

## Synthesis and Characterization of Dinuclear Rhodium Complexes containing (Benzylthiomethyl)diphenylphosphine as the Bridging Ligand. Structure of the Novel Rhodium(II) Complex $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-PhCH}_2\text{SCH}_2\text{PPh}_2)_2]^\dagger$

Yoshio Fuchita\*

Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

Yoshihisa Ohta, Katsuma Hiraki, and Masanori Kawatani

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852, Japan

Nobuaki Nishiyama

Center of Advanced Instrument Analysis, Kyushu University, Kasugakoen, Kasuga, Fukuoka 816, Japan

Treatment of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  with 5 equivalents of  $\text{PhCH}_2\text{SCH}_2\text{PPh}_2$  (btmp) gave the mononuclear Vaska-type complex *trans*- $[\text{RhCl}(\text{CO})(\text{btmp-}P)_2]$ , whereas the reaction with 2 equivalents of btmp afforded not the expected face-to-face complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-btmp})_2]$  but the chloro-bridged complex  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2][\text{RhCl}_2(\text{CO})_2]$ . The tetraphenylborate salt analogue  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2]\text{BPh}_4$  was obtained from the reaction of an ethanolic solution of  $[\text{RhCl}_2(\text{CO})_2]^-$  with 1 equivalent of btmp and  $\text{NaBPh}_4$ . Treatment of  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  with 1 equivalent of btmp afforded the carbonyl-bridged dinuclear complex  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-btmp})_2]$ , while the above reaction performed in the presence of hydrochloric acid gave the novel dinuclear rhodium(II) complex  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (**5**). Complex (**5**) was also obtained from the reaction of an ethanolic solution of  $[\text{RhCl}_2(\text{CO})_2]^-$  and 1 equivalent of btmp. Crystals of (**5**) are monoclinic, space group *C2/c*, with  $a = 14.064(3)$ ,  $b = 19.364(4)$ ,  $c = 16.930(5)$  Å,  $\beta = 116.67(2)^\circ$ , and  $Z = 4$ ; final  $R = 0.036$  for 3 529 observed reflections. The structure shows that there is a metal-metal bond  $[\text{Rh}-\text{Rh} 2.733(3)$  Å] and the two  $\mu\text{-btmp}$  ligands are co-ordinated to rhodium atoms *cis* to each other with a head-to-tail arrangement. The relationships among the synthesized complexes are discussed.

We<sup>1</sup> have previously reported the synthesis of side-by-side and A-frame type complexes of palladium containing the bidentate bridging ligand (benzylthiomethyl)diphenylphosphine (btmp). This ligand has different donor sites P and S, which seemed to increase the reactivity for acetylene insertion into the Pd-Pd bond of the side-by-side complex; phenylacetylene reacted with  $[\text{Pd}_2\text{Cl}_2(\mu\text{-btmp})_2]$  to give  $[\text{Pd}_2\text{Cl}_2(\mu\text{-PhC}=\text{CH})(\mu\text{-btmp})_2]$ , while  $[\text{Pd}_2\text{Cl}_2(\mu\text{-dppm})_2][\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{-methane}]$  was reported to show no reactivity towards phenylacetylene.<sup>2</sup> In view of this observation we anticipated that btmp might show different chemistry on rhodium complexes compared with that of dppm.

Here, we report the synthesis of four types of rhodium complexes containing btmp, *i.e.* *trans*- $[\text{RhCl}(\text{CO})(\text{btmp-}P)_2]$ ,  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2]\text{X}$  [ $\text{X} = \text{RhCl}_2(\text{CO})_2$  or  $\text{BPh}_4$ ],  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-btmp})_2]$ , and  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$ , and the relationships among these complexes. The X-ray crystal structure analysis of the novel rhodium(II) complex  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  is also described.

Recently, in the course of our study on this chemistry, Anderson and Kumar<sup>3</sup> reported the synthesis of the face-to-face rhodium complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-MeSCH}_2\text{PPh}_2)_2]$  and Anderson<sup>4</sup> reported the heterobimetallic complex  $[\text{RhPdCl}_3(\text{CO})(\mu\text{-MeSCH}_2\text{PPh}_2)_2]$ .

Analytical and physical data, and selected n.m.r. data, are listed in Tables 1 and 2, respectively.

*Synthesis of the Complexes.*—Reaction of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  with 5 equivalents of btmp produced a mononuclear Vaska-type complex *trans*- $[\text{RhCl}(\text{CO})(\text{btmp-}P)_2]$  (**1**). In the <sup>13</sup>C n.m.r. spectrum of (**1**) the *ipso*, *o*-, and *m*-carbons of the phenyl groups in the phosphine moieties appeared as triplets at  $\delta$  132.58 ( $^1J_{\text{PC}} + ^3J_{\text{PC}} = 21.2$ ), 133.73 ( $^2J_{\text{PC}} + ^4J_{\text{PC}} = 5.9$ ), and 128.24 ( $^3J_{\text{PC}} + ^5J_{\text{PC}} = 3.9$  Hz), respectively, and the methylene carbons between the P and S atoms resonated as a triplet (Table 2). These triplets were ascribed to the virtual couplings caused by the two phosphorus nuclei co-ordinated *trans* to each other. Moreover, the molar conductivity measured in acetone showed that (**1**) was a non-electrolyte. On the basis of these results and the elemental analysis, together with the observation of only one <sup>31</sup>P resonance, (**1**) was assigned the structure shown in Scheme 1.

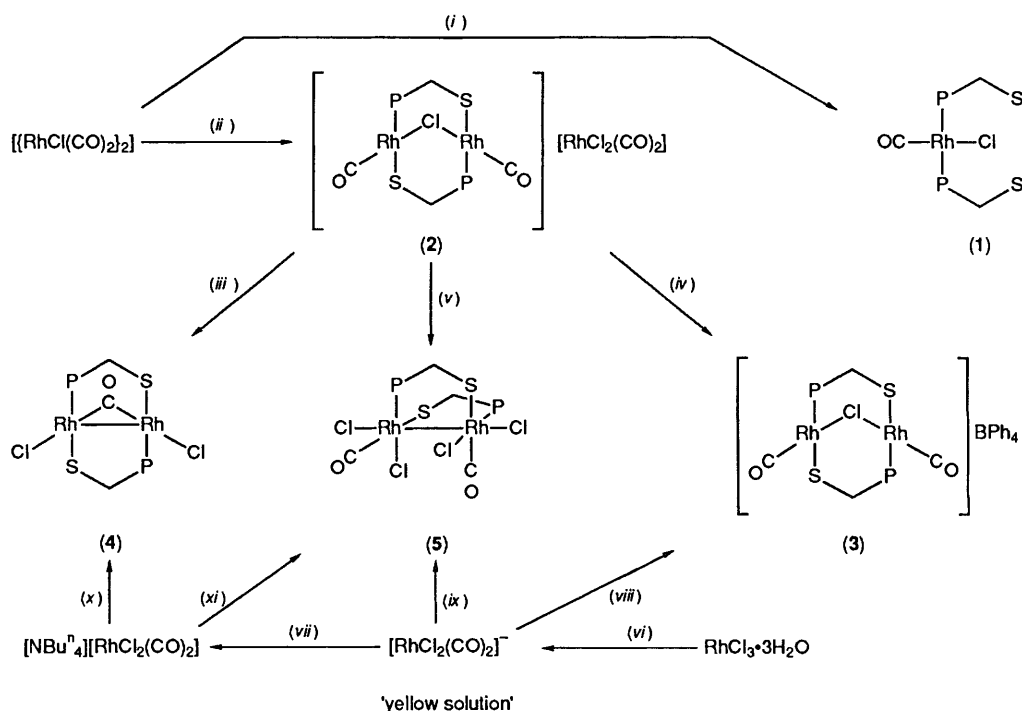
The reaction between  $[\{\text{RhCl}(\text{CO})_2\}_2]$  and 2 equivalents of btmp unexpectedly afforded a salt  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2][\text{RhCl}_2(\text{CO})_2]$  (**2**). Anderson and Kumar<sup>3</sup> reported the synthesis of a face-to-face rhodium complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-MeSCH}_2\text{PPh}_2)_2]$  using (methylthiomethyl)diphenylphosphine as the bridging ligand instead of btmp. We expected that the

### Results and Discussion

The method of preparation of the complexes and the interconversion observed are summarized in Scheme 1.

† Bis[ $\mu$ -(benzylthiomethyl)diphenylphosphine]-1:2 $\kappa^2P,S$ ; 1:2 $\kappa^2S,P$ -bis[carbonyldichlororhodium(II)] (*Rh-Rh*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.



**Scheme 1.** (i) 5 mol btmp in  $\text{CH}_2\text{Cl}_2$ ; (ii) 2 mol btmp in  $\text{CH}_2\text{Cl}_2$  or  $\text{Et}_2\text{O}$ ; (iii) in  $\text{EtOH}$ ; (iv) 1 mol  $\text{NaBPh}_4$  in  $\text{EtOH}$ ; (v) three drops concentrated  $\text{HCl}$  in  $\text{EtOH}$ ; (vi)  $\text{CO}$  in refluxing aqueous  $\text{EtOH}$ ; (vii) 1 mol  $\text{NBu}_4^+\text{Cl}^-$  in aqueous  $\text{EtOH}$ ; (viii) 1 mol of btmp and  $\text{NaBPh}_4$  in  $\text{EtOH}$ -acetone; (ix) 1 mol btmp in aqueous  $\text{EtOH}$ ; (x) 1 mol btmp in  $\text{EtOH}$ ; (xi) three drops concentrated  $\text{HCl}$  and 1 mol btmp in  $\text{EtOH}$

**Table 1.** Analytical<sup>a</sup> and physical data for the complexes

Complex	M.p. ( $\theta$ , $^\circ\text{C}$ )	Yield (%)	$\nu(\text{CO})^b/\text{cm}^{-1}$	Analysis(%)		$\Lambda_M/S \text{ cm}^2 \text{ mol}^{-1}$
				C	H	
(1) $[\text{RhCl}(\text{CO})(\text{btmp}-P)_2]^c$	48	82	1 960	58.3 (58.4)	4.75 (4.6)	0.78
(2) $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2][\text{RhCl}_2(\text{CO})_2]$	163 <sup>d</sup>	66 <sup>e</sup> 87 <sup>f</sup>	2 060s, 2 000(sh) 1 980s	44.8 (45.1)	3.5 (3.25)	108
(3) $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2]\text{BPh}_4$	137 <sup>d</sup>	70	2 005s, 1 985s	62.35 (62.85)	4.75 (4.65)	92
(4) $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-btmp})_2]$	198 <sup>d</sup>	67	1 780m	51.45 (51.85)	4.05 (4.05)	—
(5) $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$	> 300	72 <sup>g</sup> 80 <sup>h</sup>	2 080s, 2 075(sh)	48.1 (48.1)	3.8 (3.65)	—

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> In  $\text{KBr}$ . <sup>c</sup> Complex (1) was isolated as a 0.5  $\text{CH}_2\text{Cl}_2$  solvate; presence of  $\text{CH}_2\text{Cl}_2$  confirmed by  $^1\text{H}$  n.m.r. spectroscopy. <sup>d</sup> With decomposition. <sup>e</sup> Yield in  $\text{CH}_2\text{Cl}_2$ . <sup>f</sup> Yield in  $\text{Et}_2\text{O}$ . <sup>g</sup> Yield from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ . <sup>h</sup> Yield from  $[\text{NBu}_4^+][\text{RhCl}_2(\text{CO})_2]^-$ .

**Table 2.** Selected  $^{13}\text{C}$ - $\{^1\text{H}\}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  n.m.r. data<sup>a</sup>

Complex	$^{13}\text{C}$ N.m.r. <sup>b</sup>						$^{31}\text{P}$ N.m.r. <sup>c</sup>	$^1J_{\text{RhC}}/\text{Hz}$
	$\text{PhCH}_2\text{S}$	$\text{SCH}_2\text{P}$	$^1J_{\text{PC}}/\text{Hz}$	$\text{CO}$	$^1J_{\text{RhC}}/\text{Hz}$	$^2J_{\text{PC}}/\text{Hz}$		
(1)	38.80(s)	27.89(t) <sup>d</sup>	—	ca. 186.9	—	—	24.39(d)	123.7
(2)	45.46(s)	30.96(d)	27.4	181.16(d) <sup>e</sup> 181.80(dd) <sup>f</sup>	66.5 82.2	— 19.6	30.73(d)	141.6
(3)	43.09(s)	33.73(d)	27.4	— <sup>g</sup>	—	—	30.73(d)	141.6
(4)	42.93(s)	33.34(d)	27.4	228.15(tt)	47.0	7.8	35.63(d)	146.4
(5)	42.83(d) <sup>h</sup>	37.44(d)	31.3	184.40(dd)	62.6	11.8	21.29(d)	112.3

<sup>a</sup> Key: s = singlet, d = doublet, and t = triplet. <sup>b</sup> Recorded at 100 MHz in  $\text{CDCl}_3$  for complexes (1), (2), and (4), or in  $\text{CD}_2\text{Cl}_2$  for (3) and (5) at 30  $^\circ\text{C}$ ;  $\delta/\text{p.p.m.}$  relative to  $\text{SiMe}_4$ . <sup>c</sup> Recorded at 162 MHz in  $\text{CDCl}_3$  except for complex (3) ( $\text{CD}_2\text{Cl}_2$ ) at 30  $^\circ\text{C}$ ;  $\delta/\text{p.p.m.}$  relative to external 85%  $\text{H}_3\text{PO}_4$ . <sup>d</sup>  $|^1J_{\text{PC}} + ^3J_{\text{PC}}| = 11.7 \text{ Hz}$ . <sup>e</sup>  $[\text{RhCl}_2(\text{CO})_2]^-$ . <sup>f</sup>  $\mu\text{-Cl-Rh-CO}$ . <sup>g</sup> Not detected. <sup>h</sup>  $^3J_{\text{PC}} = 11.8 \text{ Hz}$ .

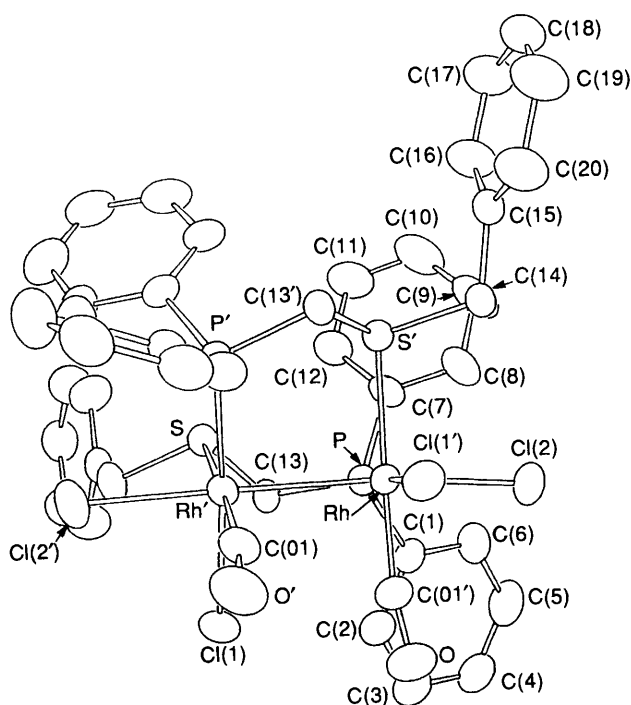


Figure. Molecular structure of  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (5) showing the principal atomic numbering

above reaction would form a face-to-face rhodium complex, but such a complex could not be isolated under several reaction conditions including exactly the same procedure reported previously.<sup>3</sup> The yield of (2) was maximum when the molar ratio of  $[\{\text{RhCl}(\text{CO})_2\}_2]$ : btmp was 3:4.5, which meant that a large excess of btmp is not necessary for the synthesis of (2). In the above reaction  $[\{\text{RhCl}(\text{CO})_2\}_2]$  acts as a halide-abstraction agent. This ability of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  was also observed in its reaction with dppm or bis(diphenylarsino)methane (dpam) which affords the chloro-bridged complex  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-L})_2][\text{RhCl}_2(\text{CO})_2]$  (L = dppm or dpam).<sup>5</sup>

The far-i.r. spectrum of complex (2) showed characteristic bands at 330 and 285  $\text{cm}^{-1}$  due to  $\nu(\text{Rh}-\text{Cl})$  of  $[\text{RhCl}_2(\text{CO})_2]^-$ ,<sup>6</sup> and the molar conductivity measured in acetone revealed that (2) is a 1:1 electrolyte. The  $^{13}\text{C}$  n.m.r. spectrum exhibited only one doublet of doublets at  $\delta$  181.80 for the carbonyl carbon signal of the cation moiety. Only one set of signals was also observed for the two methylene carbons of the btmp ligands. These data confirmed that two btmp ligands were co-ordinated to the rhodium centres *trans* to each other in a head-to-tail fashion.

It is known that hydrated rhodium(III) chloride reacts with CO in refluxing aqueous ethanol to afford dicarbonyldichlororhodate(I) as a yellow solution,<sup>7</sup> from which  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  could easily be obtained by treating with  $\text{NBu}^n_4\text{Cl}$ . Reactions of dicarbonyldichlororhodate(I) with btmp have been investigated using the 'yellow solution' and  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$ . First, a chloro-bridged cationic complex  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2]\text{-BPh}_4$  (3), an analogue of (2), was obtained by adding btmp and sodium tetraphenylborate to the yellow solution. Secondly, a carbonyl-bridged dirhodium complex  $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-btmp})_2]$  (4) was obtained by treating  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  with btmp. Thirdly, a novel dirhodium(II) complex  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (5) was afforded from either of the two  $[\text{RhCl}_2(\text{CO})_2]^-$  species. From the yellow solution, (5) was obtained by reaction with only btmp without sodium tetraphenylborate, while from  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  it was produced with btmp in the presence of hydrochloric acid.

For complex (3) the spectroscopic data were quite similar to those of (2), and moreover in the  $^{13}\text{C}$  n.m.r. spectrum characteristic signals of tetraphenylborate were observed at  $\delta$  115.67 (br s, *m*-C) and 122.09 (br s, *p*-C).<sup>8</sup>

The i.r. spectrum of complex (4) showed a carbonyl stretching frequency at lower wave-number (1780  $\text{cm}^{-1}$ ), indicating a bridging carbonyl ligand. This carbonyl carbon resonated at lower field,  $\delta$  228.15, as a triplet of triplets owing to the couplings with  $^{103}\text{Rh}$  and  $^{31}\text{P}$ . Such a resonance is normal for the bridging carbonyl ligands,<sup>8</sup> and is ascribed to a larger degree of back donation from the metals.<sup>9</sup> For the two methylene carbons of the btmp ligands, only one set of signals, a doublet (PCH<sub>2</sub>S) and a singlet (PhCH<sub>2</sub>S), were observed. Considering the fact that the methylene carbon between the P and S atoms appeared as a triplet for (1) where two btmp ligands are co-ordinated *trans* to each other (see before), the arrangement of the two btmp ligands in (4) is shown as head-to-tail.

For the novel dirhodium(II) complex (5), the i.r. spectrum showed terminal carbonyls at 2080s and 2075(sh)  $\text{cm}^{-1}$ . In the  $^{13}\text{C}$  n.m.r. spectrum the carbonyl carbon was observed as only one doublet of doublets at  $\delta$  184.40, which is normal for terminal carbonyls.<sup>8</sup> The coupling constant between P and C indicated that the carbonyl ligands are situated *cis* to the phosphine ligands. Again the methylene carbons of the btmp ligands appeared as only one set of signals. On the basis of these results and elemental analysis, (5) was assigned the formula  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$ , in which two btmp ligands are co-ordinated to rhodium in a head-to-tail arrangement. Concerning the dicarbonyltetrachlorodirhodium(II) complex of dppm, Cotton *et al.*<sup>10</sup> reported that this type of complex could be isolated by treating  $[\text{Rh}_2(\mu\text{-Cl})\text{Cl}_3(\text{CO})(\mu\text{-dppm})_2]$  with CO. However, the product easily loses one carbonyl ligand giving the monocarbonyltetrachlorodirhodium(II) complex, and so an X-ray crystal analysis has not yet been possible. On the contrary, in the case of bis(dimethylphosphino)methane (dmpm) it was reported that the complex  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-dmpm})_2]$  was formed during attempts to obtain crystals of the face-to-face complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dmpm})_2]$  and was shown by an X-ray diffraction study to have the *trans* arrangement of the two dmpm ligands.<sup>11</sup>

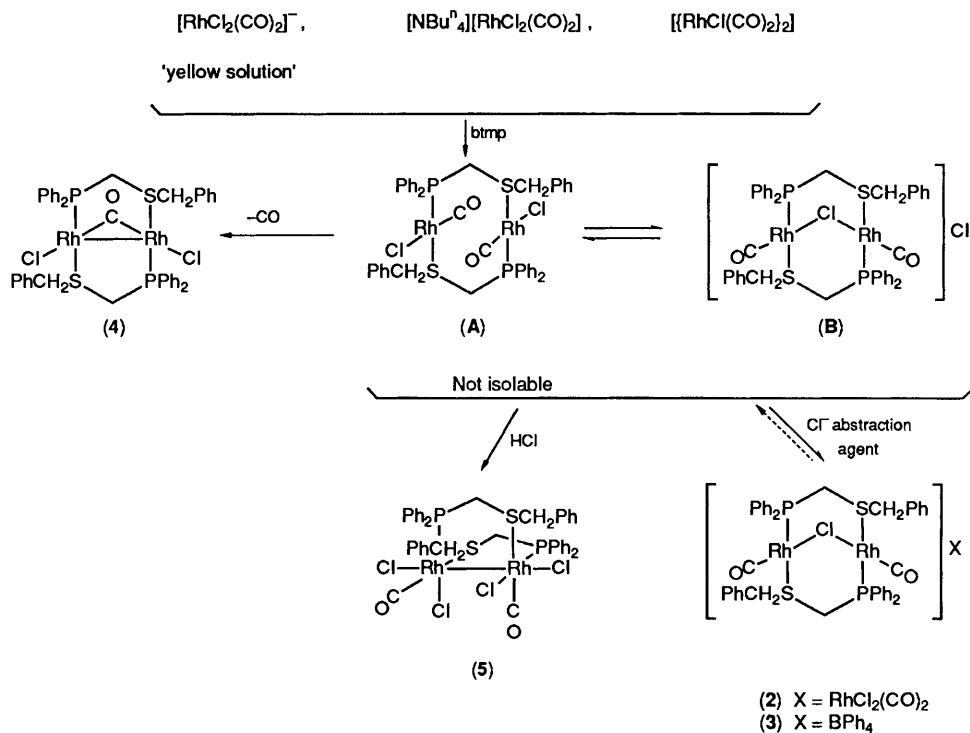
**Molecular Structure of  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (5).**—The structure of complex (5) has been established by X-ray diffraction studies (Figure, Table 3). Unexpectedly, complex (5) has a *cis* arrangement of the btmp groups bridging the two octahedral rhodium centres in a head-to-tail fashion. This is different from the *trans* arrangement of the dmpm ligands in  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-dmpm})_2]$ .<sup>11</sup> The Rh–Rh separation is 2.733(3) Å in the range for normal two-electron Rh–Rh bonds [2.617(3)–2.796(8) Å].<sup>12,13</sup> The Rh–Cl bonds opposite the Rh–Rh bond [2.470(1) Å] are longer than those opposite P–Rh bonds [2.418(1) Å], showing a high *trans* influence of the metal–metal bond.<sup>11,14</sup> The Rh–Rh–Cl angles [174.1(4)°] indicated that the Cl–Rh–Rh–Cl chain is approximately linear. The carbonyl ligands are co-ordinated *cis* to the phosphine ligands as expected and are slightly bent [Rh–C–O 168.8(3)°] owing to the steric effect of the bulky diphenylphosphino groups. The five-membered ring, constituted by Rh, Rh', S, C(13), and P atoms, has an envelope conformation with the sulphur atom 0.998 Å from the mean plane of the other atoms.

**Relationships among the Synthesized Rhodium Complexes.**—As stated before,  $[\{\text{RhCl}(\text{CO})_2\}_2]$  produced complexes (1) and (2) depending on the amounts of btmp ligand, and dicarbonyldichlororhodate species, the 'yellow solution' of  $[\text{RhCl}_2(\text{CO})_2]^-$  and  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$ , gave three types of complexes, (3)–(5).

**Table 3.** Bond distances (Å) and angles (°) in  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (5)\*

Rh-Rh'	2.733(3)	Rh-P	2.291(1)	P-C(13)	1.840(5)	S-C(13)	1.813(3)
Rh-Cl(1')	2.418(1)	Rh-S'	2.390(3)	P-C(1)	1.827(4)	S'-C(14)	1.829(6)
Rh-Cl(2)	2.470(1)	Rh-C(01')	1.867(6)	P-C(7)	1.835(5)	O-C(01)	1.135(6)
Rh'-Rh-Cl(1')	92.3(4)	Cl(2)-Rh-P	87.1(3)	C(13)-P-C(1)	101.9(2)		
Rh'-Rh-Cl(2)	174.1(4)	Cl(2)-Rh-S'	95.2(4)	C(13)-P-C(7)	104.4(4)		
Rh'-Rh-P	91.8(1)	Cl(2)-Rh-C(01')	84.2(9)	C(1)-P-C(7)	110.4(9)		
Rh'-Rh-S'	90.5(4)	P-Rh-S'	91.2(7)	Rh-S'-C(13')	103.5(2)		
Rh'-Rh-C(01')	90.0(4)	P-Rh-C(01')	94.0(6)	Rh-S'-C(14)	104.6(4)		
Cl(1')-Rh-Cl(2)	88.6(4)	S'-Rh-C(01')	174.6(1)	C(14')-S-C(13)	99.2(2)		
Cl(1')-Rh-P	175.7(2)	Rh-P-C(13)	114.5(1)	Rh-C(01')-O	168.8(3)		
Cl(1')-Rh-S'	89.7(7)	Rh-P-C(1)	113.1(8)	P-C(13)-S	108.3(8)		
Cl(1')-Rh-C(01')	84.8(6)	Rh-P-C(7)	111.6(1)				

\* Numbers in parentheses are estimated standard deviations (e.s.d.s) in the least significant digits. Atoms marked with a prime are related by  $1 - x, y, \frac{3}{2} - z$ .

**Scheme 2.** Relationships among complexes (2)–(5)

Scheme 2 shows how the complexes (2)–(5) are related to each other. Taking all the results obtained in this study and the results of Anderson and Kumar stated above into consideration, it seemed likely that the reactions of the three starting rhodium complexes with btmp, at first and in all cases, should form a face-to-face complex  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-btmp})_2]$  (A). This complex is considered to exist in equilibrium with a chloro-bridged complex (B). If some  $\text{Cl}^-$ -abstraction agent such as  $[\{\text{RhCl}(\text{CO})_2\}_2]$  or  $\text{NaBPh}_4$  is present the reaction goes in the direction of the chloro-bridged complex (2) or (3). In its absence, a carbonyl ligand could be lost and the carbonyl-bridged complex (4) produced. However, when HCl is present, that is when using the *in situ* method to prepare  $[\text{RhCl}_2(\text{CO})_2]^-$  as the 'yellow solution', further reaction with HCl occurs and the rhodium(II) complex (5) is formed. Complex (5) was probably formed by oxidative addition of HCl to the rhodium(I) species followed by elimination of  $\text{H}_2$  from the two rhodiums. In the

case of  $[\text{NBu}_4][\text{RhCl}_2(\text{CO})_2]$  when there is no HCl and no  $\text{Cl}^-$ -abstraction agent in the system, the reaction with btmp proceeds in the direction of the carbonyl-bridged complex (4). On the contrary, when hydrochloric acid is added to the reaction mixture of  $[\text{NBu}_4][\text{RhCl}_2(\text{CO})_2]$  and btmp the reaction goes to yield the rhodium(II) complex (5).

It was also found that complex (2) could be converted into (3)–(5): complex (3) was obtained by treatment with  $\text{NaBPh}_4$ , (4) by stirring in ethanol at room temperature, and (5) by the reaction with hydrochloric acid (Scheme 1). Balch and co-workers<sup>5</sup> reported that  $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-L})_2][\text{RhCl}_2(\text{CO})_2]$  (L = dppm or dpam) exists in equilibrium with  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-L})_2]$  and  $[\{\text{RhCl}(\text{CO})_2\}_2]$ . Taking this observation into consideration, it is reasonable that (2) also exists in equilibrium with  $[\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-btmp})_2]$  and  $[\{\text{RhCl}(\text{CO})_2\}_2]$ . These two species again can be converted into (4) or (5) depending on the reaction conditions as mentioned before.

**Table 4.** Atom co-ordinates for  $[\text{Rh}_2\text{Cl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (**5**) with e.s.d.s in parentheses

Atom	x	y	z
Rh	0.400 81(2)	0.443 56(2)	0.746 06(2)
P	0.333 38(8)	0.378 26(6)	0.619 79(7)
S	0.556 39(8)	0.342 23(6)	0.663 93(6)
Cl(1)	0.541 56(9)	0.514 41(6)	0.622 89(7)
Cl(2)	0.216 76(8)	0.452 91(7)	0.727 40(8)
O	0.655 8(3)	0.419 0(2)	0.343 3(3)
C(01)	0.629 2(4)	0.472 5(3)	0.314 6(3)
C(1)	0.222 9(3)	0.419 9(3)	0.527 1(3)
C(2)	0.248 3(4)	0.472 1(3)	0.482 2(3)
C(3)	0.166 0(4)	0.506 9(3)	0.411 9(3)
C(4)	0.059 5(4)	0.490 7(3)	0.387 8(3)
C(5)	0.035 4(4)	0.439 9(4)	0.432 7(4)
C(6)	0.117 3(4)	0.402 4(3)	0.503 0(3)
C(7)	0.294 6(3)	0.291 8(2)	0.639 2(3)
C(8)	0.213 7(4)	0.286 0(3)	0.666 4(3)
C(9)	0.192 9(5)	0.218 6(4)	0.689 2(4)
C(10)	0.252 4(5)	0.161 1(3)	0.688 5(4)
C(11)	0.330 8(5)	0.169 8(3)	0.663 1(4)
C(12)	0.352 3(4)	0.234 7(3)	0.637 5(3)
C(13)	0.427 4(3)	0.362 1(2)	0.573 6(3)
C(14)	0.637 9(3)	0.348 5(3)	0.605 1(3)
C(15)	0.615 3(3)	0.292 3(3)	0.536 9(3)
C(16)	0.629 4(5)	0.221 8(3)	0.559 3(4)
C(17)	0.620 2(5)	0.172 6(3)	0.496 0(4)
C(18)	0.595 5(4)	0.192 5(3)	0.411 3(4)
C(19)	0.579 0(6)	0.260 6(4)	0.389 0(4)
C(20)	0.588 9(5)	0.311 8(3)	0.452 6(4)

## Experimental

*General.*—The i.r. spectra were recorded on Jasco A-100 and Shimadzu IR 450 spectrometers and n.m.r. spectra on a JEOL JNM GX-400 instrument. Conductivity measurements were carried out for  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> acetone solutions at 25 °C on a Toa Electronics CM-6A conductometer. Melting points were determined on a Yanaco micro melting point apparatus.

Literature methods were used to prepare the compounds  $[\{\text{RhCl}(\text{CO})_2\}_2]$ ,<sup>15</sup>  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$ ,<sup>6</sup> and (benzylthiomethyl)diphenylphosphine.<sup>1</sup>

*trans*- $[\text{RhCl}(\text{CO})(\text{btmp}-P)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$ .—Solid btmp (0.207 g, 0.642 mmol) was added to a solution of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  (0.050 g, 0.129 mmol) in dichloromethane (10 cm<sup>3</sup>), and the mixture was stirred at room temperature for 3 h. The resulting pale yellow solution was concentrated, and diluted with hexane to give (1)·0.5 CH<sub>2</sub>Cl<sub>2</sub> as pale yellow crystals (0.180 g).

$[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2][\text{RhCl}_2(\text{CO})_2]$  (**2**).—(i) Solid btmp (0.040 g, 0.124 mmol) was added to a solution of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  (0.024 g, 0.062 mmol) in dichloromethane (5 cm<sup>3</sup>), and the mixture stirred at room temperature for 1 h. Benzene was added to the resulting orange solution to afford (**2**) as pale orange crystals (0.032 g).

(ii) Solid btmp (0.124 g, 0.385 mmol) was added to a solution of  $[\{\text{RhCl}(\text{CO})_2\}_2]$  (0.100 g, 0.257 mmol) in Et<sub>2</sub>O (30 cm<sup>3</sup>). Immediately, complex (**2**) (0.175 g) was precipitated from the mixture as pale orange crystals.

$[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-btmp})_2]\text{BPh}_4$  (**3**).—(i) Carbon monoxide was passed through a refluxing aqueous ethanol solution (15 cm<sup>3</sup>) of RhCl<sub>3</sub>·3H<sub>2</sub>O (0.100 g, 0.380 mmol) for 3 h. To the resulting 'yellow solution' which contains predominantly  $[\text{RhCl}_2(\text{CO})_2]^-$  (refs. 7 and 16) was successively added an acetone solution (3 cm<sup>3</sup>) of btmp (0.113 g, 0.350 mmol) and an

ethanol solution (3 cm<sup>3</sup>) of NaBPh<sub>4</sub> (0.120 g, 0.350 mmol). The precipitated orange solids were collected and washed with ethanol and Et<sub>2</sub>O to give complex (**3**) (0.169 g).

(ii) Solid NaBPh<sub>4</sub> (0.015 g, 0.043 mmol) was added to a solution of complex (**2**) (0.050 g, 0.043 mmol) in ethanol (30 cm<sup>3</sup>). The resulting mixture was stirred at room temperature for 3 h, whereupon the orange solids were precipitated, collected, and washed with ethanol and Et<sub>2</sub>O to give complex (**3**) (0.020 g).

$[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-btmp})_2]$  (**4**).—(i) Solid btmp (0.068 g, 0.211 mmol) was added to an ethanol solution (25 cm<sup>3</sup>) of  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  (0.100 g, 0.212 mmol), and the mixture was stirred for 4 h. The colour changed from pale yellow to orange. The resulting solution was concentrated to 3 cm<sup>3</sup>, whereupon dull green precipitates appeared. These solids were collected and washed with ethanol and Et<sub>2</sub>O to give complex (**4**) (0.067 g).

(ii) An ethanol solution (50 cm<sup>3</sup>) of complex (**2**) (0.070 g, 0.060 mmol) was stirred at room temperature for 1 d, during which (**4**) was precipitated as a dull green solid (0.040 g).

$[\text{RhCl}_4(\text{CO})_2(\mu\text{-btmp})_2]$  (**5**).—(i) To a 'yellow solution' prepared by bubbling carbon monoxide through an aqueous ethanol solution (35 cm<sup>3</sup>) of RhCl<sub>3</sub>·3H<sub>2</sub>O (0.200 g, 0.760 mmol) was added solid btmp (0.245 g, 0.760 mmol), and the mixture was stirred at room temperature for 1 d. Precipitated red solids were collected and washed with ethanol and Et<sub>2</sub>O to afford complex (**5**) (0.285 g).

(ii) Solid btmp (0.055 g, 0.171 mmol) was added to an ethanol solution (30 cm<sup>3</sup>) of  $[\text{NBu}^n_4][\text{RhCl}_2(\text{CO})_2]$  (0.080 g, 0.170 mmol). After the btmp added had dissolved completely, three drops of concentrated HCl was added and the mixture was stirred for 1 d. The precipitated red solids were collected and washed with acetone and Et<sub>2</sub>O to give complex (**5**) (0.071 g).

(iii) Three drops of concentrated HCl was added to an ethanol solution (30 cm<sup>3</sup>) of complex (**2**) (0.100 g, 0.083 mmol). The mixture was stirred for 1 d, whereupon red solids were precipitated and washed with acetone and Et<sub>2</sub>O to give (**5**) (0.061 g).

*Single Crystal X-Ray Diffraction Analysis of Complex (5).*—Suitable crystals were grown by diffusion of hexane into a solution of complex (**5**) in CH<sub>2</sub>Cl<sub>2</sub> in a refrigerator.

*Crystal data.* C<sub>42</sub>H<sub>38</sub>Cl<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Rh<sub>2</sub>S<sub>2</sub>, *M* = 1048.46, monoclinic, space group *C2/c* (no. 15), *a* = 14.064(3), *b* = 19.364(4), *c* = 16.930(5) Å, β = 116.67(2)°, *D<sub>c</sub>* = 1.628 g cm<sup>-3</sup>, *U* = 4 120(3) Å<sup>3</sup> [by least-squares refinement of 23 reflections, 7.72 < θ < 13.91°, λ(Mo-K<sub>α</sub>) = 0.710 73 Å], *Z* = 4, *F*(000) = 2 104, μ = 12.58 cm<sup>-1</sup>. The molecule is located on a special position. The two halves of the molecule are related by a crystallographic binary axis passing through (½, *y*, ¾).

A red crystal (0.20 × 0.31 × 0.35 mm) was employed for X-ray measurements using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K<sub>α</sub> radiation. A total of 5 294 reflections were measured with ω–2θ scanning (1 < θ < 28°, –18 < *h* < 18, 0 < *k* < 25, 0 < *l* < 22) followed by correction for Lorentz-polarization and spherical absorption correction (reflections having *h* + *k* = odd were not measured). Intensities of standard reflections gave no significant variation during data collection. 3 529 Reflections were considered as observed [*I* > 3σ(*I*)].

*Solution and refinement.* The positions of all non-H atoms were obtained by direct methods and Fourier synthesis. The structure was refined by full-matrix least squares on *F* including positional parameters for all atoms, anisotropic thermal parameters for all non-H atoms, and isotropic ones (fixed at *B*<sub>iso</sub> = 4.0 Å<sup>2</sup>) for all H atoms. The final *R* and *R'* {*w* = 4*F*<sub>o</sub><sup>2</sup>/[σ(*F*<sub>o</sub>)<sup>2</sup>]} were 0.036 and 0.059, respectively. Final

maximum electron density in the Fourier difference map was  $0.332 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors and  $f'$ ,  $f''$  values were obtained from ref. 17. Computer programs: Enraf-Nonius SDP-Plus program package<sup>18</sup> and ORTEP II<sup>19</sup> for all calculations. The final atomic co-ordinates and their standard deviations are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

### References

- 1 Y. Fuchita, K. I. Hardcastle, K. Hiraki, and M. Kawatani, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1961.
- 2 C-L. Lee, C. T. Hunt, and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2498.
- 3 G. K. Anderson and R. Kumar, *J. Organomet. Chem.*, 1988, **342**, 263.
- 4 G. K. Anderson, *J. Organomet. Chem.*, 1989, **368**, 385.
- 5 M. M. Olmstead, C. H. Lindsay, L. S. Benner, and B. L. Balch, *J. Organomet. Chem.*, 1979, **179**, 289.
- 6 L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.
- 7 J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1437.
- 8 B. E. Mann and B. F. Taylor, in <sup>13</sup>C NMR Data for Organometallic Compounds, eds. P. M. Maitlis, F. G. A. Stone, and R. West, Academic Press, London, 1981, Tables 2.4 and 2.8.
- 9 M. Cowie and S. K. Pwight, *Inorg. Chem.*, 1980, **19**, 2508.
- 10 F. A. Cotton, C. T. Eagle, and A. C. Price, *Inorg. Chem.*, 1988, **27**, 4362.
- 11 J. A. Jenkins, J. P. Ennett, and M. Cowie, *Organometallics*, 1988, **7**, 1845.
- 12 C. P. Kubiak, C. Woodcock, and R. Eisenberg, *Inorg. Chem.*, 1982, **21**, 2119 and refs. therein.
- 13 M. Cowie and S. K. Dwight, *Inorg. Chim. Acta*, 1978, **31**, L407 and refs. therein.
- 14 M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1977, **23**, L33.
- 15 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.
- 16 B. R. James and G. L. Rempel, *Chem. Commun.*, 1967, 158.
- 17 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, table 2.2B.
- 18 Enraf-Nonius Structure Determination Package-Plus, Enraf-Nonius, Delft, 1985.
- 19 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.

Received 9th April 1990; Paper 0/01581D