

## The Syntheses and Characterisation of, and the Determination of $^1J(^{103}\text{Rh}-^{103}\text{Rh})$ in $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\{\mu\text{-CH}_2\text{CR}(\text{CH}_2\text{CR}=\text{CH}_2)\text{CH}_2\}]$ (R = H or Me) and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]^{2+}$ ( $n = 1$ or $2$ )

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Reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\text{Cl}_2]$  with  $\text{CH}_2=\text{CRCH}_2\text{MgCl}$  gave  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\{\mu\text{-CH}_2\text{CR}(\text{CH}_2\text{CR}=\text{CH}_2)\text{CH}_2\}]$  (**3**, R = H; **4**, R = Me). Reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2(\text{MeCN})_2]^{2+}$  with  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  gave  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]^{2+}$  (**5**,  $n = 1$ ; **6**,  $n = 2$ ). The complexes (**3**)–(**6**) were characterised largely by their n.m.r. spectra which also allowed the determination of  $^1J(^{103}\text{Rh}-^{103}\text{Rh})$  as 13.5 for (**3**), 13.2 for (**4**), 12.4 for (**5**), and 11.9 Hz for (**6**). After allowance for gyromagnetic ratios and *s*-electron densities at the nuclei, these coupling constants are comparable with a  $^1J(^{196}\text{Pt}-^{196}\text{Pt})$  coupling of *ca.* 8 000 Hz.

We have recently developed an extensive chemistry of molecules containing the  $(\text{C}_5\text{Me}_5)_2\text{Rh}(\mu\text{-CH}_2)_2\text{Rh}(\text{C}_5\text{Me}_5)$  skeleton and where the rhodiums are formally in the +4 oxidation state.<sup>1–3</sup> In order to account for the observed diamagnetism and the short rhodium–rhodium distances in the X-ray crystal structures, the presence of metal–metal bonds are postulated. The chemistry is dominated by a substantial stability of this skeleton which allows a wide variety of substituents to be put at each of the rhodiums and allows the molecules to exist in either *cis* or *trans* geometries. We have described the synthesis of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\text{R}_2]$  (R = Et, Pr<sup>n</sup>, or Bu<sup>n</sup>) by reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\text{Cl}_2]$  (**1**) with  $\text{RMgCl}$ .<sup>3</sup> We here describe the rather unexpected products, (**3**) and (**4**), obtained when complex (**1**) is treated with  $\text{CH}_2=\text{CRCH}_2\text{MgCl}$  (R = H or Me) as well as the reactions of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2(\text{MeCN})_2]^{2+}$  (**2**) with bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) to give the bridged complexes (**5**) and (**6**). The n.m.r. spectra of (**3**)–(**6**) allow the opportunity to determine the rhodium–rhodium coupling constants in such dinuclear complexes.

### Results and Discussion

**Synthesis and Structure of Complexes (3) and (4).**—Reaction of the dichloro-complex (**1**)<sup>2</sup> with allylmagnesium chloride gave a complex with the same elemental analysis as the expected di- $\sigma$ -allyl product, but with quite different spectroscopic properties. Thus, although both the <sup>1</sup>H and the <sup>13</sup>C n.m.r. spectra (Table 1) showed the presence of only one type of C<sub>5</sub>Me<sub>5</sub>, the high-frequency (low-field)  $\mu$ -methylene region showed four distinct resonances in the <sup>1</sup>H n.m.r., two doublets with  $J(\text{H}-\text{H})$  2.5 Hz (at  $\delta$  6.94 and 7.65) and two doublets of triplets with  $J(\text{H}-\text{H})$  2.5 and  $J(\text{Rh}-\text{H})$  2 Hz (at  $\delta$  7.40 and 7.88). Similarly the <sup>13</sup>C spectrum showed the presence of two distinct methylenic carbons (at  $\delta$  153.7 and 157.6), but each coupled to two equivalent rhodiums. The spectra were not temperature dependent. These data indicate that the molecule is dinuclear with two rhodiums and that it has only a single plane of symmetry, which is perpendicular to and bisects the Rh–Rh bond. Analysis of the remaining signals showed the presence of one  $\sigma$ -bonded allyl (multiplets at  $\delta$  4.82 and 5.80 and a doublet at 1.90 in the <sup>1</sup>H spectrum); this was confirmed by characteristic peaks in the i.r. at 1 640 and 3 070 cm<sup>-1</sup>. The position and multiplicity of the signal at  $\delta$  1.90 showed it to arise from the  $\sigma$ -allyl CH<sub>2</sub>–, bonded to a carbon bearing one hydrogen. The three remaining signals, multiplets at  $\delta$  0.49, 0.92, and 1.82 integrated in the ratio 2:2:1

and arose from the five protons of the other C<sub>3</sub> group, no longer an allyl. These were shown to arise from a propane-1,3-diyl group since off-resonance decoupling experiments showed that the two lowest frequency (highest field) multiplets coupled to each other, to a single rhodium and to the highest frequency signal, which did not itself couple to rhodium. The two lower frequency signals arose from two equivalent CH<sub>2</sub> groups, bearing inequivalent hydrogens, each attached to only one Rh. These methylenes also appeared (again at low frequency, in sharp contrast to the methylenes bridging the rhodiums) as one doublet [ $J(\text{Rh}-\text{C})$  30 Hz] at  $\delta$  28.0 in the carbon spectrum. These data are entirely consistent with the structure shown for (**3**); the spectra for the dimethyl derivative (**4**) obtained from  $\text{CH}_2=\text{CMeCH}_2\text{MgCl}$  are very similar and indicate an analogous structure.

The <sup>13</sup>C n.m.r. resonances of the Rh–CH<sub>2</sub> groups of the bridging CH<sub>2</sub>CR(CH<sub>2</sub>CR=CH<sub>2</sub>)CH<sub>2</sub> group are typical ABX spectra, see Figure (d) for R = H. The splitting of the central two lines of the pattern requires that the two <sup>103</sup>Rh nuclei have different chemical shifts due to a <sup>12</sup>C/<sup>13</sup>C isotope shift. There are then four parameters to extract from the pattern,  $^1J(^{103}\text{Rh}-^{103}\text{Rh})$ ,  $^1J(^{103}\text{Rh}-^{13}\text{C})$ ,  $^2J(^{103}\text{Rh}-^{13}\text{C})$ , and  $\Delta\delta(^{103}\text{Rh})$ , the <sup>12</sup>C/<sup>13</sup>C isotope shift, but due to the centrosymmetrical nature of the pattern there are only three independent line separations. As a consequence, the line positions can be matched for any assumed value to  $^2J(^{103}\text{Rh}-^{13}\text{C})$ , see Figure (a)–(c). Examination of these calculated spectra shows that if the relative intensities of the inner and outer pairs of lines are included the best fit is obtained in Figure (b), while Figure (a) and (c) are taken as representing the extreme acceptable patterns to fit the data. This analysis gives for complex (**3**),  $^1J(^{103}\text{Rh}-^{103}\text{Rh}) = 13.5 \pm 0.5$  Hz,  $^1J(^{103}\text{Rh}-^{13}\text{C}) = 30.0 \pm 0.5$  Hz,  $^2J(^{103}\text{Rh}-^{13}\text{C}) = 0.0 \pm 0.5$  Hz, and  $\Delta\delta(^{103}\text{Rh}) = 0.36 \pm 0.02$  p.p.m.; for complex (**4**),  $^1J(^{103}\text{Rh}-^{103}\text{Rh}) = 13.2 \pm 0.5$  Hz,  $^1J(^{103}\text{Rh}-^{13}\text{C}) = 29.6 \pm 0.5$  Hz,  $^2J(^{103}\text{Rh}-^{13}\text{C}) = 0.0 \pm 0.5$  Hz, and  $\Delta\delta(^{103}\text{Rh}) = 0.34 \pm 0.02$  p.p.m.

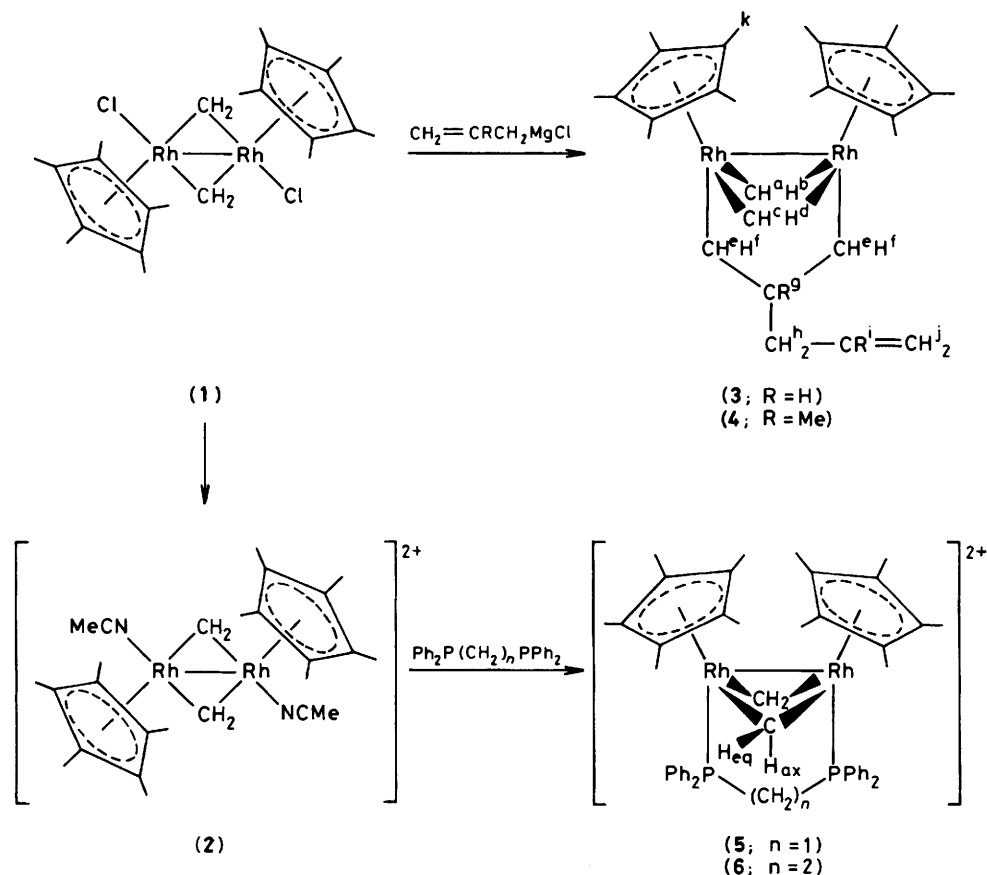
Our first thoughts on the mechanism by which (**3**) [or (**4**)] was formed centred around a two-step process in which one allylic nucleophile first displaced the chloride at one rhodium to give a chloro-allyl intermediate, which was then attacked on the central allylic carbon by the second allylic nucleophile (Scheme 1).

However, several attempts to detect or trap the postulated intermediate, (A) or (B), were in vain. Reaction of (**1**) with one equivalent of the allylic Grignard reagent  $\text{CR}_2=\text{CRCH}_2\text{MgCl}$  gave a mixture of (**1**) and (**3**) [or (**4**)] and attempts to treat this mixture with a second equivalent of a different nucleophile (*e.g.*

**Table 1.** N.m.r. spectra of complexes (3) and (4) ( $\delta$ /p.p.m., in  $\text{CDCl}_3$ )\*

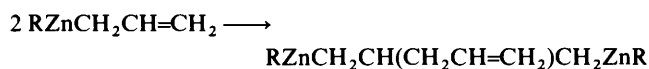
	a or d	b or c	e or f	g	h	i	j	k
<b><math>^1\text{H}</math> N.m.r.</b>								
(3)	7.40 (dt) (2.5) [2] 7.88 (dt) (2.5) [2]	6.94 (d) (2.5) 7.65 (d) (2.5)	0.49 (m) 0.92 (m)	1.82 (m)	1.90 (dd) (6)	5.80 (m)	4.82 (m)	1.67 (s)
(4)	7.54 (dt) (2.5) [2] 7.55 (dt) (2.5) [2]	7.43 (d) (2) 7.71 (d) (2)	0.93 (m) 1.29 (m)	1.02 (s)	2.04 (s)	1.77 (s)	4.60 (m) 4.72 (m)	1.66 (s)
<b><math>^{13}\text{C}</math> N.m.r.</b>								
	Rh-CH <sub>2</sub> -Rh		RhCH <sub>2</sub> -C	$\rightarrow$ C-R	C-CH <sub>2</sub> -C	-CR=	=CH <sub>2</sub>	C <sub>5</sub> Me <sub>5</sub>
(3)	157.6 (t), [30.0]	153.7 (t) [31.3]	28.0 (m) [30]	140.3	46.4	36.5	112.7	9.4 98.8
(4)	148.3 (t), [30.2]	149.3 (t) [30.2]	36.1 (m) [29.6]	146.2 Me, 25.6	61.8	37.2 Me, 39.9	113.0	9.3 99.0

\* Coupling constants (Hz) to  $^1\text{H}$  are given in parentheses, to  $^{103}\text{Rh}$  in square brackets.



LiMe) gave no useful product. The equilibrium must therefore be very much towards complexes (1) and (3) [or (4)] rather than to (A) [or (B)] and we surmise that the reaction in fact proceeds directly to the di- $\sigma$ -allyl compound (C) which then rearranges (Scheme 2).

The thermal rearrangements of  $\sigma$ -allyl-zinc compounds to the dinuclear 2-allylpropane-1,3-diylzinc have recently been reported by Lehmkuhl *et al.*<sup>4</sup> (see below). The reactions we observe appear very similar and probably proceed by similar routes (Scheme 2).



$\mu$ -Bis(diphenylphosphino)-ethane and -methane Complexes:  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\{\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}][\text{PF}_6]_2$  (5,  $n = 1$ ; 6,  $n = 2$ ).—Reaction of the bis-acetonitrile complex (2) with bis(diphenylphosphino)methane in acetone gave a high yield of complex (5); an analogous reaction of (2) with 1,2-bis(diphenylphosphino)ethane gave (6). Both complexes were

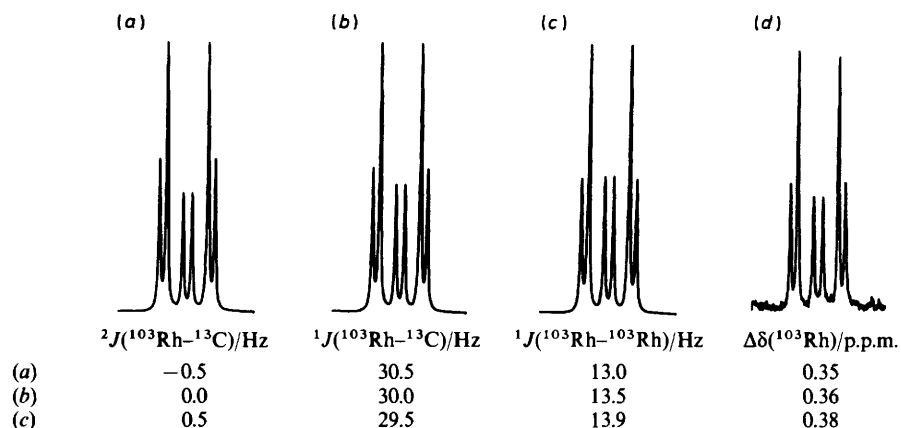
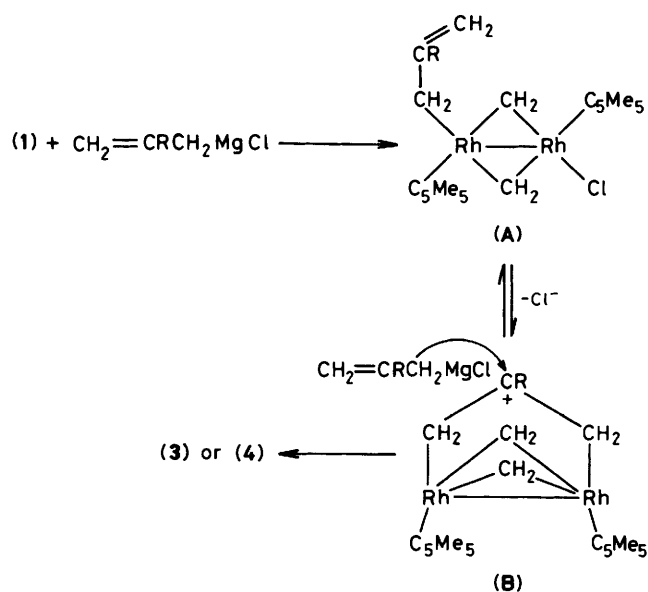


Figure. Computer simulations (a)–(c) of the  ${}^{13}\text{C}\{-{}^1\text{H}\}$  n.m.r. spectrum of the  $\text{RhCH}_2\text{C}$  resonance of complex (3) using the parameters given above; (d) observed spectrum

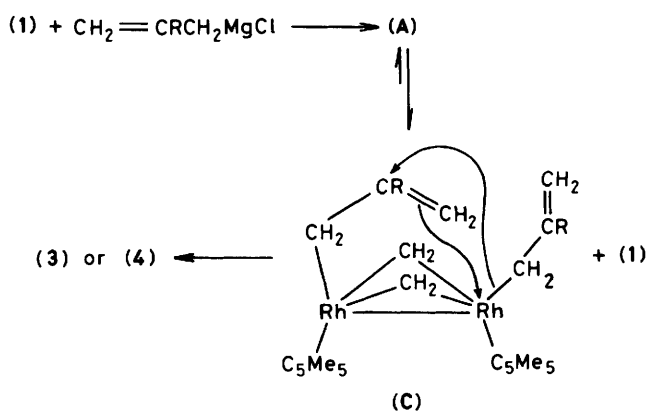


Scheme 1.

dinuclear dications and their structures were determined from analyses of their n.m.r. spectra.

The  ${}^1\text{H}$  spectrum of complex (5) showed the presence of only one type of  $\text{C}_5\text{Me}_5$  [doublet at  $\delta$  1.74,  $J(\text{P}-\text{H})$  4 Hz] and of one type of methylene bridging two rhodiums (Table 2). The proton patterns of the  $\mu$ -methylenes were typical for the *cis* arrangement expected except that the higher frequency (lower field) signal ( $\delta$  9.98) was a doublet of triplets, arising from the coupling of the equatorial hydrogens to two phosphorus nuclei ( $J$  11 Hz) and to one axial hydrogen ( $J$  2.2 Hz) but *not* to rhodium. The lower frequency (higher field) methylene resonance ( $\delta$  9.52) was a doublet of triplets arising from the coupling to the higher frequency pair of hydrogens ( $J$  2 Hz), and to the two rhodiums ( $J$  1.5 Hz), but *not* to phosphorus.

The  ${}^1\text{H}$  n.m.r. spectrum of (6) is very similar to that of complex (5) and similar assignments are made by comparison. However, the appearance of the  $\text{PCH}_2\text{CH}_2\text{P}$  resonances as a broad multiplet as well as the relative broadness of the  $\text{RhCH}_2\text{Rh}$  signals suggests that this molecule may be undergoing a dynamic process of intermediate rate. This was



Scheme 2.

not further investigated but it may well involve a flexing of the 1,2-bis(diphenylphosphino)ethane ligand with respect to the rest of the molecule.

The identity of the methylene resonances was shown by nuclear Overhauser enhancement experiments; when the phenyl protons were irradiated, the higher frequency methylene resonance was markedly enhanced while the lower frequency one was reduced. The opposite effect, enhancement of the lower frequency resonance, was observed when the  $\text{C}_5\text{Me}_5$  protons were irradiated.

Molecular models of (5) and (6) suggest that the  $\text{C}_5\text{Me}_5$  rings will exert a distorting effect on the methylene bridges, similar to that in the *cis*-dimethyl complex [ $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\text{-Me}_2$ ],<sup>1</sup> causing them to pucker towards the diphosphine ligand. In that case, the methylenic hydrogens nearest the phosphine phenyls will be the axial ones, which we therefore identify as giving the higher frequency resonance. Similarly the models indicate that the  $\text{C}_5\text{Me}_5$  rings are closer to the equatorial methylenic hydrogens, which therefore give rise to the lower frequency resonances. This is the same assignment as for the methylenes in *cis*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2\text{Me}_2]$ . The reason for the observation of coupling to phosphorus of the axial but not of the equatorial methylenic protons may be due to a Karplus-type relationship. The models suggest that the dihedral angle between  $\text{P}-\text{Rh}$  and  $\text{C}-\text{H}$  (axial) is likely to be near  $0^\circ$ , while that between  $\text{P}-\text{Rh}$  and  $\text{C}-\text{H}$  (equatorial) is likely to be

**Table 2.** N.m.r. spectra of complexes (5) and (6) [ $\delta$ /p.p.m., in (CD<sub>3</sub>)<sub>2</sub>CO] \*

	C <sub>5</sub> Me <sub>5</sub>	RhCH <sub>2</sub> Rh	PCH <sub>2</sub>	Phenyl
<sup>1</sup> H for (5)	1.74 (d) (4)	9.52 (dt) <i>J</i> (H-H) 2, [1.5] 9.98 (dt)	3.69 (t) (11)	7.6 (m)
<sup>1</sup> H for (6)	1.72 (d) (4)	10.21 (s, br) 10.43 (t) (11.7)	2.40 (m, br)	7.76 (m, br)
<sup>13</sup> C-{ <sup>1</sup> H} for (5)	10.5 (s) 109.83 (d) (2)	173.4 (tt) [24] (6)	26.6 (t) (26)	C <sub>i</sub> 126.7 (m) C <sub>o</sub> 130.0 (m) C <sub>m</sub> 134.5 (m) C <sub>p</sub> 133.4 (s)
<sup>13</sup> C-{ <sup>1</sup> H} for (6)	9.8 (s) 110.4 (s)	170.9 (tt) ( <i>ca.</i> 6) [ <i>ca.</i> 23]	23.8 (d) (31)	C <sub>i</sub> 126.0 (d) (30) C <sub>o</sub> 129.5 (d) (9.8) C <sub>m</sub> 133.5 (d) (8.5) C <sub>p</sub> 132.4 (s)

\* Coupling constants (Hz) to <sup>31</sup>P are given in parentheses, to <sup>103</sup>Rh in square brackets.

around 90°. In saturated organic systems <sup>3</sup>*J*(H-H) is at a maximum and at a minimum respectively for these two dihedral angles.

The more coplanar arrangement of the equatorial hydrogens and the two rhodiums may facilitate the coupling to rhodium which is observed here.

The <sup>13</sup>C n.m.r. spectra of complexes (5) and (6) (Table 2) were also in complete agreement with the proposed structures.

The <sup>31</sup>P n.m.r. spectra of the ligands in complexes (5) and (6) are typical 12 line [AX]<sub>2</sub> spectra centred at  $\delta$  + 44.0 in (5) and + 43.8 in (6). The analysis of this system leads to the coupling constants for complex (5), *J*(AA') = ± 12.4 ± 0.3 Hz, *J*(XX') = ± 35.4 ± 0.3 Hz, *J*(AX) = ∓ 159.3 ± 0.3 Hz, and *J*(AX') = ∓ 0.9 ± 0.3 Hz; for complex (6), *J*(AA') = ± 11.9 ± 0.3, *J*(XX') = ± 1.3 ± 0.3 Hz, *J*(AX) = ∓ 165.9 ± 0.3 Hz, and *J*(AX') = ∓ 1.6 ± 0.3 Hz.

Since the change in the number of bridging CH<sub>2</sub> in the diphosphine ligand from one in (5) to two in (6) is expected to have a large effect on <sup>2,3</sup>*J*(<sup>31</sup>P-<sup>31</sup>P) but little effect on <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh), while <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>31</sup>P) will be large<sup>5</sup> and <sup>2</sup>*J*(<sup>103</sup>Rh-<sup>31</sup>P) small the assignments are A = <sup>103</sup>Rh and X = <sup>31</sup>P. Thus the rhodium-rhodium coupling constants are 12.4 Hz for (5) and 11.9 Hz for complex (6).

**Rh-Rh Coupling Constants.**—The observation of <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) is so far rather rare with few literature reports. The reported values for <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) cover a relatively wide range, from 4.2 and 4.4 Hz for [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(CO)<sub>3</sub>] and [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(NO)<sub>2</sub>] respectively,<sup>6</sup> to 35 Hz for [Rh<sub>2</sub>(hmpy)<sub>4</sub>] (Hhmpy = 2-hydroxy-6-methylpyridine).<sup>7</sup> In addition a value of 17 Hz has been found<sup>8</sup> for [Rh<sub>2</sub>(CH=CH<sub>2</sub>)(CMe=CHMe)(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>]. The value of *ca.* 12 Hz for <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) appears at first sight to be quite small, when compared with the much larger values observed for other metals. However it is important to use comparable numbers. Qualitatively it has been shown that the contact term in the coupling constant<sup>9</sup> is given by equation (1) where *h* is Planck's constant,  $\gamma_A$  and  $\gamma_B$  the

$$J_{AB} = \frac{32h}{9} \left( \frac{\gamma_A}{2\pi} \right) \left( \frac{\gamma_B}{2\pi} \right) \pi \mu_0 \mu_B^2 S_A^2(0) S_B^2(0) P_{S_A S_B}^{\alpha} \quad (1)$$

gyromagnetic ratios of nuclei A and B,  $\mu_0$  the permeability of a vacuum,  $\mu_B$  the Bohr magneton, *S*<sub>A</sub><sup>2</sup>(0) and *S*<sub>B</sub><sup>2</sup>(0) the electron density at the nucleus, and *P*<sub>S<sub>A</sub>S<sub>B</sub></sub><sup>α</sup> the *s*-bond order.

Despite the approximations inherent in equation (1) it appears to be qualitatively valid for coupling constants between transition metals. Thus in order to compare <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) with *J*<sub>AB</sub> it is necessary not only to correct for  $\gamma_A \gamma_B$  as is usual but also *S*<sub>A</sub><sup>2</sup>(0) *S*<sub>B</sub><sup>2</sup>(0). Approximate *S*<sub>A</sub><sup>2</sup>(0) values are available in the literature,<sup>10</sup> but are rarely used. To compare <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>195</sup>Pt) and <sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) it is usual to use reduced coupling constants, *K*, according to equation (2). Thus

$$K_{AB} = J_{AB} h^{-1} \left( \frac{2\pi}{\gamma_A} \right) \left( \frac{2\pi}{\gamma_B} \right) \quad (2)$$

<sup>1</sup>*J*(<sup>103</sup>Rh-<sup>103</sup>Rh) of 12 Hz corresponds to a <sup>1</sup>*K*(<sup>103</sup>Rh-<sup>103</sup>Rh) of 10<sup>23</sup> cm<sup>-3</sup> while a <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>195</sup>Pt) of 7 500 Hz corresponds to a <sup>1</sup>*K*(<sup>195</sup>Pt-<sup>195</sup>Pt) of 13.5 × 10<sup>23</sup> cm<sup>-3</sup>, implying that the rhodium-rhodium *s*-bond order is small. However, by using optical hyperfine splitting constants, it has been estimated that *S*<sub>Pt</sub>(0)<sup>2</sup> = 223.1 × 10<sup>24</sup> cm<sup>-3</sup> and *S*<sub>Rh</sub>(0)<sup>2</sup> = 59.4 × 10<sup>24</sup> cm<sup>-3</sup>. Thus as equation (1) contains *S*<sub>A</sub>(0)<sup>2</sup> *S*<sub>B</sub>(0)<sup>2</sup>, it can be predicted that <sup>1</sup>*K*(<sup>195</sup>Pt-<sup>195</sup>Pt) should be *ca.* 14 times larger than <sup>1</sup>*K*(<sup>103</sup>Rh-<sup>103</sup>Rh) due purely to differences in *s*-electron density at the nucleus. There is therefore no significant difference in *s*-bond order between the compounds (3)–(6) reported in this paper and, say, [Pt<sub>2</sub>Cl<sub>2</sub>(μ-Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] where <sup>1</sup>*J*(<sup>195</sup>Pt-<sup>195</sup>Pt) = 8 197 Hz.<sup>11</sup>

The <sup>12/13</sup>C isotope shifts,  $\Delta\delta$ (<sup>103</sup>Rh) = 0.34 for (4) and 0.36 for (3) p.p.m. are in the range reported by Salzer *et al.*<sup>12</sup> for <sup>103</sup>Rh bound to C<sub>5</sub>H<sub>5</sub> in two dimeric complexes and consistent with a value of *ca.* 0.2 p.p.m. which was found by Goodfellow and co-workers<sup>13</sup> in [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>4</sub>Rh<sub>4</sub>H<sub>4</sub>]<sup>2+</sup>

## Experimental

The n.m.r. spectra were measured on JEOL PFT-100 (<sup>31</sup>P, 40.48 MHz) and Bruker WH 400 (<sup>13</sup>C, 100.62 MHz) n.m.r. spectrometers in (CD<sub>3</sub>)<sub>2</sub>CO (<sup>31</sup>P) and CDCl<sub>3</sub> (<sup>13</sup>C). The data are presented in Tables 1 and 2. Microanalyses were by the University of Sheffield Microanalytical Service.

[(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Rh<sub>2</sub>(μ-CH<sub>2</sub>)<sub>2</sub>{μ-CH<sub>2</sub>CH(CH<sub>2</sub>CH=CH<sub>2</sub>)-CH<sub>2</sub>}] (3).—Complex (1) (100 mg, 0.174 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer, Suba-seal, and nitrogen inlet and outlet. After flushing with nitrogen for a few minutes, dry toluene (10 cm<sup>3</sup>) was added by syringe.

Once all the complex (1) had dissolved, allylmagnesium chloride in diethyl ether ( $8 \text{ cm}^3$ ,  $0.25 \text{ mol dm}^{-3}$ ) was injected into the solution (over *ca.* 5 min). During this period the colour of the solution turned from deep wine-red to a light yellow. The solution was further stirred (5 min); acetone-water (1:1.3  $\text{cm}^3$ ) was added to remove the excess Grignard reagent. The crude solution was then evaporated to dryness. The white-yellow residue was extracted into *n*-pentane ( $3 \times 15 \text{ cm}^3$ ); removal of solvent from the pentane extracts gave a yellow-red oil which upon addition of ice-cold methanol ( $3 \text{ cm}^3$ ) gave yellow needles (60 mg, 59%) of complex (3) which were isolated by filtration (Found: C, 57.9; H, 7.5.  $\text{C}_{28}\text{H}_{44}\text{Rh}_2$  requires C, 57.3; H, 7.5%). I.r. (KBr disc):  $\nu(\text{C}=\text{C})$ , 1 640;  $\nu(\text{C}=\text{CH}_2)$ , 3 070  $\text{cm}^{-1}$ .

Complex (4) was prepared similarly (50% yield) from  $\text{CH}_2=\text{CMeCH}_2\text{MgCl}$  and complex (1) (Found: C, 58.0; H, 7.9.  $\text{C}_{30}\text{H}_{48}\text{Rh}_2$  requires C, 58.6; H, 7.8%). I.r.:  $\nu(\text{C}=\text{C})$ , 1 635;  $\nu(\text{C}=\text{CH}_2)$ , 3 080  $\text{cm}^{-1}$ .

$[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)]_2[\text{PF}_6]_2$  (5).

—Complex (2;  $\text{PF}_6^-$  salt) (150 mg,  $1.71 \times 10^{-4}$  mmol) was dissolved in acetone ( $4 \text{ cm}^3$ ) and the solution stirred. A solution of bis(diphenylphosphino)methane (79 mg,  $2.05 \times 10^{-4}$  mmol) in acetone ( $2 \text{ cm}^3$ ) was then added dropwise (over *ca.* 5 min). During this time the solution darkened noticeably to a deep orange colour. After further stirring (15 min) diethyl ether ( $10 \text{ cm}^3$ ) was added gradually giving a fine yellow precipitate which was isolated by filtration yielding 0.160 g (76%) of the yellow-orange complex (5) (Found: C, 48.1; H, 5.0; N, 0.0.  $\text{C}_{47}\text{H}_{56}\text{F}_{12}\text{P}_4\text{Rh}_2$  requires C, 47.9; H, 4.8; N, 0%). I.r.:  $\nu(\text{PF})$ , 835  $\text{cm}^{-1}$ .  $^{31}\text{P}$  N.m.r. [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  44.0 (m) and  $-144.4$  (septet) [ $J(\text{P}-\text{F})$  708 Hz,  $\text{PF}_6^-$ ] (reference external 85%  $\text{H}_3\text{PO}_4$ ).

Complex (6) was prepared similarly (in 81% yield) by reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CH}_2)_2(\text{MeCN})_2][\text{CF}_3\text{SO}_3]_2$  with 1,2-bis(diphenylphosphino)ethane in acetone (Found: C, 49.3; H, 5.0; S, 6.0.  $\text{C}_{50}\text{H}_{58}\text{F}_6\text{O}_6\text{P}_2\text{Rh}_2\text{S}_2$  requires C, 50.0; H, 4.8; S, 5.3%). I.r.:  $\nu(\text{SO}_3)$ , 1 148 and 1 268  $\text{cm}^{-1}$ .  $^{31}\text{P}$  N.m.r. [ $(\text{CD}_3)_2\text{CO}$ ]:  $\delta$  43.8 (m).

#### Acknowledgements

We thank the S.E.R.C. for support and Mr. G. A. Wright for synthesis of starting materials.

#### References

- 1 K. Isobe, D. G. Andrews, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 809; K. Isobe, A. Vázquez de Miguel, P. M. Bailey, S. Okeya, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1983, 1441; A. Vázquez de Miguel, M. Gómez, K. Isobe, B. F. Taylor, B. E. Mann, and P. M. Maitlis, *Organometallics*, 1983, **2**, 1724.
- 2 K. Isobe, P. M. Bailey, P. Schofield, J. T. Gauntlett, A. Nutton, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 425; N. J. Meanwell, A. J. Smith, H. Adams, S. Okeya, and P. M. Maitlis, *Organometallics*, 1983, **2**, 1705; K. Isobe, S. Okeya, N. J. Meanwell, A. J. Smith, H. Adams, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1215.
- 3 S. Okeya, B. F. Taylor, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1983, 971; S. Okeya, N. J. Meanwell, B. F. Taylor, K. Isobe, A. Vázquez de Miguel, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1984, 1453.
- 4 H. Lehmkuhl, I. Doring, R. McLane, and H. Nehl, *J. Organomet. Chem.*, 1981, **221**, 1.
- 5 See, for example, P. S. Pregosin and R. W. Kunz,  $^{31}\text{P}$  and  $^{13}\text{C}$  N.M.R. of Transition Metal Phosphine Complexes, vol. 16 in the series 'N.M.R. Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, Heidelberg, and New York, 1979.
- 6 R. J. Lawson and J. R. Shapeley, *Inorg. Chem.*, 1978, **17**, 2963.
- 7 M. Berry, C. D. Garner, and B. E. Mann, *Inorg. Chem.*, 1984, **23**, 1500.
- 8 P. Caddy, M. Green, L. E. Smart, and N. White, *J. Chem. Soc., Chem. Commun.*, 1978, 839.
- 9 A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, 1971, **55**, 950.
- 10 G. W. Smith, Research Publication GMR-444, General Motors Corporation, Warren, Michigan, 1964.
- 11 N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, and J. L. Spencer, *J. Chem. Res.*, 1978, 228 (S) 2962 (M).
- 12 A. Salzer, T. Egolf, and W. von Philipsborn, *Helv. Chim. Acta*, 1982, **65**, 1145.
- 13 J. S. Ricci, T. F. Koetzle, R. J. Goodfellow, P. Espinet, and P. M. Maitlis, *Inorg. Chem.*, 1984, **23**, 1828.

Received 23rd July 1984; Paper 4/1283