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**Synthesis and characterization of  
 bis-(diphenylphosphinoethane)-substituted hexarhodium  
 clusters:  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ ,  
 $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$   
 and  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$ .  
 X-Ray crystal structures of  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$   
 and  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  clusters**

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**Abstract**

Two major products of the photoreaction between  $\text{Rh}_6(\text{CO})_{16}$  and bis-(diphenylphosphinoethane) (dppe) were isolated and characterized as  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  with  $\mu_2$ -bridging bidentate dppe and  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$  where one P atom of dppe is terminally coordinated, the other being oxidized and thus non-coordinated. Substitution of the labile acetonitrile ligand in  $\text{Rh}_6(\text{CO})_{15}\text{NCMe}$  by dppe yields  $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  with dppe bridging two  $\text{Rh}_6$  cores. The structures of  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  and  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  have been determined by single-crystal X-ray diffraction studies.

Solution structures of  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ ,  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$ ,  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$  and  $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  have been established by IR, and  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy.

**Introduction**

Diphosphine ligands  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ , dpmm;  $n = 2$ , dppe;  $n = 4$ , dppb) react under thermal conditions with the cluster  $\text{Rh}_6(\text{CO})_{16}$  affording substituted derivatives  $\text{Rh}_6(\text{CO})_{16-2x}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_x$ , where  $x = 1, 2$  or 3 for dpmm [1]

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and  $x = 2$  or  $3$  for dppe [2]. In those clusters diphosphines occupy bridge positions on "Rh<sub>6</sub>" octahedra. An unusual mode of diphosphine coordination was proposed for cluster Rh<sub>6</sub>(CO)<sub>15</sub>(η<sup>1</sup>-dppe) [2] where only one phosphorus atom is bound to rhodium. The other one is connected to oxygen atom of the (μ<sub>3</sub>-CO) group. This assumption was based only on chemical analysis and the considerable low-field shift of the (μ<sub>3</sub>-CO) group in the <sup>13</sup>C NMR spectrum of this compound.

In our previous paper [3] we elaborated two effective and selective methods of Rh<sub>6</sub>(CO)<sub>16</sub> activation in substitution reactions: photoexcitation in the lowest band of the cluster electronic spectrum and replacement of one terminal CO group by a labile acetonitrile ligand. In the present communication we report the results of these routes on application to the synthesis of Rh<sub>6</sub>(CO)<sub>16</sub> diphosphine derivatives, and the crystal and solution structures of the products obtained.

## Experimental

Rh<sub>6</sub>(CO)<sub>16</sub> (I) was obtained by refluxing for 5 h a hexane solution of Rh<sub>4</sub>(CO)<sub>12</sub>, which was synthesized according to the literature procedure [4]. Rh<sub>6</sub>(CO)<sub>15</sub>NCMe (II) and Rh<sub>6</sub>(CO)<sub>15</sub>PPh<sub>3</sub> (III) were prepared as described previously [3]. Corresponding <sup>13</sup>CO-labelled products were obtained from Rh<sub>4</sub>(CO)<sub>12</sub> (20% enriched). All solvents were dried over appropriate reagents and distilled prior to use. Products were separated in air by column chromatography on silica (Silpearl). <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker AM-500 instrument with Cr(acac)<sub>3</sub> as a relaxation agent. IR spectra were measured on a Specord M80 spectrophotometer. Photolysis was carried out using a 500 W Hg lamp (DRT-500).

### Photoreaction of I with dppe

A solution of I (180 mg; 0.17 mmol) and dppe (210 mg; 0.52 mmol) in chloroform (200 cm<sup>3</sup>) was irradiated in a Pyrex valve ( $\lambda_{\text{irr}} > 300$  nm) with vigorous stirring. Reaction was monitored by IR spectroscopy, and after complete conversion of the starting cluster I (disappearance of  $\nu(\text{CO})$  2076 cm<sup>-1</sup>) the solution was concentrated by rotary evaporation, diluted with hexane and transferred to a silica column (4 × 8 cm). Chromatography using hexane/chloroform (1/1) as an eluant gave three bands, in the order of elution: (1) a light-brown band containing unreacted Rh<sub>6</sub>(CO)<sub>16</sub>; (2) a dark-brown band, Rh<sub>6</sub>(CO)<sub>14</sub>(μ<sub>2</sub>, η<sup>2</sup>-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>) (IV) (112 mg, 47%); and (3) a band indicating a trace amount of an unidentified product. Subsequent elution with methyl ethyl ketone/chloroform (1/10) gave a grey-brown wide band of Rh<sub>6</sub>(CO)<sub>15</sub>(η<sup>1</sup>-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>P(O)Ph<sub>2</sub>) (V) (85 mg; 35%).

### Preparation of {Rh<sub>6</sub>(CO)<sub>15</sub>}<sub>2</sub>(μ<sub>2</sub>, η<sup>1</sup>: η<sup>1</sup>-Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>) (VI)

A solution of dppe (37 mg; 0.092 mmol) in chloroform (3 cm<sup>3</sup>) was added dropwise with vigorous stirring to a freshly prepared solution of II (100 mg; 0.094 mmol) in chloroform (5 cm<sup>3</sup>). The reaction mixture was stirred for an additional 10 min, diluted with hexane (30 cm<sup>3</sup>) and transferred to a silica column (2.5 × 6 cm). Chromatography with hexane/chloroform (3/2) gave the following bands in order of elution: (1) a trace amount of I; and (2) a dark-brown band of VI, 115 mg, 90%. Analytical data and some spectral characteristics of the compounds obtained (IV–VI) are summarized in Table 1.

Table 1  
Analytical and spectroscopic data for the complexes III-VI

Compound	Analysis (Found (calc.) (%))		IR $\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) $\text{CHCl}_3$	NMR <sup>a</sup> $^3\text{P}\{^1\text{H}\}$ $\text{CDCl}_3$
	C	H		
$\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$ <sup>b</sup> (III)			2100w, 2066s, 2036m, 2024sh, 1788m,br	25.3 (d, $J(\text{Rh}-\text{P})$ 134)
$\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$ <sup>c</sup> (V)			2100w, 2066s, 2036m, 2020sh, 1788m,br $\nu(\text{P}=\text{O})$ 1184	30.9 (d, $J(\text{P}-\text{P}')$ 38) 21.3 (dd, $J(\text{P}-\text{P}')$ 38, $J(\text{Rh}-\text{P})$ 135)
$\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ (VI)	27.09 (27.19)	1.26 (0.98)	2100w, 2066s, 2036m, 1788m,br	23.3 (d, $J(\text{Rh}-\text{P})$ 136)
$\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ (IV)	33.80 (34.12)	1.76 (1.72)	2090m, 2058vs, 2026m, 2002w, 1784m,br	25.8 (d, $J(\text{Rh}-\text{P})$ 134)

<sup>a</sup> Chemical shifts in ppm, relative to 85%  $\text{H}_3\text{PO}_4$ , coupling constants ( $J$ ) in Hz. <sup>b</sup> Data taken from ref. 4. <sup>c</sup> Satisfactory analysis for this complex was not obtained.

### Crystal structure determination

Single crystals of IV suitable for an X-ray study were grown by slow diffusion of heptane in a chloroform solution of IV. Single crystals of III were grown by slow evaporation of solvent from a pentane solution of III at 2°C. X-ray single crystal diffraction experiments for III and IV were carried out with an automated four-circle diffractometer, Siemens P3/PC (graphite-monochromated Mo- $K_\alpha$  radiation). All calculations were performed using the SHELXTL PLUS program package.

For III the X-ray diffraction experiment was performed at 158 K. Crystal data:  $C_{33}H_{15}O_{15}PRh_6$ , monoclinic, space group  $P2_1/c$ ,  $a$  9.648(2),  $b$  22.532(5),  $c$  16.986(4) Å,  $\beta$  92.70(2)°,  $V$  3689(1) Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc.}}$  2.34 g cm<sup>-3</sup>,  $\mu(\text{Mo-}K_\alpha)$  27 cm<sup>-1</sup>. Intensities of 4167 independent reflections were measured by the  $\theta/2\theta$  scan technique ( $2\theta < 50^\circ$ ), of which 3409 reflections with  $I > 2\sigma(I)$  were used in the calculations. The structure was solved by direct methods. Least-squares refinement of all non-hydrogen (anisotropic approximation) and hydrogen (isotropic approximation) atoms converged at  $R = 0.037$  ( $R_w = 0.036$ ). The weighting scheme  $w = 1/[\sigma^2(F) + 0.0001F_0^2]$  was used, its goodness of fit being 1.56.

For IV the X-ray diffraction experiment was performed at room temperature. Crystal data:  $C_{40}H_{24}O_{14}P_2Rh_6$ , orthorhombic, space group  $Pna2_1$ ,  $a$  18.525(6),  $b$  11.481(2),  $c$  21.055(5) Å,  $V$  4478(4) Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc.}}$  2.09 g cm<sup>-3</sup>,  $\mu(\text{Mo-}K_\alpha)$  23 cm<sup>-1</sup>. Intensities of 2788 independent reflections were measured by the  $\theta/2\theta$  scan technique ( $2\theta < 54^\circ$ ), of which 2451 reflections with  $I > 2\sigma(I)$  were used in the calculations. The structure was solved by direct methods. All Rh, P, O atoms and carbon atoms of dppe were refined in the anisotropic approximation; other carbon atoms were treated isotropically because of the low number of reflections measured. Least-squares refinement (a total of 489 refined parameters) converged at  $R = 0.037$  ( $R_w = 0.036$ ). Refinement of both enantiomorphic models gave essentially the same discrepancy factors, owing to pseudo-symmetric arrangement of rhodium and phosphorus atoms. Hydrogen atoms were not located. The weighting scheme  $w = 1/[\sigma^2(F) + 0.0001F_0^2]$  was used, its goodness of fit being 1.33.

The atomic coordinates for III and IV are listed in Tables 2 and 3.

## Results and discussion

The photochemical reaction between  $Rh_6(CO)_{16}$  and a three-fold excess of dppe in chloroform may be presented by Scheme 1.

The formation of the  $Rh_6(CO)_{15}(\eta^1\text{-dppe})$  intermediate in the proposed reaction sequence is usual for the coordination of any bidentate ligand. We could not isolate the highly reactive intermediate  $Rh_6(CO)_{15}(\eta^1\text{-dppe})$ , which can give rise to complex IV with the coordinated second phosphorus atom of dppe (in the absence of oxygen), or to compound V with the latter atom oxidized (in the presence of O<sub>2</sub>, even in trace amounts). It should be noted also that we cannot completely rule out the possibility of phosphorus atom oxidation in the course of reaction mixture separation on silica; the ligand coordination promotes oxidation in any case.

The molecular structure of IV was confirmed by a single-crystal X-ray diffraction study. The X-ray structure of III was also determined for comparison.

Both 86-electron octahedral clusters (Figs. 1, 2) may be regarded as derivatives of  $Rh_6(CO)_{16}$  with one (III) or two (IV) terminal CO groups substituted by phosphorus atoms. Of the remaining CO ligands four (both in III and IV) are

Table 2

Atomic coordinates ( $\times 10^4$ , for  $H \times 10^3$ ) in the structure of III

Atom	x	y	z	Atom	x	y	z
Rh(1)	4667(1)	2780(1)	6435(1)	C(14)	8780(11)	3211(4)	7115(6)
Rh(2)	7492(1)	2885(1)	6102(1)	C(15)	5754(10)	4533(4)	6416(6)
Rh(3)	6793(1)	2997(1)	7619(1)	C(21)	5312(11)	1210(4)	6407(6)
Rh(4)	4900(1)	3878(1)	7192(1)	C(22)	5706(13)	971(5)	5702(7)
Rh(5)	5602(1)	3766(1)	5643(1)	C(23)	6763(12)	546(5)	5680(7)
Rh(6)	7618(1)	3994(1)	6800(1)	C(24)	7451(13)	372(6)	6373(8)
P(1)	3964(3)	1773(1)	6415(2)	C(25)	7050(12)	599(5)	7091(7)
O(1)	1749(8)	3093(3)	5913(4)	C(26)	5998(11)	1016(5)	7099(6)
O(2)	8724(9)	1655(4)	6262(5)	C(31)	2857(10)	1569(4)	7219(5)
O(3)	9356(8)	3087(4)	4734(5)	C(32)	1856(12)	1958(5)	7455(6)
O(4)	7531(9)	1796(3)	8296(5)	C(33)	913(13)	1816(5)	7990(6)
O(5)	7526(8)	3478(4)	9263(4)	C(34)	947(13)	1261(5)	8332(7)
O(6)	1877(9)	4255(4)	7066(5)	C(35)	1932(12)	858(5)	8122(6)
O(7)	5357(9)	4523(4)	8741(5)	C(36)	2867(13)	1005(5)	7575(7)
O(8)	2810(9)	4191(4)	4962(5)	C(41)	2794(11)	1552(4)	5561(6)
O(9)	7167(8)	4294(4)	4293(5)	C(42)	2600(13)	1904(5)	4900(6)
O(10)	9687(9)	4519(4)	5687(5)	C(43)	1696(13)	1713(6)	4278(7)
O(11)	8651(9)	4715(4)	8221(5)	C(44)	1029(13)	1192(6)	4331(7)
O(12)	5492(7)	2548(3)	4710(4)	C(45)	1209(14)	842(6)	4991(8)
O(13)	3858(7)	2775(3)	8170(4)	C(46)	2072(15)	1023(6)	5608(8)
O(14)	9934(7)	3133(3)	7350(4)	H(22)	539(10)	111(4)	522(6)
O(15)	5534(7)	5031(3)	6322(4)	H(23)	710(10)	37(4)	515(6)
C(1)	2851(12)	2949(4)	6103(5)	H(24)	807(11)	5(5)	642(6)
C(2)	8186(11)	2090(5)	6200(6)	H(25)	765(11)	40(5)	765(6)
C(3)	8649(12)	3021(5)	5244(7)	H(26)	567(11)	123(5)	765(6)
C(4)	7225(11)	2230(5)	7995(6)	H(32)	186(10)	234(5)	721(6)
C(5)	7210(11)	3304(4)	8658(6)	H(33)	28(11)	212(5)	811(6)
C(6)	2974(13)	4101(5)	7095(7)	H(34)	32(13)	117(5)	869(7)
C(7)	5158(12)	4273(5)	8173(6)	H(35)	185(11)	39(5)	837(6)
C(8)	3840(13)	4010(5)	5186(6)	H(36)	338(13)	70(5)	744(7)
C(9)	6579(12)	4084(4)	4791(7)	H(42)	324(12)	224(5)	488(7)
C(10)	8928(13)	4338(5)	6097(7)	H(43)	165(12)	200(5)	385(7)
C(11)	8244(11)	4462(5)	7693(7)	H(44)	39(11)	110(4)	393(6)
C(12)	5650(10)	2768(5)	5330(6)	H(45)	79(9)	40(4)	512(5)
C(13)	4543(11)	2926(4)	7690(5)	H(46)	219(11)	86(5)	601(6)

$\mu_3$ -bridging. Bond geometry in III and IV is similar (Table 4) and strongly resembling  $Rh_6(CO)_{16}$  [5] and its phosphine and phosphite derivatives studied earlier [6–8].

Local mirror symmetry of the cluster core of III ( $m$  plane passing through the Rh(1), Rh(6), C(14), C(15) and P(1) atoms) is violated by phosphine phenyl rings. The C(2)O(2) carbonyl group closely contacts with the C(21)···C(26) ring (C(2)···C(21) 3.44, C(2)···C(22) 3.55, O(2)···C(24) 3.15, O(2)···C(23) 3.26, O(2)···C(25) 3.24 Å), while its locally symmetrical equivalent C(4)O(4) has no such shortened contacts. Probably this difference is responsible for the non-equivalence of the  $^{13}C$  NMR signals of these CO groups (see below).

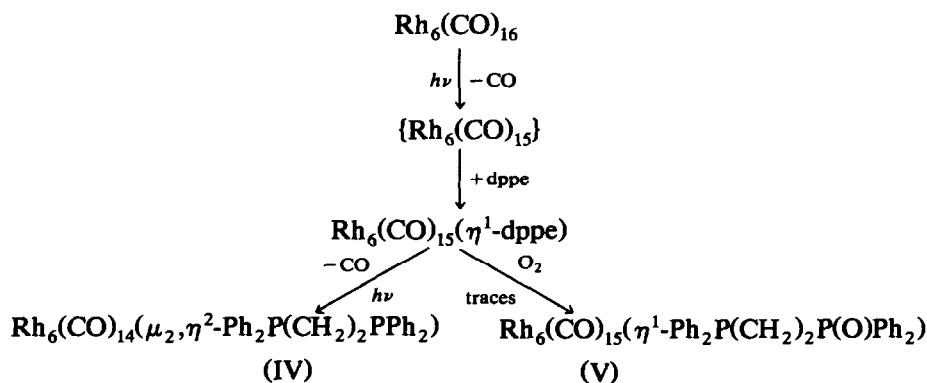
In the structure of IV, the positions of heavy atoms (Rh and P) and CO groups correspond to a higher crystallographic symmetry (space group  $Pnam$  with the cluster in a special position on the  $m$  plane) than the positions of the other atoms

Table 3

Atomic coordinates ( $\times 10^4$ ) in the structure of IV

Atom	x	y	z	Atom	x	y	z
Rh(1)	5485(1)	693(1)	9681(2)	C(11)	6876(13)	-2572(25)	8201(12)
Rh(2)	5585(1)	778(1)	8351(2)	C(12)	4658(9)	960(13)	9005(12)
Rh(3)	6788(1)	194(1)	9067(2)	C(13)	6496(12)	72(20)	10061(11)
Rh(4)	6009(1)	-1588(2)	9647(2)	C(14)	6625(11)	183(18)	8034(10)
Rh(5)	4825(1)	-1029(1)	8941(2)	C(15)	5432(9)	-2618(15)	8952(13)
Rh(6)	6096(1)	-1508(2)	8340(2)	C(16)	5476(11)	3735(15)	9294(8)
P(1)	5525(3)	2653(5)	9956(3)	C(17)	6065(9)	3668(14)	8793(7)
P(2)	5791(3)	2725(4)	8129(3)	C(21)	6306(11)	3081(18)	10443(10)
O(1)	4603(11)	231(15)	10838(9)	C(22)	6780(12)	4004(18)	10296(10)
O(3)	4722(11)	535(16)	7147(8)	C(23)	7352(12)	4251(20)	10725(11)
O(4)	7675(7)	2394(12)	9135(9)	C(24)	7422(13)	3685(21)	11287(12)
O(5)	8206(8)	-1146(13)	9073(18)	C(25)	6929(15)	2812(29)	11443(10)
O(6)	5271(12)	-2476(17)	10847(9)	C(26)	6366(12)	2476(21)	11038(10)
O(7)	7220(12)	-3264(23)	9837(15)	C(31)	4737(12)	3262(18)	10407(8)
O(8)	3761(11)	-1721(23)	9967(10)	C(32)	4851(13)	4243(21)	10790(10)
O(9)	3840(11)	-1502(22)	7826(10)	C(33)	4247(13)	4773(19)	11023(13)
O(10)	5506(12)	-2025(17)	7024(9)	C(34)	3588(12)	4414(20)	10942(11)
O(11)	7308(12)	-3311(20)	8189(15)	C(35)	3458(13)	3416(19)	10542(9)
O(12)	4111(5)	1409(9)	8966(9)	C(36)	4056(11)	2811(17)	10280(10)
O(13)	6800(8)	164(13)	10540(7)	C(41)	4997(11)	3534(17)	7825(8)
O(14)	6992(8)	349(14)	7602(8)	C(42)	5142(13)	4668(19)	7581(12)
O(15)	5269(7)	-3616(8)	8920(10)	C(43)	4554(13)	5332(19)	7405(12)
C(1)	4925(11)	422(17)	10392(10)	C(44)	3844(13)	4917(20)	7454(12)
C(3)	5077(11)	631(18)	7572(10)	C(45)	3735(11)	3853(20)	7666(10)
C(4)	7324(9)	1609(15)	9118(9)	C(46)	4314(11)	3152(19)	7837(11)
C(5)	7684(12)	-668(17)	9104(12)	C(51)	6504(12)	2988(22)	7549(10)
C(6)	5535(13)	-2104(23)	10391(12)	C(52)	7121(14)	3570(20)	7690(11)
C(7)	6783(14)	-2612(25)	9750(12)	C(53)	7661(13)	3684(24)	7198(16)
C(8)	4129(13)	-1420(20)	9578(13)	C(54)	7576(16)	3196(22)	6630(14)
C(9)	4212(12)	-1355(19)	8246(11)	C(55)	6929(15)	2619(23)	6462(11)
C(10)	5719(12)	-1877(20)	7513(12)	C(56)	6401(15)	2545(24)	6929(12)

in the molecule. The dppe ligand has a chiral conformation, reducing the symmetry to the observed  $Pna2_1$ . The Rh(1)P(1)C(16)C(17)P(2)Rh(2) chelate ring adopts a



Scheme 1.

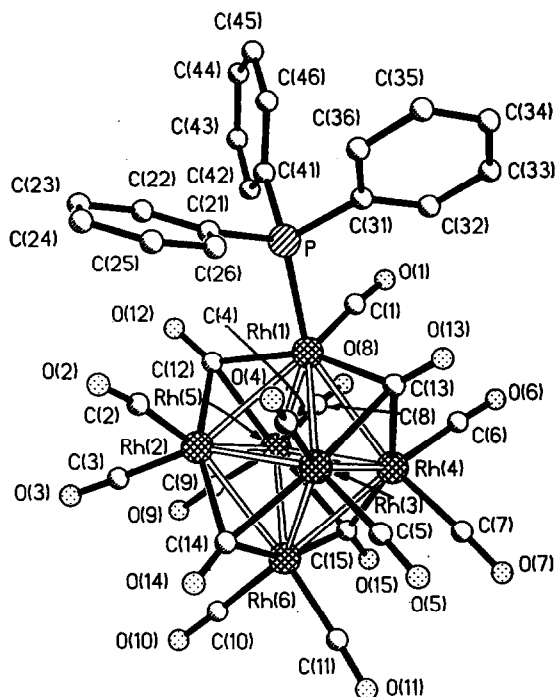


Fig. 1. Molecular structures of III in crystals (hydrogen atoms are omitted).

twist conformation, the Rh(1), Rh(2), P(1) and P(2) atoms being coplanar within  $+0.06 \text{ \AA}$ , and C(16) and C(17) being displaced out of their plane by  $0.40 \text{ \AA}$  and  $-0.57 \text{ \AA}$  (*i.e.* in opposite directions).

Phosphorus atoms of dpppe in IV substitute two *cis* carbonyl ligands of the neighbouring rhodium atoms. A similar type of  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) coordination was observed in  $\text{Rh}_6(\text{CO})_6(\mu_3\text{-CO})_4(\text{dppm})_3$  [7] and  $\text{Rh}_6(\text{CO})_{10}(\mu_3\text{-CO})_4(\text{dppm})$ , studied by X-ray powder diffraction [8]. It should be noted that IV has the same spectral characteristics (IR  $\nu(\text{CO})$ ,  $^{13}\text{C}$  NMR chemical shifts) as those given in ref. 2 for  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-dpppe})$ . Hence, the latter compound is assumed to be identical with IV, and the coordination pattern proposed for dpppe in ref. 2, with one phosphorus atom bound to rhodium and another interacting with a  $\mu_3$ -carbonyl ligand, should be eliminated.

The average Rh–Rh bond distances in III ( $2.774(34) \text{ \AA}$ ) and IV ( $2.779(26) \text{ \AA}$ ) are essentially the same as in the parent  $\text{Rh}_6(\text{CO})_{16}$  cluster ( $2.776(1) \text{ \AA}$ ) [5], though the individual values vary significantly. In III the Rh(1)–Rh(2) and Rh(1)–Rh(3) bonds, *cis* to the  $\text{PPh}_3$  ligand, are the longest ( $2.820$  and  $2.847 \text{ \AA}$ ), while the third bond of the same face, Rh(2)–Rh(3), is the shortest ( $2.706 \text{ \AA}$ ). Similar distortions of a  $\text{Rh}_6$  octahedron were observed in  $\text{Rh}_6(\text{CO})_8(\mu_3\text{-CO})_4[\text{P}(\text{OPh})_3]_4$  [5] and attributed to ligand–ligand repulsion. In IV the Rh–Rh distance variations are less systematic.

$^{13}\text{C}$  NMR (Fig. 3) and  $^{31}\text{P}$  (Table 1) spectroscopic data of IV are consistent with local  $C_2$  symmetry of the  $\text{Rh}_6(\mu_3\text{-CO})_4(\overline{\text{PP}})$  framework ( $\overline{\text{PP}} = \text{dpppe}$ ). Phosphorus

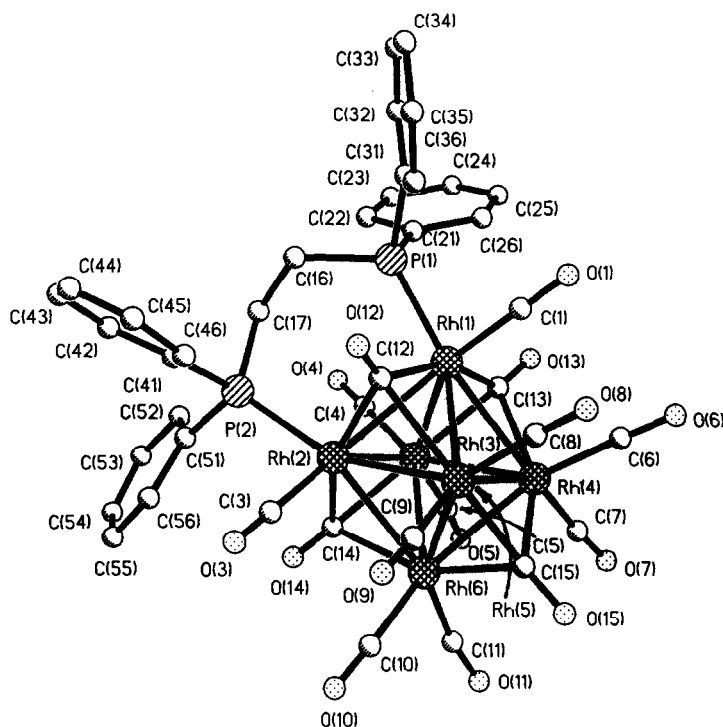


Fig. 2. Molecular structures of IV in crystals (hydrogen atoms are omitted).

atoms of dppe are equivalent and display one doublet signal in the  $^{31}\text{P}\{^1\text{H}\}$  spectrum. In the low field pattern of the  $^{13}\text{C}\{^1\text{H}\}$  spectrum there are three distorted quartets of the relative intensity 1:2:1, corresponding to four  $\mu_3$ -CO groups of which two are equivalent owing to the mirror plane passing through the Rh(3) and Rh(5) atoms and the centers of the Rh(1)–Rh(2) and Rh(4)–Rh(6) bonds (Fig. 2).

The ideal spectrum of the terminal CO ligands in IV should display four doublet signals of double intensity and two doublets of single intensity corresponding to  $C_s$  symmetry observed in the crystal. However, the experimental spectrum (high-field part of Fig. 3) reveals nine doublets of which only one has double intensity. This spectral pattern corresponds to the lower symmetry of the t-CO arrangement in solution, and may be due to the considerable influence of the reduced symmetry of coordinated dppe (see the crystal structure of IV) on NMR signals of terminal CO groups.

NMR investigation of the complexes III, V and VI has shown that all of these compounds are fluxional in solution at ambient temperatures. Variable temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  are given in Fig. 4. At or below  $-55^\circ\text{C}$  the spectrum of a stereochemically rigid system was observed. It is readily observed that the solution structure, determined on the basis of the limiting low temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, is very similar to the solid state one. The ideal symmetry of the  $\text{Rh}_6(\text{CO})_{15}\text{L}$  structural unit is  $C_s$  and its  $^{13}\text{C}$  NMR spectrum should display three low-field resonances of  $\mu_3$ -CO groups (2/1/1) of complex



Table 4

Bond lengths (Å) in molecules III and IV

	III	IV		III	IV
Rh(1)–Rh(2)	2.820(1)	2.808(6)	Rh(4)–Rh(6)	2.748(1)	2.757(6)
Rh(1)–Rh(3)	2.847(1)	2.797(3)	Rh(4)–C(6)	1.92(1)	1.89(3)
Rh(1)–Rh(4)	2.791(1)	2.794(2)	Rh(4)–C(7)	1.89(1)	1.87(3)
Rh(1)–Rh(5)	2.770(1)	2.798(4)	Rh(4)–C(13)	2.34(1)	2.28(2)
Rh(1)–P(1)	2.368(3)	2.326(6)	Rh(4)–C(15)	2.17(1)	2.16(2)
Rh(1)–C(1)	1.85(1)	1.85(2)	Rh(5)–Rh(6)	2.748(1)	2.729(3)
Rh(1)–C(12)	2.14(1)	2.11(2)	Rh(5)–C(8)	1.92(1)	1.91(3)
Rh(1)–C(13)	2.166(9)	2.16(2)	Rh(5)–C(9)	1.90(1)	1.89(2)
Rh(2)–Rh(3)	2.706(1)	2.774(4)	Rh(5)–C(12)	2.31(1)	2.31(2)
Rh(2)–Rh(5)	2.783(1)	2.798(3)	Rh(5)–C(15)	2.17(1)	2.14(2)
Rh(2)–Rh(6)	2.768(1)	2.790(2)	Rh(6)–C(10)	1.94(1)	1.92(3)
Rh(2)–P(2)		2.316(5)	Rh(6)–C(11)	1.92(1)	1.91(3)
Rh(2)–C(2)	1.92(1)		Rh(6)–C(14)	2.14(1)	2.27(2)
Rh(2)–C(3)	1.90(1)	1.90(2)	Rh(6)–C(15)	2.24(1)	2.19(2)
Rh(2)–C(12)	2.17(1)	2.21(2)	P(1)–C(16)		1.87(2)
Rh(2)–C(14)	2.20(1)	2.15(2)	P(1)–C(21)	1.82(1)	1.84(2)
Rh(3)–Rh(4)	2.770(1)	2.786(3)	P(1)–C(31)	1.83(1)	1.88(2)
Rh(3)–Rh(6)	2.778(1)	2.794(4)	P(1)–C(41)	1.86(1)	
Rh(3)–C(4)	1.88(1)	1.91(2)	P(2)–C(17)		1.84(2)
Rh(3)–C(5)	1.92(1)	1.93(2)	P(2)–C(41)		1.85(2)
Rh(3)–C(13)	2.19(1)	2.17(2)	P(2)–C(51)		1.82(2)
Rh(3)–C(14)	2.19(1)	2.20(2)	C(16)–C(17)		1.52(3)
Rh(4)–Rh(5)	2.758(1)	2.725(4)			
			Average		
			C–O (terminal)	1.13(1)	1.13(2)
			C–O ( $\mu_3$ )	1.16(3)	1.16(2)

structure (ddd, dt, dt), five doublets of terminal COs of double intensity and one dd resonance corresponding to a terminal CO group coordinated to a rhodium atom bound to a phosphine ligand. The latter CO is coupled not only with  $^{103}\text{Rh}$  but also with the  $^{31}\text{P}$  of the adjacent phosphine.

Limiting low-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  and

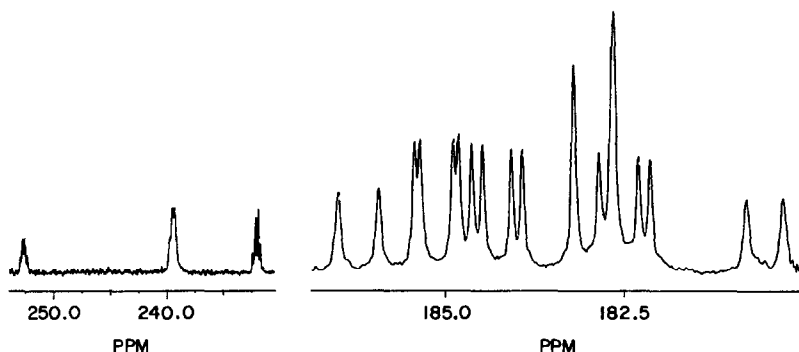


Fig. 3.  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $\text{Rh}_6(\text{CO})_{14}(\mu_2, \eta^2\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ ,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ . Mean values of the coupling constants are:  $J(\text{Rh}-\text{C})$  27 Hz for  $\mu_3$ -CO and  $J(\text{Rh}-\text{C})$  68 Hz for t-CO.

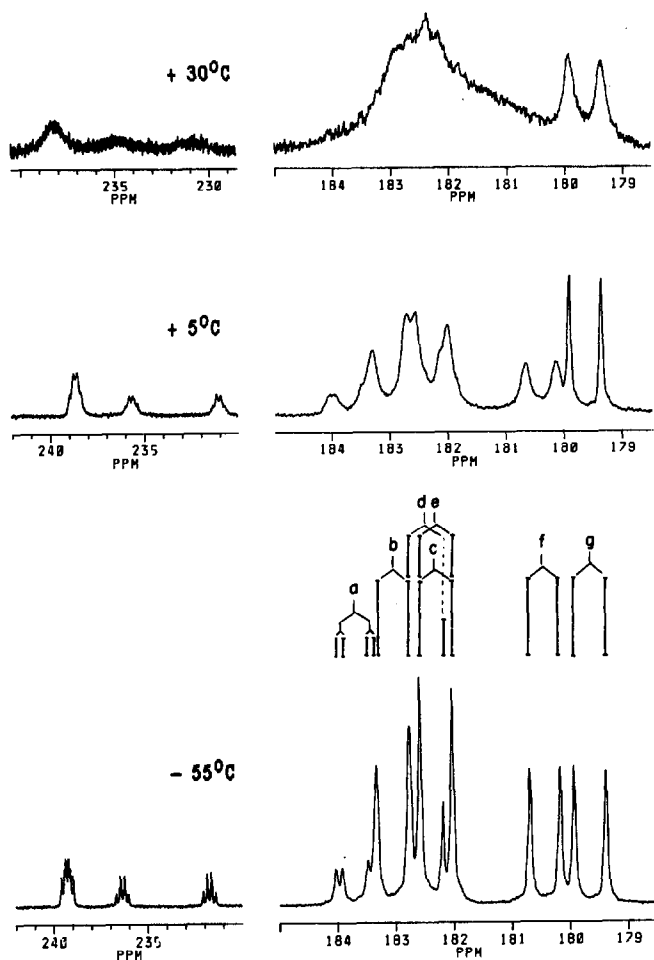


Fig. 4. Variable temperature  $^{13}\text{C}\{^1\text{H}\}$  spectra of  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  in  $\text{CDCl}_3$ . A schematic representation of the terminal CO signals is given in the upper part of the low-temperature spectrum. Mean values of the coupling constants are:  $J(\text{Rh}-\text{C})$  28 Hz for  $\mu_3\text{-CO}$ ,  $J(\text{Rh}-\text{C})$  68 Hz for t-CO and  $^2J(\text{P}-\text{C})$  13 Hz.

$\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$  (Figs. 4, 5) resemble each other and closely match the ideal spectral pattern described above. The complex signals of  $\mu_3\text{-CO}$  groups (ddd, dt, dt) appear in experimental spectra as three distorted quartets (2/1/1) owing to the very similar values of the coupling constants ( $J(\text{Rh}-\text{C})$ ) corresponding to interaction with slightly inequivalent rhodium atoms. High-field patterns corresponding to the terminal carbonyl groups display dd resonances (signals "a" in Figs. 4 and 5) of single intensity, four doublets of double intensity (signals b, c, f and g) and two doublets of single intensity (d, e signals). The only deviation from the ideal spectra consists of splitting of one doublet of double intensity into two closely placed resonances (d and e). We believe that this deviation is connected with a slight distortion of the idealized structure caused by steric interaction between the phenyl rings of the diphosphine and the terminal CO group revealed in the solid state structure. The spectral evidence permits the

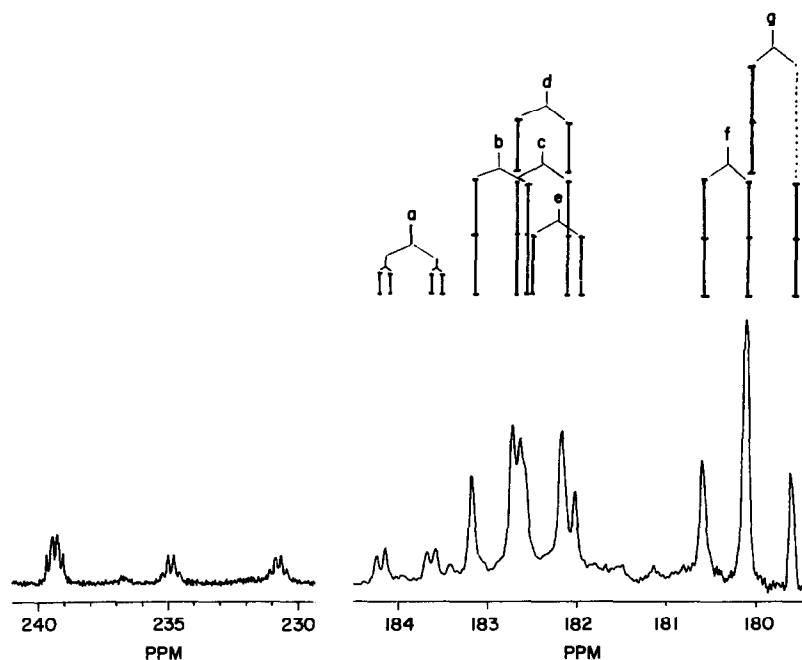
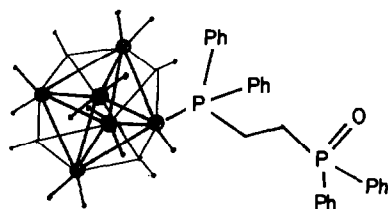


Fig. 5.  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$ ,  $\text{CDCl}_3$ ,  $-55^\circ\text{C}$ . A schematic representation of the terminal CO signals is given in the upper part of the figure. Mean values of the coupling constants are  $J(\text{Rh}-\text{C})$  28 Hz for  $\mu_3\text{-CO}$ ,  $J(\text{Rh}-\text{C})$  68 Hz for t-CO and  $^2J(\text{P}-\text{C})$  12 Hz.

conclusion that  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  and  $\text{Rh}_6(\text{CO})_{15}(\eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2)$  at temperatures below  $-55^\circ\text{C}$  have the same CO arrangement of the “ $\text{Rh}_6$ ” framework as found for  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$  in the solid state. This means that dppe in V, as well as  $\text{PPh}_3$  in III, is coordinated via only one phosphorus atom.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of V contains two signals of equal intensity (Table 1). The high-field doublet of doublets may be assigned to a phosphorus atom coordinated to rhodium. A typical  $^{103}\text{Rh}-^{31}\text{P}$  coupling (see for example  $J(\text{Rh}-\text{P})$  136 Hz in IV and 134 Hz in  $\text{Rh}_6(\text{CO})_{15}\text{PPh}_3$ ) and chemical shift position confirm such an assignment. The lower value coupling is due to interaction with the second phosphorus atom of dppe. The signal of this atom has a considerable low-field shift ( $\Delta\delta = 43$  ppm) with respect to the phosphorus resonance in the free ligand ( $-11.95$  ppm). The low-field shift of such value, as well as the presence of the  $\text{P}=\text{O}$  frequency in the IR spectrum of V, testifies in favor of the oxidation of the “dangling” phosphorus atom and formation of phosphine oxides. All spectral data mentioned above are consistent with the structure of V presented below.



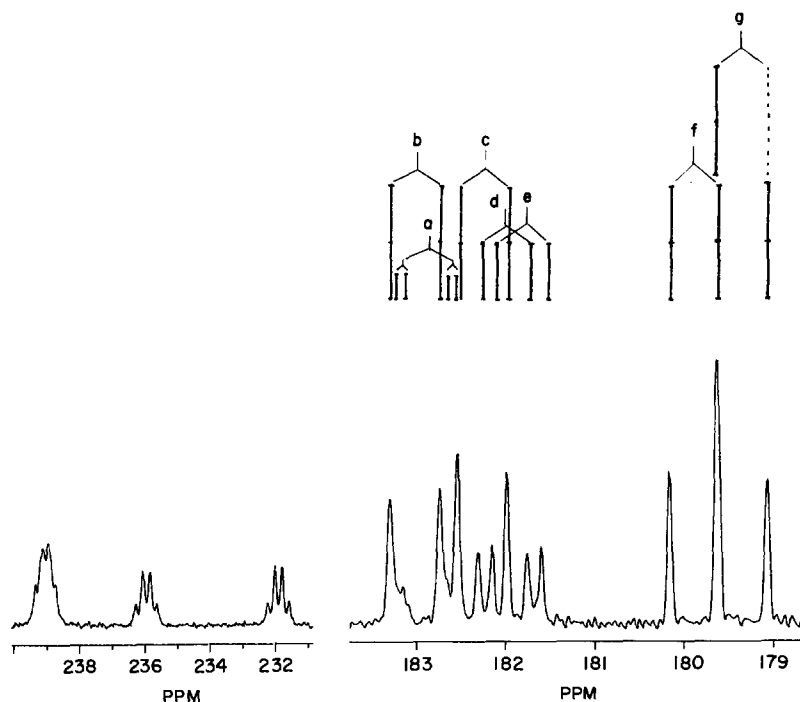
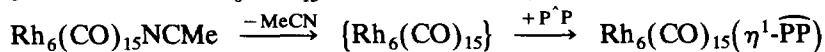
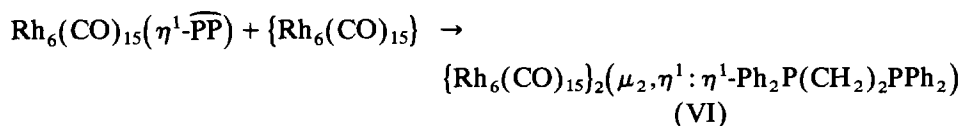


Fig. 6.  $^{13}\text{C}\{^1\text{H}\}$  spectrum of  $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ ,  $\text{CDCl}_3$ ,  $-55^\circ\text{C}$ . The upfield region of the spectrum was obtained with the use of a line narrowing procedure (resolution enhancement factors are  $\text{LB} = -11.0$ ,  $\text{GB} = 0.5$ ). A schematic representation of the terminal CO signals is given in the upper part of the figure. Mean values of the coupling constants are:  $J(\text{Rh}-\text{C})$  28 Hz for  $\mu_3\text{-CO}$  and  $J(\text{Rh}-\text{C})$  69 Hz for t-CO.

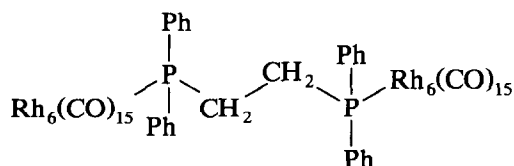
The reaction of diphosphine with coordinatively unsaturated species  $\{\text{Rh}_6(\text{CO})_{15}\}$  generated from  $\text{Rh}_6(\text{CO})_{15}\text{NCMe}$  gives the  $\eta^1$ -coordinated intermediate:



In the presence of a two-fold excess of  $\text{Rh}_6(\text{CO})_{15}\text{NCMe}$ , the  $\eta^1$ -intermediate is readily captured by  $\{\text{Rh}_6(\text{CO})_{15}\}$ , giving the double-linked cluster  $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$ :



Spectral and analytical characteristics of the product VI are given in Table 1. These data and the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum given in Fig. 6 are consistent with the following formulation of VI:



In fact, the  $^{31}\text{P}$  ( $^1\text{H}$ ) NMR spectrum of VI displays only one signal, the position of this resonance (as well as the  $^{103}\text{Rh}$ - $^{31}\text{P}$  coupling constant) being very close to that of coordinated phosphorus in IV and V. Therefore, the two phosphorus atoms of dppe in this molecule are equivalent and coordinated in terminal positions of "Rh<sub>6</sub>" frameworks.

According to the proposed structure,  $\{\text{Rh}_6(\text{CO})_{15}\text{PPh}_2\text{CH}_2\}$  units of VI are equivalent to each other and may be regarded as monosubstituted derivatives  $\text{Rh}_6(\text{CO})_{15}\text{L}$ , structurally analyzed above. In fact, the IR spectral pattern of VI in the carbonyl region exactly corresponds to those of monosubstituted clusters V and III (Table 1). Moreover, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\{\text{Rh}_6(\text{CO})_{15}\}_2(\mu_2, \eta^1: \eta^1\text{-Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)$  (Fig. 6) is very close to those of V and III. All these facts clearly show that dppe in VI links two Rh<sub>6</sub> cluster cores, the structure of the diphosphine-bound  $\{\text{Rh}_6(\text{CO})_{15}\}$  unit in VI resembling that in monosubstituted derivatives V and III.

Thus, the application of the previously proposed synthetic methods gave three modes of dppe coordination on the "Rh<sub>6</sub>" framework: (1) the well-known  $\eta^2, \mu_2$ -derivative, (2) a double diphosphine linked cluster and (3) a cluster with  $\eta^1$ -bound diphosphine and an oxidized second P atom.

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### References

- 1 D.F. Foster, B.S. Nicholls and A.H. Smith, *J. Organomet. Chem.*, 236 (1982) 395.
- 2 K. Nomija and H. Suzuki, *J. Organomet. Chem.*, 168 (1979) 115.
- 3 S.P. Tunik, A.V. Vlasov, A.B. Nikol'skii, V.V. Kryvikh and M.I. Rybinskaya, *Metallorg. Khim.*, 3 (1990) 387.
- 4 S. Martinengo, P. Chini and G. Giordano, *J. Organomet. Chem.*, 27 (1971) 389.
- 5 E.R. Corey, L.F. Dahl and W. Beck, *J. Am. Chem. Soc.*, 85 (1963) 1202.
- 6 G. Ciani, M. Manassero and V.G. Albano, *J. Chem. Soc., Dalton Trans.*, (1981) 515.
- 7 A. Ceriotti, G. Ciani, L. Garlaschelli, U. Sartorelli and A. Sironi, *J. Organomet. Chem.*, 229 (1982) C9.
- 8 J.A. Clucas, M.M. Harding and S.J. Maginn, *J. Chem. Soc., Chem. Commun.*, (1988) 185.