in benzene. The spectrum was tilted by 45° and is shown as a contour plot with a projection showing the ³¹P chemical shift positions. Peaks marked with arrows are instrumental artifacts, and can be identified since they do not correctly reflect in the plane of symmetry in the J dimension (shown by a dashed line in the contour plot). Their positions and intensities also change according to the acquisition parameters, unlike the genuine peaks. Several such artifacts shown in the projection (e.g. at δ – 14.6) are off the vertical scale in the contour representation.



Fig. 2. ³¹P{¹H} NMR spectrum of RhCl(PMe₃)(dppm), (a) observed, (b) calculated, (c) n.O.e. difference spectrum obtained by pre-irradiation at the PMe₃ proton resonance, and subtraction of a control spectrum obtained with off-resonance ¹H pre-irradiation.

Table 1. Spectral parameters for $RhX(PR_3)(dppm)$, R = Me, Ph



x	cf ^a	CH₂SiMe₃ ^a	CH ₂ CMe ₂ Ph ^a	CH ₂ CMe ₃ ^a	ce ^b
δ _A ^C	-40.2	-24.1	-26.8	-22.9	-38.5 ^d
^б в	-12.7	-13.7	-16.9	-14.3	+32.7
δ _C	-10.2	-19.7	-11.6	-17.4	-13.3
$\frac{J_{AB}}{B}^{e}$	407.7	378.8	343.7	371.1	382.9
<u>J</u> AC	-96.4	-63.3	-57.6	-56.7	-99.6
$\frac{J}{AD}$	-112.7	-135.2	-148.8	-145.6	-118.8
<u>J</u> _{BC}	-37.1	-38.0	-38.5	-38.0	-33.7
<u>J</u> BD	-131.1	-156.3	-170.1	-168.1	-134.8
<u>J</u> CD	-158.2	-103.9	-96.1	-94.5	-159.5
	l			1	

a RhX(PMe₃)(dppm), ^b RhCℓ(PPh₃)(dppm), ^c in benzene, containing 10% benzene, and referenced to external 85% H₃PO₄ (δ 0.0) at 101.25 MHz,

d In CH₂C ℓ_2 - 10% d₆-acetone and referenced to external 85% H₃PO₄ (δ 0.0) at 101.25 MHz,

^e Coupling constants are determined by iterative spectral analysis. The standard deviation in the calculated transition frequency was < 0.2 Hz in all cases. Good agreement between the observed and calculated spectra can be obtained only by setting the relative values of $\underline{J}_{PP}^{(trans)}$ and $\underline{J}_{PP}^{(cis)}$ to be opposite in sign. The absolute signs could not be determined by this approach and we have assumed $\underline{J}_{PP}^{(trans)}$ to be positive.



Fig. 3. Pulse sequence for observation of the heteronuclear ³¹P{¹H} nuclear Overhauser effect. To obtain the n.O.e., the CW decoupling is tuned to the appropriate proton resonance. To obtain a control spectrum for subtraction, the CW decoupling is moved far off resonance but left operating to minimise sample temperature variation. To minimize the effects of long term instabilities, both sets of data are collected simultaneously by switching the CW frequency from one frequency to the other at regular intervals and storing the two sets of data separately.



(4)

nevertheless, remains an ambiguity in assigning these spectral constants to specific phosphorus atoms (1a vs 1b).

Although in principle these could be distinguished by selective proton decoupling experiments, the presence of long range ¹H-³¹P coupling to the phenyl groups results in very complex spectra. We instead made use of the significant ${}^{31}P{}^{1}H$ nuclear Overhauser effect, using the experimental sequence shown in Fig. 3. Single frequency 'H pre-irradiation at a specific proton resonance allows a selective ${}^{31}P{}^{1}H$ n.O.e. to build up, and allows the non-selective n.O.e. from the broadband irradiation in the cycle to decay between transients. From a spectrum obtained in this way is subtracted a control in which the single frequency ¹H decoupling is off-resonance, giving a difference spectrum which shows only the effects due to the ³¹P{¹H} n.O.e. Pre-irradiation of the proton resonance corresponding to the PMe₃ gave a difference spectrum (Fig. 2c) which shows only enhancement ($\eta \simeq 1.10$) of the low field signals, indicating that the high field signals $(\eta \simeq 1.017)$ are not due to the PMe₃ group and therefore, that assignment 1b is correct. We note that the actual transitions enhanced are complex due to the significant degree of second order character present in the spectrum, and the probable presence of three spin effects,⁸ although this does not affect our qualitative conclusions. This experiment represents, as far as we are aware, the first such application of heteronuclear n.O.e. difference spectroscopy.

RhCl(PMe₃)(dppm) does not react with hydrogen (2 atm., 70°C), ethylene (2 atm., 25°C), NaBH₄ and Na metal (25°C). It reacts with LiAlH₄, MeLi, and EtLi, but complex mixtures were obtained and attempts to isolate pure compounds were unsuccessful.

(2) Bis (diphenylphosphino)methane(trimethylphosphine) -trimethylsilylmethylrhodium(I)

In toluene, RhCl(PMe₃)(dppm) reacts with one equivalent of Me₃SiCH₂Li to give the air-sensitive complex RhCH₂SiMe₃(PMe₃)(dppm) which can be readily crystallised from 40 to 60° petroleum as red crystals in 80% yield; it is monomeric in benzene.

The observed and simulated ${}^{31}P{}^{1}H$ spectra are shown in Fig. 4 and spectral parameters are given in the Table.

Unlike the parent compound, $Rh(CH_2SiMe_3)(PMe_3)$ -(dppm) reacts readily with hydrogen at 1 atm. pressure at room temperature to give a mixture from which no crystalline product could be isolated. The 'H NMR spectrum of the mixture shows the absence of the trimethylsilylmethyl group on the rhodium, but no hydride is observed in either IR or 'H NMR spectra.

Since $Rh(CH_2SiMe_3)(PMe_3)(dppm)$ slowly (ca. 12 hr) catalyses the isomerisation of hex-1-ene to hex-2-ene under 1 atm. of hydrogen (but not N₂ or Ar) at room



Fig. 4. Observed (a) and calculated (b) ³¹P{¹H} spectrum of Rh(CH₂SiMe₃)(PMe₃)(dppm).

temperature a transient hydrido species is presumably 100°C involved. At with 20 atm. hydrogen Rh(CH₂SiMe₃)(PMe₃)(dppm) slowly (ca. 12 hr) hydrogenates hex-1-ene to hexane (100% conversion). Hydroformylation of hex-1-ene to a mixture of 2-methylhexanol and heptaldehyde (straight branched chain isomer, ratio 3:1) under 30 atm. of CO/H₂ (1:1) also occurs slowly. The solution IR spectrum of the residual solution shows a terminal CO stretch at 1960 cm⁻¹; interaction of the complex with CO alone at 1 atm. gives a mixture with CO stretches at 1960 and 1940 cm⁻¹. Attempts to isolate these carbonyl species in a pure state have failed.

(3) Bis(diphenylphosphino)methane(trimethylphosphine) -neopentyl- and neophylrhodium(I)

Alkylation with one equivalent of neopentylmagnesium bromide or of neophylmagnesium chloride in THF give high yields of the corresponding alkyls which can be obtained from petroleum as orange air-sensitive crystals. Both compounds are monomeric in benzene.

The ${}^{31}P{}^{1}H$ observed and simulated spectra for the





Fig. 6. Observed (a) and calculated (b) ³¹P{¹H} spectrum of Rh(CH₂CMe₂Ph)(PMe₃)(dppm).

alkyls are shown in Figs. 5 and 6 respectively. Spectral parameters are in Table 1.

For all the complexes RhX(PR₃)(dppm) we can conclude that the magnitude of the homonuclear ${}^{31}P_{-}{}^{31}P$ coupling constants are in the order $J(P_A-P_B) \ge J(P_A-P_C) > J(P_B-P_C)$ and also that the signs of the coupling constants J(trans) and J(cis) are opposite to each other.

(4) Bis(diphenylphosphino)methane(trimethylphosphine) - η^{5} -cyclopentadienylrhodium(I) and Bis(diphenylphosphino)methane η^{5} -cyclopentadienylrhodium(I)

The interaction of RhCl(PMe₃)(dppm) in toluene with one equivalent of C₅H₅Na leads to orange-red air-sensitive crystals of Rh(η^{5} -C₅H₅)(PMe₃)(dppm). The NMR data indicate unidentate dppm as in (2) and the structure has been confirmed by X-ray diffraction⁹ (Fig. 7).

The ³¹P{¹H} spectrum shows a doublet at δ -23.21 [$J(P_A - P_C) = \pm 97.6$ Hz], a doublet of doublets at δ -2.20 [$J(Rh-P_B) = \pm 208.6$ Hz; $J(P_B - P_C) = \pm 55.3$ Hz] and a doublet of doublet of doublets at δ 47.94 [$J(Rh-P_C = \pm 231.9$ Hz; $J(P_A - P_C) = \pm 97.6$ Hz; $J(P_B - P_C) = \pm 55.3$ Hz]. Heteronuclear ³¹P-¹⁰³Rh coupling is not observed for the δ -23.21 resonance so that this can be assigned to the non-bonded phosphorus atom. These spectral parameters are consistent with those observed for the other complexes studied (Table 1).

On heating the complex in refluxing toluene, PMe₃ is lost and Rh(η^5 -C₅H₅)(dppm) is formed quantitatively. The compound forms orange-red air-sensitive crystals and is monomeric in benzene. The NMR data is consistent with the chelate structure (3). Thus, the ³¹P{¹H} NMR spectrum shows a doublet with heteronuclear ³¹P-¹⁰³Rh coupling of 190.2 Hz at δ - 11.72 ppm. The ¹H NMR spectrum shows a doublet [J(¹⁰³Rh-C₅H₅) = 0.7 Hz] for the cyclopentadienyl protons.

(5) Bis(diphenylphosphino)methane(triphenylphosphine chlororhodium(I)

Interaction of excess dppm with RhCl(PPh₃)₃ in toluene at room temperature for 18 hr gives RhCl(PPh₃)(dppm) in 90% yield. The compound is sparingly soluble in toluene but can be crystallised as orange crystals from CH₂Cl₂ in which it is monomeric; it is a non-conductor in MeNO₂.

Assignment of the ³¹P{¹H} parameters is subject to the same ambiguity as for RhCl(PMe₃)(dppm). Three distinct sets of signals were observed (Figs. 8a, b). The two sets due to the dppm ligand were assigned by carrying out a heteronuclear n.O.e. experiment similar to that described for RhCl(PMe₃)(dppm), but in which the CH₂ protons in the dppm ligand were pre-irradiated. Significant ($\eta \approx$ 1.12) enhancements are seen in the difference spectrum (Fig. 8c) for the two sets of high field signals, suggesting the assignment of these to the dppm ligand and of the low field set ($\eta = 1.01$) to the PPh₃ phosphorus atom. These assignments are completely consistent with those made for RhCl(PMe₃)(dppm) (Table 1).

(6) Bis[bis(diphenylphosphino)methane] methylrhodium-(I)

Interaction of excess $bis(diphenylphosphino)methane with RhCl(PPh_3)_3 in toluene at room temperature for four days gives the known³ RhCl(dppm)_2 in 90% yield. It is monomeric in benzene. The compound reacts with one equivalent of methyl lithium in toluene to give orange-red crystals of RhMe(dppm)_2 which is monomeric in benzene and is a non-conductor in nitromethane and hence must be 5-coordinate. The room temperature ³¹P{¹H} NMR spectrum shows essentially an AB quartet with further heteronuclear ³¹P-¹⁰³Rh coupling; at -60°C a complicated AA'BB'X pattern is observed in which the AB' and A'B couplings are approx. 300 Hz.$



Fig. 7. The structure of $Rh(\eta^5-C_5H_5)(PMe_3)(dppm)$ as determined by X-ray diffraction. $Rh-P(PMe_3) = 2.214(2)$ Å; Rh-P(dppm) = 2.188(2)Å; Rh-C = 2.251-2.313(8)Å.



Fig. 8. Observed (a) and calculated (b) ³¹P{¹H} spectrum of RhCl(PPh₃)(dppm), (c) n.O.e. difference spectrum obtained by pre-irradiation at the dppm CH₂ proton resonance, and subtraction of a control spectrum obtained with off-resonance ¹H pre-irradiation.

Unfortunately, an accurate analysis of this spectrum could not be obtained, possibly as a result of the effects of fluxionality still present in the spectrum. The ³¹P data are, however, consistent with a trigonal bipyramidal geometry (4) and non-rigidity at room temperature. The tbp geometry should produce an AA'BB'X pattern whereas a square pyramidal geometry should show a doublet (i.e. an A₄X pattern) resulting from heteronuclear ³¹P-¹⁰³Rh splitting of the four equivalent phosphorus nuclei. An X-ray diffraction study⁴ on a related cationic complex, [Rh(dppm)₂CO]BF₄, has confirmed a trigonal bipyramidal structure.

With one equivalent of C_5H_5Na , RhCl(dppm)₂ in toluene reacts to give high yields of Rh(η -C₅H₅)(dppm).

EXPERIMENTAL

Microanalyses by Pascher, Bonn, and Imperial College laboratories. Molecular weights: cryoscopically in benzene. Melting points were determined in sealed capillaries under vacuum.

All operations were performed under oxygen-free nitrogen or in vacuo. Tetrahydrofuran, toluene, benzene and petroleum (b.p. 40-60°C) were dried over sodium-benzophenone and distilled under nitrogen before using.

Instruments

NMR: Perkin-Elmer R32 (¹H, 90 MHz), Bruker WM250 (¹H, 250; ³¹P{¹H}, 101.25 MHz); data in δ ppm referenced to SiMe₄ and 85% H₃PO₄ (external) at 26°C in C₆D₆ unless otherwise stated. IR: Perkin-Elmer 683; spectra in cm⁻¹ and Nujol mulls unless otherwise stated. Conductivity data were obtained on a Mullard conductivity bridge type E7566/3 with a matching conductivity cell.

All iterative NMR spectral analysis were performed using an interactive graphical program written by Burgess and Rzepa.

Detailed NMR procedures

Two dimensional δ/J resolved spectra were recorded using a preliminary version of the Bruker ASPECT 2000 software and the following acquisition parameters: data size 512 (F₁)×4k (F₂), spectral width 760 Hz (F₁) and 6 kHz (F₂) giving a digital resolution of 1.47 Hz (F₁) and 2.94 Hz (F₂). A delay of 40 s (*ca.* 5T₁) between 90° – τ_1 - 180° – τ_1 -acquire (τ_2) pulse cycles was used and four transients were acquired for each value of τ_1 (quadrature detection) to give a total acquisition time of 17 hr. The data was multiplied by half cosine window functions before Fourier transformation and the resulting two dimensional spectrum tilled by 45°. Peak positions in this spectrum could be obtained to an accuracy of ±1.5 Hz, although the contour representation (Fig. 1) is shown with an exponential weighting function and a deliberately low contour level to improve clarity of presentation.

Nuclear Overhauser effect difference spectra were obtained at ambient temperatures, with 2800 transients being acquired for both the control and the CW 'H pre-irradiation experiments. The following micro-program sequence was used on the ASPECT 2000: The two frequency list files contain the decoupler frequencies for selective and broad-band irradiation.

(1) Bis(diphenylphosphino)methane(trimethylphosphine)chlororhodium(I)

Bis(diphenylphosphino)methane (1.74 g, 4.52 mmol) was added to a toluene solution (100 cm^3) of $[\text{Rh}(\text{PMe}_3)_4]\text{Cl}$ (2.0 g, 4.52 mmol). The mixture was refluxed for 24 hr. Volatile materials were removed under vacuum, and the residue extracted into hot toluene $(2 \times 30 \text{ cm}^3)$, filtered, concentrated to *ca*. 50 cm³ and cooled at -20°C to give orange crystals, which were collected and washed with petroleum. Yield; > 2.6 g, 95%; m.p., 210-1°C. [Found: C, 55.8 (56.1); H, 5.0 (5.2); P, 15.6 (15.5); Cl, 5.6 (5.9)%; M 580 (598.5)]. NMR. ¹H: 1.07 s, (9), PMe; 3.74 br, s, (2), PCH₂P; 7.0-7.9 m (20) Ph₂P. ³¹P{¹H}: see Table 1.

IR. 3035w, 3025w, 1670w, 1585w, 1570w, 1480m, 1436s, 1422m, 1360w, 1340w, 1310m, 1300w, 1283m, 1280m, 1185m, 1160w, 1100s, 1080m, 1070m, 1025w, 1000w, 955vs, 940s, 875w, 850w, 840w, 790w, 756s, 740s, 730s, 700s, 670m, 660w, 545s, 510s, 492w, 470w, 460w, 450w, 445w, 420w.

(2) Bis(diphenylphosphino)methane(triphenylphosphine)chlororhodium(I)

Bis(diphenylphosphino)methane (1.9 g, 4.95 mmol) was added to a toluene solution (100 cm³) of RhCl(PPh₃)₃ (2.0 g, 2.16 mmol) at room temperature. The solution was stirred for 18 hr. The yellow precipitate was collected, washed with toluene (2 × 20 cm³) and dried *in vacuo* to give 1.2 g pure RhCl(dppm)(PPh₃). A further 0.3 g was obtained by concentrating the combined filtrate to *ca*. 50 cm³ and cooling at -20° C. The compound can be recrystallised from CH₂Cl₂ to give orange crystals. Total yield; 1.5 g, 90%; m.p., 170-2°C. [Found: C, 65.9 (65.8); H, 4.7 (4.7); P, 11.8 (11.9); Cl, 4.4 (4.5)%. *M* 780 (784.5)].

NMR. ¹H: (CDCl₃): 4.95 s, (2), PCH_2P ; 6.7–7.8 br, m (35); $(Ph_2P)_2CH_2$ and Ph_3P . ³¹P{¹H}: see Table 1.

IR. 3052w, 1584w, 1568w, 1480m, 1435s, 1310m, 1275m, 1182m, 1178m, 1155w, 1092s, 1070m, 1025m, 998m, 915w, 848w, 752s, 735s, 723s, 695s, 672m, sh, 615w, 550m, 520s, 510s, 495s, 478m, 465m, 436m, 420m.

(3) Bis[bis(diphenylphosphino)methane]chlororhodium(I)

Bis(diphenylphosphino)methane (2.0 g, 5 mmol) was added to a solution of RhCl(PPh₃)₃ (2.0 g, 2.2 mmol) in 200 cm³ of toluene at room temperature. The solution was stirred for 4 d. The orange solution was evaporated and the residue extracted into toluene $(2 \times 30 \text{ cm}^3)$. The combined filtrated was concentrated to *ca.* 30 cm³ and cooled at -20° C to give orange-red crystals. Yield; 1.7 g, 90%; m.p., 88-90°C (lit., 97°C dec.) [Found: C, 66.3 (66.2); H, 4.9 (4.9); P, 13.4 (13.7); Cl, 3.8 (3.8 (3.9)%. M, 920 (906.5)].

NMR. ¹H: 3.83 br, s (4), P CH₂P; 6.90 and 7.68 br, s (40), P h_2 P. ³¹P{¹H}: -16.1 d, J(Rh-P) = 105.7 Hz.

IR. 3025w, 1585w, 1570w, 1494w, 1482m, 1436s, 1366w, 1306w, 1184w, 1155w, 1096s, 1090msh, 1028w, 998w, 756m, 734s, 729s, sh, 702s, sh, 696s, 670w, 618w, 553w, 522s, 512s, 501m, sh, 492w, 440w, 421w.

1	ZE	14	02	27	LO TO 9 TIMES: 700
2	RE PDEC	15	CW	28	DO
3	ZE	16	DI	29	EXIT
4	S1	17	BB		
5	DO	18	S2	D1	3 sec
6	WR PDEC	19	02	D2	0.05 sec
7	IF PDEC	20	D2	S 1	24 H
8	LO TO 1 TIMES: 2	21	GO 13	S2	4 H
9	RF PDEC	22	DO		
10	RF	23	WR PDEC		
11	RE PDEC	24	IF PDEC		
12	RL FREOL	25	IF FREQL		
13	S1	26	LO TO 11 TIMES: 2		

(4) Bis(diphenylphosphino)methane(trimethylphosphine)trimethylsilylmethylrhodium(I)

Trimethylsilylmethyllithium (1.6 cm³, 1.7 M in petroleum; 2.68 mmol) was added to a toluene solution (100 cm³) of RhCl(dppm)(PMe₃) (1.6 g, 2.68 mmol) at -40° C. The mixture was allowed to warm to room temperature slowly and stirred for an additional 8 hr. Volatile materials were removed under reduced pressure and the residue was extracted with petroleum (3 × 40 cm³). The combined filtrate was concentrated to *ca*. 60 cm³ and cooled at -20° C to give red crystals. Yield: 1.4 g, 80%; m.p., 115-6°C. [Found: C, 58.7 (59.1); H, 6.5 (6.5); P, 14.4 (14.3); Si, 3.9 (4.3)%. M, 640 (650)].

NMR. H: 0.29 s (2), CH_2SiMe_3 ; 0.31 s (9), CH_2SiMe_3 ; 1.08 d (9), ${}^{2}J(P-H) = 6$ Hz, PMe_3 ; 3.93 t, (2) ${}^{2}J(P-H) = 8$ Hz, $PCH_{22}P$; 7.03-7.73 m, (20), Ph_2P . ${}^{31}P{}^{1}H{}$: see Table 1.

IR. 3050w, 3030w, 1950br, w, 1895br, w, 1820br, w, 1610m, 1586m, 1497m, 1478s, 1435vs, 1420m, 1306w, 1280w, 1280w, 1248w, 1180w, 1155w, 1105m, 1095s, 1065w, 1050w, 1026w, 1000w, 945s, 880m, 850s, 835m, 785w, 740s, 728vs, 692vs, 665m, 615w, 545m, 535s, 520s, 510s, 490w, 482w, 469w.

(5) Bis(diphenylphosphino)methane(trimethylphosphine)neopentylrhodium(I)

In a similar way from neopentylmagnesium bromide $(2.0 \text{ cm}^3, 0.42 \text{ M} \text{ in Et}_2\text{O}; 0.82 \text{ mmol})$ and a THF solution (80 cm^3) of RhCl(dppm)(PMe₃) (0.47 g, 0.79 mmol) at -78° C. The petroleum extract was concentrated to *ca*. 60 cm³ and cooled to -20° C to give orange crystals. Yield: 0.4 g, 75%; m.p., 154–5°C. [Found: C, 62.2 (62.5); H, 6.6 (6.6); P, 14.2 (14.6)%. *M*, 610 (634)].

NMR. ¹H: 1.11 d (9), J(P-H) = 6.5 Hz, PMe_3 ; 1.37 s (9), CH₂CMe₃; 1.93 br, m (2), CH₂CMe₃ 3.95 t (2), $J(P-CH_2) =$ 16.8 Hz, PCH₂P; 7.0–7.8 br, m (20) Ph₂P. ³¹P{¹H}: see Table 1.

IR. 3035w, 3028w, 1585m, 1570w, 1482m, 1434s, 1420w, 1348m, 1307w, 1300w, 1278m, 1229m, 1175w, 1092s, 1081m, 1069w, 1029m, 1000m, 948s, 930m, 842w, 760w, 755m, 740vs, 725s, 715m, 700vs, 665w, 615w, 540m, 509m, 488m, 440m, 430m, 420m.

(6) Bis(diphenylphosphino)methane(trimethylphosphine)neophylrhodium(I)

As in (4), but using neophyl magnesium chloride $(1.9 \text{ cm}^3, 0.6 \text{ M} \text{ in } \text{Et}_2\text{O}; 1.14 \text{ mmol})$ and a THF solution (80 cm^3) of RhCl(dppm)(PMe₃) (0.6 g, 1 mmol) at -78° C. The petroleum extract was concentrated to *ca*. 60 cm³ and cooled to -20° C to give orange crystals. Yield: 0.56 g, 80%; m.p., 168–9°C. [Found: C, 65.5 (65.5); H, 6.5 (6.3); P, 13.3 (13.4)%. *M* 670 (696)]. NMR. ¹H: 0.84d (9), *J*(P-H) = 7.1 Hz, PMe₃; 1.73 s (8), UNR.

NMR. 'H: 0.84 d (9), J(P-H) = 7.1 Hz, PMe_3 ; 1.73 s (8), CH_2CMe_2Ph ; 3.9 br, m (2), PCH_2P ; 6.8–8.4 br, m (25), Ph_2P and $PhMe_2C$. ³¹P{¹H}: see Table 1.

IR. 3030m, 3015m, 1970w, 1955w, 1880w, 1810w, 1486m, 1560m, 1480s, 1431s, 1418s, 1345m, 1297m, 1279s, 1233w, 1190w, 1176w, 1095s, 1082s, 1067m, 1040m, 1027m, 1015m, 1000w, 940vs, 930vs, 842m, 767m, 758m, 749s, 735s, sh, 720vs, 692vs, 670m, sh, 662s, 640w, 618w, 560m, 535m, 510m, 485m, 430m, 415w.

(7) Bis(diphenylphosphino)methane(trimethylphosphine)- η^5 cyclopentadienylrhodium(I)

Sodium cyclopentadienide $(1 \text{ cm}^3, 1.12 \text{ M} \text{ in THF}; 1.12 \text{ mmol})$ was added to a toluene solution (50 cm^3) of RhCl(dppm)(PMe₃) (0.65 g, 1.09 mmol) at -50° C. The mixture was allowed to warm and stirred at room temperature for 12 hr. Volatile materials were removed under reduced pressure. The residue was extracted into petroleum $(3 \times 40 \text{ cm}^3)$ and filtered. The combined filtrate was concentrated to *ca*. 60 cm³ and cooled to -20° C to give red crystals. Yield: 0.5 g, 75%; m.p., 112–3°C. [Found: C, 63.4 (63.0); H, 5.8 (5.7); P, 14.6 (14.8)%. M 600 (628)].

NMR. H: 0.85 d (9), J(P-H) = 8.7 Hz, PMe_3 ; 3.3 d (2), J(P-H) = 7.6 Hz, PCH_2P ; 5.4 s (5), $\eta^5-C_5H_3$; 7.0–8.0 br, m (20), Ph_2P . ³¹P{¹H}: -23.21 d, J(P-P) = 97.6 Hz, $Ph_2P-CH_2(Ph_2)PRh$; -2.2 d of d, J(Rh-P) = 208.6 Hz, J(P-P) = 55.3 Hz, PMe_3 ; 47.9 d of d, J(Rh-P) = 231.9 Hz; (J(P-P) = 97.6; J(P-P) = 55.3 Hz, $RhPPh_2CH_2PPh_2$.

IR. 3020w, 1610w, 1586w, 1486m, 1480m, 1434s, 1420m, 1330w, 1308m, 1298m, 1279m, 1190w, 1180w, 1160w, 1130w, 1095m, sh, 1090s, 1060w, 1040w, 1024m, 1009m, 1000m, 992m, 948vs, 930s, 875m, 848m, 825w, 770m, 759s, 745s, sh, 730vs, 695vs, 675s, 660m, 620w, 550w, 510s, 500s, 471m, 464m, 450m, 390m.

(8) Bis(diphenylphosphino)methane- η^5 -cyclopentadienylrhodium(I)

(a) A toluene solution (50 cm³) of $(\eta^5-C_5H_5)Rh(dppm)(PMe_3)$ (0.3 g, 0.47 mmol) was refluxed for 18 hr. The solution was evaporated to dryness. The residue was washed with petroleum (2 × 30 cm³), extracted into toluene (20 cm³) and filtered. The filtrate was concentrated to *ca*. 2 cm³ and cooled at - 78°C to give orange crystals. Yield: 0.25 g, 95%; m.p., 199-200°C. [Found: C, 65.6 (65.2); H, 5.1 (4.9), P, 10.9 (11.2)%. *M* 530 (552)].

NMR. ¹H: 3.90 t of d (2), J(P-H) = 10.6 Hz, J(Rh-H) = 1.5 Hz, PCH₂P; 5.50 d (5), $J(Rh-C_5H_5) = 0.6$ Hz, η^5 -C₅H₅; 7.04-7.75 br, m (20), Ph_2P . ³¹P{¹H}: -11.59 d, J(Rh-P) = 163.4 Hz.

IR. 3070w, 3050w, 1940br, w, 1960br, w, 1825br, w, 1580m, 1570m, 1480m, 1435s, 1327w, 1305w, 1275w, 1260m, 1180m, 1156w, 1100m, 1090s, 1080s, 1025m, 1000m, 870w, 850w, 810w, 770s, 750s, 730s, 695s, 660w, 618w, 550s, 512s, 490w, 482w, 470m, 423m.

(b) Sodium cyclopentadienide $(0.5 \text{ cm}^3, 1.12 \text{ M} \text{ in THF}; 0.56 \text{ mmol})$ was added to a THF solution (30 cm^3) of RhCl(dppm)₂ (0.4 g; 0.44 mmol) at 0°C. The solution was warmed and stirred at room temperature for 18 hr. The deep red solution was evaporated and the residue extracted into 20 cm³ of toluene and filtered. The filtrate was concentrated to *ca*. 10 cm³ and then 20 cm³ of diethyl ether were added to the solution and cooled at -20° C. Dppm first crystallised and was removed, after which the filtrate was concentrated to *ca*. 5 cm³ and cooled at -20° C to give orange crystals. Yield: 0.22 g, 90%.

(9) Bis[bis(diphenylphosphino)methane]methylrhodium(I)

Methyllithium (0.5 cm³, 1.1 *M*; 0.55 mmol) was added to a toluene solution (40 cm³) of RhCl(dppm)₂ at 0°C, and the solution stirred at room temperature for 18 hr. when the solvent was removed. The residue was extracted into toluene (2×20 cm³), the combined filtrate concentrated *ca*. 20 cm³ and cooled at -20° C, to give orange-red crystals. Yield: 0.37 g, 80%; m.p., 218°C. [Found: C, 69.1 (69.1); H, 5.1 (5.3); P, 14.2 (14.0)% *M* 860 (886)]. NMR. ¹H. 0.29 s (3), Rh-CH₃; 3.83 b, s (2), PCH₂P; 4.08 b, t

NMR. 'H: 0.29 s (3), Rh– CH_3 ; 3.83 b, s (2), P CH_2 P; 4.08 b, t (2), $J(P-CH_2) = 9$ Hz, PCH_2 P; 6.7–6.9, br, m (40) Ph_2 P. ³¹P{¹H}: AA'BB'M spectrum, -19.04, J(Rh-P) = 122 Hz, J(P-P) = 302 Hz; -26.24, J(Rh-P) = 101 Hz, J(P-P) = 302 Hz.

IR. 3025w, 1582w, 1480m, 1432s, 1428s, sh, 1300w, 1272w, 1170w, 1150w, 1110m, 1095s, 1065w, 1025m, 1000w, 992w, 878m, 852m, 740s, 730m, 722m, 696s, 666w, 540m, 521s, 512m, sh, 508s, 483m, 420m.

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REFERENCES

- ¹M. Cowie and T. G. Southern, *Inorg. Chem.* 1982, 21, 246; W. A. Fordyce and G. A. Crosby, *J. Am. Chem. Soc.* 1982, 104, 985; B. R. James and D. Mahajan, *Can. J. Chem.* 1980, 58, 996; M. Cowie and S. K. Dwight, *Inorg. Chem.* 1979, 18, 1209; A. R.
- Sanger, J. Chem. Soc. Dalton Trans. 1977, 120.
- ²M. D. Fryzuk, Inorg. Chim. Acta 1981, 54, L265.
- ³B. R. James and D. Mahajan, Can. J. Chem. 1979, 57, 180.
- ⁴L. H. Pignolet, H. D. Doughty, S. C. Nowicki and A. L. Casalnuovo, *Inorg. Chim.* 1980, 19, 2172.
- ⁵ Preliminary Note: K. W. Chiu, H. S. Rzepa, R. N. Sheppard, G. Wilkinson and W. K. Wong, J. Chem. Soc. Chem. Commun. 1982, 482; see also J. J. Colquhoun and W. McFarlane, J. Chem. Soc. Chem. Commun. 1982, 484.
- ⁶R. A. Jones, F. Mayor Real, G. Wilkinson, M. B. Hursthouse, A. M. R. Galas and K. M. A. Malik, J. Chem. Soc., Dalton Trans. 1980, 511.
- ⁷W. McFarlane and D. S. Rycroft, *Nuclear Magnetic Resonance* (Edited by G. A. Webb), Specialist Periodical Report, Vol. 10, p. 180. Royal Society of Chemistry, London (1981).
- ⁸J. H. Noggle and R. E. Shirmer, The Nuclear Overhauser Effect. Academic Press, New York (1971).
- ⁹J. I. Davies and A. C. Skapski, Imperial College, private communication.