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# Reactions of the complexes $[\text{Re}_2(\text{CO})_9(\eta^1-\text{P}-\text{P})]$ (P-P = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>, n = 1-6) with Me<sub>3</sub>NO: formation of close-bridged complexes $[\text{Re}_2(\text{CO})_8(\mu-\text{P}-\text{P})]$ and phosphine oxide complexes $[\text{Re}_2(\text{CO})_9\{\text{P}-\text{P}(\text{O})\}]$

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### Abstract

Reactions of  $[\text{Re}_2(\text{CO})_{10}]$  with Me<sub>3</sub>NO and diphosphines  $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2, n = 1-6]$  yield mixtures of the monodentate-coordinated diphosphine complexes  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}\text{P}-\text{P})]$  (P-P = Ph\_2P(CH\_2)\_nPPh\_2, n = 1-6) (yields 5-40%) and bridged dimers  $[\{\text{Re}_2(\text{CO})_9\}_2(\mu\text{-}\text{P}-\text{P})]$  (5-50%). These complexes were isolated as either equatorial or axial isomers, or a mixture of two isomers. Reactions of the monodentate complexes with Me<sub>3</sub>NO yield close-bridged complexes  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\text{P}-\text{P})]$  and phosphine oxide complexes  $[\text{Re}_2(\text{CO})_9\{\text{P}-\text{P}(\text{O})\}]$ . The structures of the close-bridged complexes 1 (n = 3) and 2 (n = 4), were determined by Xray crystallography. The Re-Re bond in the close-bridged complex with the longest phosphine chain (n = 6) is readily cleaved in CDCl<sub>3</sub> to give the complex [{*cis*-ReCl(CO)<sub>4</sub>}\_2(\mu\text{-dpph})] (3) as the product, the structure of which was also determined by X-ray crystallography.

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#### 1. Introduction

Diphosphine ligands have played a major role in modern coordination chemistry [1]. Their ability to form chelate and bridged complexes is widely known. However, except for dppm complexes [2], few complexes containing monodentate-coordinated diphosphines have been reported, and these have not been systematically studied.

The only known  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$  complex (P-P=diphosphine) is the dppf complex [dppf=1,1'-bis(diphenylphosphino)ferrocene], which was synthesized by reaction of  $[\text{Re}_2(\text{CO})_9(\text{solvent})]$  (obtained by

Me<sub>3</sub>NO-decarbonylation of  $[Re_2(CO)_{10}]$  with excess dppf [3]. It is noteworthy that Me<sub>3</sub>NO can, in principle, also decarbonylate the monodentate–dppf complex and cause the formation of the close-bridged complex  $[Re_2(CO)_8(\mu$ -dppf)]. This octacarbonyl complex has not been reported, however. Several  $[Re_2(CO)_8(\mu$ -P–P)] complexes have been prepared by Brown and coworkers [4], but no crystal structures or <sup>31</sup>P NMR data were reported.

In this paper, we report the synthesis of the complexes  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}\text{P}-\text{P})]$   $(\text{P}-\text{P}=\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2,$ n = 1-6) (Fig. 1) and their reactions with Me<sub>3</sub>NO to yield the close-bridged complexes  $[\text{Re}_2(\text{CO})_8(\mu\text{-}\text{P}-\text{P})]$ and the phosphine oxide complexes  $[\text{Re}_2(\text{CO})_9\{\text{P}-\text{P}(\text{O})\}]$  (Fig. 2) as the major products. X-ray crystallographic studies of the close-bridged complex 1

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n	Name	Abbreviation
1	bis(diphenylphosphino)methane	dppm
2	1,2-bis(diphenylphosphino)ethane	dppe
3	1,3-bis(diphenylphosphino)propane	dppp
4	1,4-bis(diphenylphosphino)butane	dppb
5	1,5-bis(diphenylphosphino)pentane	dpppe
6	1,6-bis(diphenylphosphino)hexane	dpph

Fig. 1. General structure of the monodentate-coordinated complexes [ $Re_2(CO)_9(\eta^1-P-P)$ ].

(P–P = dppp) and **2** (P–P = dppb) show that the accommodation of diphosphine chains between two mutually bonded Re atoms creates significant strain on the molecules. Due to the immense steric strain on the molecule, the Re–Re bond of  $[\text{Re}_2(\text{CO})_8(\mu\text{-dpph})]$ readily cleaves to give  $[\{cis-\text{ReCl}(\text{CO})_4\}_2(\mu\text{-dpph})]$  (**3**) the structure of which was determined by X-ray crystallography. For the first time, the <sup>31</sup>P chemical shifts of the close-bridged complexes are analyzed for the ring contributions.

#### 2. Experimental

### 2.1. General

All reactions were routinely performed under pure dry nitrogen using standard Schlenk techniques [5,6]. All solvents for the reactions were also vacuum degassed before use. The solvents were of reagent grade and were freshly purified and dried by published procedures [7]. Chemical reagents, unless otherwise stated, were commercial products and were used without further purification. Pre-coated silica TLC plates of layer thickness 0.25 mm were purchased from Merck. Fourier transform infrared spectra were recorded with a Perkin–Elmer 1725X FT-IR Spectrometer. Phosphorus-31 NMR spectra were recorded at room temperature on a Bruker DRX400 spectrometer at 162 MHz. The phosphorus chemical shifts are quoted from the proton-decoupled spectra, and are reported in ppm to the higher frequency of external 80% H<sub>3</sub>PO<sub>4</sub>. Elemental analyses were performed using a LECO CHNS-932 instrument.

### 2.2. Synthesis of the complexes $[Re_2(CO)_9(\eta^1-P-P)]$ $(P-P=Ph_2P(CH_2)_nPPh_2, n = 1-6)$

Solid Me<sub>3</sub>NO · 2H<sub>2</sub>O (0.0511 g, 0.46 mmol) was added to a continuously stirred solution of  $[Re_2(CO)_{10}]$ (0.3132 g, 0.48 mmol) in 50 ml of THF at room temperature. The yellow reaction mixture so formed was stirred under reduced pressure. After all the Me<sub>3</sub>NO · 2H<sub>2</sub>O solid had dissolved, stirring was continued for another 30 min, and half of the solvent was removed under reduced pressure. The remaining solution was stirred for a further 15 min before it was slowly transferred to a stirred solution of the diphosphine (P–P) (0.44 mmol) in 24 ml of THF via a PTFE transfer tube. The resultant yellow solution was stirred under nitrogen for about 1 h. Half of the solvent was then removed and stirring was continued for another 50 min, after which the solution was evaporated to dryness to give a yellow residue.

2.2.1. Workup procedure for the complexes  $[Re_2(CO)_9-(\eta^1-P-P)]$   $[P-P=Ph_2P(CH_2)_nPPh_2, n = 1, 3-6]$ 

The yellow residue was redissolved in a minimum quantity of CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on silica TLC plates. A diethyl ether–hexane (1:3) mixture eluted two closely-spaced yellow bands. A very light yellow solid was recovered from each of the two bands by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–MeOH mixture. The first band (that of the higher  $R_f$  value, typically ca. 0.70) yielded the monodentate-coordinated complex [Re<sub>2</sub>(CO)<sub>9</sub>( $\eta^1$ -P–P)] and the second band ( $R_f$  typically ca. 0.60) yielded the "dimer" complex [{Re<sub>2</sub>(CO)<sub>9</sub>}<sub>2</sub>( $\mu$ -P–P)] (Fig. 3). The yields of both products, except for the dppm complexes, are very sensitive to experimental conditions, and when the yield of the monodentate complex was low, there was always a corresponding increase in the yield of the dimer. The



Fig. 2. General structures of the close-bridged [ $Re_2(CO)_8(\mu-P-P)$ ] and phosphine oxide [ $Re_2(CO)_9\{P-P(O)\}$ ] complexes.



Fig. 3. General structure of the dimer complexes [ $\{Re_2(CO)_9\}_2(\mu-P-P)$ ].

yields and elemental analysis data are given in Table 1, and IR and <sup>31</sup>P NMR data are given in Tables 2 and 3, respectively.

# 2.2.2. Workup Procedure for the complex $[Re_2(CO)_9-(\eta^1-dppe)]$

About 3 ml of CH<sub>2</sub>Cl<sub>2</sub> was added to the yellow residue. A suspension was obtained, which was centrifuged to yield the light yellow [{Re<sub>2</sub>(CO)<sub>9</sub>}<sub>2</sub>( $\mu$ -dppe)] solid and a yellow supernatant. The yellow supernatant was chromatographed on silica TLC plates. Elution with CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:3) followed by further recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-MeOH mixture yielded the pure complex [Re<sub>2</sub>(CO)<sub>9</sub>( $\eta$ <sup>1</sup>-dppe)]. The yields, elemental analysis data and spectroscopic data are given in Tables 1–3.

Table 1

There's and analytical data for $[Ke_2(CO)_9(1] - F - F)]$ and $[Ke_2(CO)_9(2(\mu - F - F))]$ complexe	Yields and	analytical	data for	$[Re_2(CO)_9]$	$(\eta^1 - P - P)$	and [{R	$e_2(CO)_9$	u-P-P)] complex
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P–P	[Re <sub>2</sub> (CO) <sub>9</sub> (η <sup>1</sup> -I	$[\text{Re}_2(\text{CO})_9(\eta^1-P-P)]$			$[{Re_2(CO)_9}_2(\mu-P-P)]$		
	Yield (%)	Ca	Ha	Yield (%)	$C^{a}$	Ha	-
dppm	40	40.6 (40.5)	2.0 (2.2)	10	31.2 (31.6)	1.4 (1.4)	
dppe	5-20	40.6 (41.1)	2.7 (2.4)	15-50	31.9 (32.1)	1.9 (1.5)	
dppp	15-25	42.2 (41.7)	2.5 (2.5)	5-10	32.5 (32.5)	1.6 (1.6)	
dppb	6-18	42.5 (42.3)	2.9 (2.7)	15-20	32.8 (33.0)	1.7 (1.7)	
dpppe	14-30	43.0 (42.9)	2.9 (2.8)	9–15	32.9 (33.4)	1.7 (1.8)	
dpph	14–20	43.7 (43.5)	2.9 (3.0)	6–10	34.1 (33.8)	1.9 (1.9)	

<sup>a</sup>Observed value; calculated value in brackets.

Table 2

Solution (CH<sub>2</sub>Cl<sub>2</sub>) IR absorptions for [Re<sub>2</sub>(CO)<sub>9</sub>( $\eta^1$ -P–P)] and [{Re<sub>2</sub>(CO)<sub>9</sub>}<sub>2</sub>( $\mu$ -P–P)] complexes in the carbonyl stretching region (cm<sup>-1</sup>)

P–P	$[Re_2(CO)_9(\eta^1-P-P)]$	$[{Re_2(CO)_9}_2(\mu-P-P)]$
dppm	<i>eq</i> , 2103(m), 2034(m), 1991(s), 1960(m), 1931(m) <i>ax</i> , 2104(m), 2034(m), 1994(s), 1960(m), 1936(m)	<i>ax–ax</i> , 2105(m), 2035(m), 1998(s), 1963(m), 1938(m)
dppe dppp	<i>ax</i> , 2104(m), 2034(m), 1994(s), 1962(m), 1934(m) <i>ax</i> , 2105(m), 2033(m), 1995(m), 1958(m), 1936(m)	<i>ax–ax</i> , 2105(m), 2035(m), 1996(s), 1964(m), 1936(m) <sup>a</sup> <i>ax–ax</i> , 2105(m), 2034(m), 1996(s), 1960(m), 1936(m)
dppb	<i>eq</i> , 2103(m), 2034(m), 1992(s), 1961(m), 1930(m) <i>ax</i> , 2104(m), 2033(m), 1994(s), 1960(m), 1935(m)	<i>eq-eq</i> , 2103(m), 2034(m), 1993(s), 1961(m), 1930(m) <i>ax-ax</i> , 2105(m), 2035(m), 1995(s), 1961(m), 1935(m)
dpppe dpph	<i>ax</i> , 2105(m), 2033(m), 1994(s), 1959(m), 1935(m) <i>ax</i> , 2105(m), 2033(m), 1994(s), 1959(m), 1935(m)	<i>ax–ax</i> , 2105(m), 2033(m), 1995(s), 1960(m), 1935(m) <i>ax–ax</i> , 2105(m), 2033(m), 1994(s), 1960(m), 1935(m)

<sup>a</sup> Recorded in toluene.

Table 3				
<sup>31</sup> P NMR data, $\delta_{\rm p}$	(ppm), for $[Re_2(CO)_9(r)]$	$^{1}-P-P$ and [{Re <sub>2</sub> (CO) <sub>9</sub>	$\frac{1}{2}(\mu - P - P)$ ] recorded in	CDCl <sub>3</sub>

P-P	$[Re_2(CO)_9(\eta^1\text{-}P\text{-}P)]^b$	$[{Re_2(CO)_9}_2(\mu-P-P)]$
dppm	$eq$ , -10.3(d), -25.7(d), $J_{p-p} = 48$ Hz $ax$ , 6.3(d), -23.5(d), $J_{p-p} = 104$ Hz	<i>ax–ax</i> , 5.9(s)
dppe dppp	<i>ax</i> , 9.6(d), $-11.5$ (d), $J_{p-p} = 39.5$ Hz <i>ax</i> , 5.6(s), $-16.9$ (s)	$ax-ax, 8.1(s)^a$ ax-ax, 5.5(s)
dppb	eq, -11.5(s), -16.2(s) ax, 5.6(s), -16.9(s)	<i>eq–eq</i> , –11.6(s) <i>ax–ax</i> , 5.5(s)
dpppe dpph	<i>ax</i> , 6.1(s), -14.6(s) <i>ax</i> , 6.0(s), -14.7(s)	<i>ax–ax</i> , 6.3(s) <i>ax–ax</i> , 5.9(s)

<sup>a</sup>Recorded in deuterated toluene.

<sup>b</sup> The higher field signal was assigned to the phosphorus atom of the free phosphino end and the lower field signal was assigned to the equatorial or axial coordinated phosphorus atom.

2.2.3. Isomerization reactions of  $eq-[Re_2(CO)_9(\eta^1-P-P)]$ and  $eq, eq-[\{Re_2(CO)_9\}_2(\mu-P-P)](P-P=dppm, dppb)$ 

A sample of either  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$  or  $[\{\text{Re}_2(\text{CO})_9\}_2(\mu\text{-}P\text{-}P)]$  (equatorial isomers, about 10 mg) was placed in a small Schlenk tube with a stirring bar, and toluene (about 2 ml) was added. The solution was vacuum-degassed, and the tube was refilled with nitrogen. A slow flow of nitrogen was maintained through the tube via an outlet needle inserted through the rubber septum. The solution was magnetically stirred, and heated to boiling with a heat gun. After 10 min of boiling, the solvent was removed under reduced pressure to yield a solid residue of the axial isomer. The IR and <sup>31</sup>P NMR spectroscopic data are given in Tables 2 and 3 respectively.

### 2.3. Reactions of the complexes $[Re_2(CO)_9(\eta^1-P-P)]$ $(P-P=Ph_2P(CH_2)_nPPh_2, n = 1-6)$ with $Me_3NO$

In a typical experiment,  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$  (0.036 mmol) was dissolved in 5 ml of freshly distilled and degassed THF. A 0.012 M solution of Me<sub>3</sub>NO · 2H<sub>2</sub>O in THF–MeOH (49:1) mixture (3 ml, 0.036 mmol of Me<sub>3</sub>NO) was then added dropwise under nitrogen. The resultant solution was degassed again and stirred under nitrogen for 4 h at room temperature. The solution was then evaporated to dryness and the yellow residue was redissolved in a minimum quantity of CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on silica TLC plates. Elution with acetone–hexane (1:3) mixture followed by further recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–hexane mixture yielded the

complexes  $[\text{Re}_2(\text{CO})_8(\mu-\text{P}-\text{P})]$  (typical  $R_f$  0.43) and  $[\text{Re}_2(\text{CO})_9\{\text{P}-\text{P}(\text{O})\}]$  (typical  $R_f$  0.32). The yields, elemental analysis, IR and <sup>31</sup>P NMR spectroscopic data are given in Tables 4–6. In the reaction of  $[\text{Re}_2(\text{CO})_9(\eta^1-\text{P}-\text{P})]$  (P–P = dppb, dpppe and dpph), mixtures of *eq-eq*, *ax–eq* or *ax–ax* [Re<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -P–P)] products were isolated first, which then isomerized to the *eq–eq* isomers after leaving the solution at room temperature for 2–3 days.

## 2.4. Crystallography

Single crystals of both complexes 1 and 2 were grown by slow evaporation of solutions in CH<sub>2</sub>Cl<sub>2</sub>-hexane mixtures at ca. 5 °C. Those of complex 3 were similarly grown from solutions in CDCl<sub>3</sub>-hexane mixtures. Crystals were mounted on quartz fibres (1, 2) or sealed in a glass capillary (3). X-ray data were collected on a Siemens SMART CCD system, using Mo K $\alpha$  radiation, at ambient temperatures [295(2) K], with 6s (1) or 10s (2 and 3) exposures. Data were corrected for Lorentz and polarisation effects with the SMART suite of programs [8], and for absorption effects with sADABS [9]. Structural solution and refinement were carried out with the SHELXTL suite of programs [10].

Final unit cell parameters were determined from 5874, 6628 and 9371 reflections, for 1, 2 and 3, respectively. The structures were solved by either direct methods, or by a Patterson map to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. H atoms were placed in calculated

Table 4

Yields and analytical data for  $[Re_2(CO)_8(\mu-P-P)]$  and  $[Re_2(CO)_9\{P-P(O)\}]$  complexes

Starting material [ $Re_2(CO)_9(\eta^1-P-P)$ ] P–P:	$[\text{Re}_2(\text{CO})_8(\mu\text{-}\text{P}-\text{P})]$			$[\operatorname{Re}_2(\operatorname{CO})_9\{\operatorname{P-P}(\operatorname{O})\}]$			
	Yield (%)	C <sup>a</sup>	Ha	Yield (%)	$C^a$	$\mathrm{H}^{\mathrm{a}}$	
<i>eq</i> , dppm	76	40.2 (40.4)	2.3 (2.3)	5	39.5 (39.8)	2.2 (2.1)	
ax, dppm	42	40.0 (40.4)	2.2 (2.3)	_	_	_	
ax, dppe	32	40.8 (41.0)	2.3 (2.4)	9	40.8 (40.5)	2.5 (2.3)	
ax, dppp	17	41.9 (41.7)	2.8 (2.6)	17	40.9 (41.1)	2.7 (2.5)	
<i>eq</i> , dppb	42	42.2 (42.3)	2.9 (2.8)	11	41.4 (41.6)	2.7 (2.6)	
ax, dppb	14	42.1 (42.3)	2.9 (2.8)	8	41.7 (41.6)	2.6 (2.6)	
ax, dpppe	14	42.7 (42.8)	2.9 (2.9)	17	41.9 (42.2)	3.0 (2.8)	
ax, dpph	11	43.0 (43.4)	3.1 (3.0)	8	42.7 (42.8)	3.0 (2.9)	

<sup>a</sup>Observed value; calculated value in brackets.

Table	5
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Solution (CH<sub>2</sub>Cl<sub>2</sub>) IR absorptions of  $[Re_2(CO)_8(\mu-P-P)]$  and  $[Re_2(CO)_9\{P-P(O)\}]$  in the carbonyl stretching region (cm<sup>-1</sup>)

P–P	$[Re_2(CO)_8(\mu-P-P)]$	$[Re_2(CO)_9{P-P(O)}]$
dppm	2072(m), 2019(m), 1978(s), 1956(w), 1940(w), 1914(m)	eq, 2105(w), 2036(m), 1994(s), 1962(m), 1938(m)
dppe	2070(m), 2016(m), 1978(s), 1944(m), 1911(m)	ax, 2106(w), 2034(m), 1996(s), 1959(m), 1937(m)
dppp	2068(m), 2014(m), 1976(s), 1938(m), 1910(m)	ax, 2105(w), 2033(m), 1995(s), 1960(m), 1936(m)
dppb	2066(m), 2009(m), 1975(s, sh), 1937(m), 1910(m)	ax, 2104(w), 2034(m), 1994(s), 1962(m), 1934(m)
dpppe	2065(m), 2009(m), 1977(s, sh), 1934(m), 1907(m)	ax, 2105(w), 2033(m), 1994(s), 1958(m), 1935(m)
dpph	2067(m), 2006(w), 1966(s), 1918(m, sh)	ax, 2105(w), 2033(m), 1994(s), 1960(m), 1935(m)

eq or ax: equatorial or axial isomer.

Table 6 <sup>31</sup>P NMR data,  $\delta_p(ppm)$ , of  $[Re_2(CO)_8(\mu-P-P)]$  and  $[Re_2(CO)_9\{P-P(O)\}]$ , recorded in CDCl<sub>3</sub>

Starting material [Re <sub>2</sub> (CO) <sub>0</sub> (n <sup>1</sup> -P–P)] P–P:	$[\text{Re}_2(\text{CO})_8(\mu-\text{P}-\text{P})]$	$[\text{Re}_2(\text{CO})_0 \{P - P(\text{O})\}]$
ag dppm	0.3 (s)	$aa 224 (d) -37 (d) L_{mm} = 7 Hz$
ax, dppe	4.2 (s)	$ax, 31.7$ (d), 9.0 (d), $J_{(P,P)} = 51$ Hz
ax, dppp	-17.5 (s)	ax, 32.8 (s), 6.0 (s)
<i>eq</i> , dppb		
ax, dppb	-1.0 (s) <sup>a</sup> , $-9.3$ (s)	<i>ax</i> , 32.4 (s), 4.9 (s)
ax, dpppe	-1.0 (s) <sup>a</sup> , $-8.3$ (s)	ax, 32.1 (s), 5.0 (s)
ax, dpph	11./ (s), $-1.0$ (s) <sup>a</sup> , $-14.5$ (s)	<i>ax</i> , 32.3 (s), 4.8 (s)

<sup>a</sup> After completing the isomerization to the *eq*-*eq* isomer, only this signal was observed.

Table 7

Crystallographic data for $[Re_2(CO)_8(\mu-dppp)]$ (1)		Selected bond lengths (Å) and angles (°) for $[Re_2(CO)_8(\mu-d)]$			
Empirical formula Formula weight Temperature (K) Wavelength (Å)	$\begin{array}{c} C_{35}H_{26}O_8P_2Re_2\\ 1008.90\\ 293(2)\\ 0.71073\\ \end{array}$	Re(1)-Re(1a) Re(1)-C(11) Re(1)-C(13) Re(1)-C(14) P(1)-C(12)	3.1075(3) 1.913(4) 1.954(4) 1.978(5)	P(1)-C(1) O(11)-C(11) O(12)-C(12) O(13)-C(13) O(14)-C(14)	
Space group	orthornombic Pnna	Re(1)-C(12) Re(1)-P(1)	1.984(5) 2.4811(9)	C(14) = C(14) C(1) = C(2)	
Unit cell dimensions a (Å) b (Å) c (Å) V (Å <sup>3</sup> ) Z $D_{(calc)}$ (Mg/m <sup>3</sup> ) Absorption coefficient (mm <sup>-1</sup> ) F(000)	14.6848(2) 23.1878(5) 10.3998(2) 3541.2(1) 4 1.892 6.969 1920	$\begin{array}{c} C(11)-Re(1)-C(13)\\ C(11)-Re(1)-C(14)\\ C(13)-Re(1)-C(14)\\ C(11)-Re(1)-C(12)\\ C(13)-Re(1)-C(12)\\ C(14)-Re(1)-C(12)\\ C(11)-Re(1)-P(1)\\ C(13)-Re(1)-P(1)\\ C(14)-Re(1)-P(1)\\ \end{array}$	91.6(2) 96.1(2) 86.9(2) 93.4(2) 90.9(2) 170.4(2) 87.8(1) 176.9(1) 96.1(1)	$\begin{array}{l} C(12)-Re(1)-P(1)\\ C(11)-Re(1)-Re(1a)\\ C(13)-Re(1)-Re(1a)\\ C(14)-Re(1)-Re(1a)\\ C(12)-Re(1)-Re(1a)\\ P(1)-Re(1)-Re(1a)\\ C(1)-P(1)-Re(1)\\ C(2)-C(1)-P(1)\\ C(1)-C(2)-C(1a)\\ \end{array}$	
Crystal size (mm <sup>3</sup> ) $\theta$ range for data collection (°) Index ranges	$0.325 \times 0.250 \times 0.200$ 2.15-29.32 -19 \le 19, -31 \le k \le 21, -13 \le l \le 9				
Reflections collected Independent reflections [ $R_{int}$ ] Completeness to $\theta = 29.32^{\circ}$ Absorption correction Maximum and minimum transmission	21 422 4530 [0.0321] 93.3% SADABS 0.341697 and 0.212105	<b>3. Results and disc</b> 3.1. Synthesis of $(P-P = Ph_2P(CH))$	the comp $f_2)_n PPh_2$ , if	lexes $[Re_2(CO)_9(\eta n = 1-6)]$	
Refinement method Data/restraints/parameters Goodness-of-fit on $F^2$ Final <i>R</i> indices $[I > 2\sigma(I)]$ <i>R</i> indices (all data) Extinction coefficient Largest differential peak and hole (e Å <sup>-3</sup> )	full-matrix least-squares on $F^2$ 4530/0/214 1.121 $R_1 = 0.0258, wR_2 = 0.0470$ $R_1 = 0.0439, wR_2 = 0.0532$ 0.00122(4) 0.684 and -0.856	The reactions of $[\text{Re}_2(\text{CO})_{10}]$ with the diph (P–P) and Me <sub>3</sub> NO invariably yielded a mi $[\text{Re}_2(\text{CO})_9(\eta^1\text{-P}\text{-P})]$ (monodentate complex, Fi $[\{\text{Re}_2(\text{CO})_9\}_2(\mu\text{-P}\text{-P})]$ (dimer complex, Fig. presence of Me <sub>3</sub> NO leads to oxidative decarbo of $[\text{Re}_2(\text{CO})_{10}]$ , which results in the formation intermediate species $[\text{Re}_2(\text{CO})_9(\text{solvent})]$ Res			

positions and given isotropic thermal parameters at 1.2 times that of the C atoms to which they are attached. All non-hydrogen atoms were given anisotropic thermal parameters in the final model. An extinction parameter was also refined for 1. A half molecule of CH<sub>2</sub>Cl<sub>2</sub> was found in 2. This was refined with isotropic thermal parameters and with the C-Cl bond lengths restrained to be equal. A molecule of  $CDCl_3$  was found in 3, and this was refined fully. Crystallographic data for 1, 2 and 3 are summarized in Tables 7, 9 and 11, respectively. Selected bond lengths and angles for the complexes are given in Tables 8, 10 and 12 respectively.

Table 8 Selected bond lengths (Å) and angles (°) for $[\text{Re}_2(\text{CO})_8(\mu\text{-dppp})]$ (1)						
Re(1)-Re(1a)	3.1075(3)	P(1)-C(1)	1.839(4)			
Re(1)-C(11)	1.913(4)	O(11)-C(11)	1.142(5)			
Re(1)-C(13)	1.954(4)	O(12)-C(12)	1.132(5)			
Re(1) - C(14)	1.978(5)	O(13)-C(13)	1.137(4)			
Re(1) - C(12)	1.984(5)	O(14)-C(14)	1.143(5)			
$\operatorname{Re}(1) - \operatorname{P}(1)$	2.4811(9)	C(1)–C(2)	1.519(5)			
C(11)-Re(1)-C(13)	91.6(2)	C(12)-Re(1)-P(1)	86.1(1)			
C(11)-Re(1)-C(14)	96.1(2)	C(11)-Re(1)-Re(1a)	174.3(1)			
C(13)-Re(1)-C(14)	86.9(2)	C(13)-Re(1)-Re(1a)	83.6(1)			
C(11)-Re(1)-C(12)	93.4(2)	C(14) - Re(1) - Re(1a)	86.6(1)			
C(13)-Re(1)-C(12)	90.9(2)	C(12)-Re(1)-Re(1a)	83.8(1)			
C(14)-Re(1)-C(12)	170.4(2)	P(1)-Re(1)-Re(1a)	96.9(2)			
C(11)-Re(1)-P(1)	87.8(1)	C(1) - P(1) - Re(1)	122.2(1)			
C(13)-Re(1)-P(1)	176.9(1)	C(2)–C(1)–P(1)	116.3(2)			
C(14)-Re(1)-P(1)	96.1(1)	C(1)-C(2)-C(1a)	116.6(4)			

P-P]

osphines xture of g. 1) and 3). The onvlation on of an intermediate species [Re2(CO)9(solvent)]. Reaction of this intermediate with the diphosphine results in the formation of the monodentate complex. Further reaction of the monodentate complex with another molar equivalent of the solvent-stabilized intermediate would produce the dimer. The isolation of dimer reflects the high reactivity of the monodentate complex with [Re<sub>2</sub>(CO)<sub>9</sub>(solvent)].

The monodentate complexes and dimers were isolated as either equatorial or axial isomers, or a mixture of two isomers (Fig. 4). Distinction between axial and equatorial complexes was mainly based on <sup>31</sup>P NMR spectra, as the resonance for the axial isomer occurs 10-20 ppm downfield of that for the equatorial isomer [11]. In addition, the coordination shift ( $\Delta \delta = \delta_{coord} - \delta_{free}$ )

Table 9

Crystallographic data for  $[Re_2(CO)_8(\mu-dppb)]$  (2)

Empirical formula	$C_{36.5}H_{29}ClO_8P_2Re_2$
Formula weight	1065.39
Temperature (K)	293(2)
Wavelength	0.71073
Crystal system	monoclinic
Space group	$P2_{1}/n$
Unit cell dimensions	
a (Å)	12.8610
$b(\dot{A})$	17.4869(2) Å
$c(\dot{A})$	17.8955(1) Å
β(°)	107.85(1)
$V(A^3)$	3830.92(6)
Z	4
$D_{(calc)}$ (Mg/m <sup>3</sup> )	1.847
Absorption coefficient (mm <sup>-1</sup> )	6.515
F(000)	2036
Crystal size (mm <sup>3</sup> )	$0.400\times0.300\times0.140$
$\theta$ range for data collection (°)	2.03-29.27
Index ranges	$-17 \leqslant h \leqslant 15, 0 \leqslant k \leqslant 23, 0 \leqslant l \leqslant 23$
Reflections collected	24 732
Independent reflections $[R_{int}]$	9463 [0.0283]
Completeness to $\theta = 29.27^{\circ}$	90.6%
Absorption correction	SADABS
Maximum and minimum	0.368256 and 0.191728
transmission	
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	9463/1/446
Goodness-of-fit on $F^2$	1.165
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0307, wR_2 = 0.0613$
R indices (all data)	$R_1 = 0.0430, wR_2 = 0.0667$
Largest differential peak and	0.662 and -0.747
hole (e $A^{-3}$ )	

Table 10 Selected bond lengths (Å) and angles (°) for  $[Re_2(CO)_8(\mu-dppb)]$  (2) 3.1791(2) P(1)-C(1)1.855(4) Re(1)-Re(2)Re(1)-C(14) 1.913(5) O(11)-C(11) 1.134(5)Re(1)-C(12) 1.952(5) O(12)-C(12) 1.146(6) Re(1)-C(13) 1.991(5) O(13)-C(13) 1.150(5) Re(1)-C(11)2.001(5)O(14) - C(14)1.155(5)Re(1) - P(1)2.513(1)O(21)-C(21) 1.152(6) O(22)-C(22) Re(2)-C(24)1.929(5) 1.148(5)Re(2)-C(22)1.960(5) O(23)-C(23) 1 1 3 9 (6) Re(2)-C(21)1.980(5) O(24) - C(24)1.150(5)2.001(5)1.535(7) Re(2)-C(23)C(1)-C(2)Re(2) - P(2)2.502(1)C(2)-C(3)1.519(7) 1.838(5) 1.540(6) C(3)-C(4) P(2)-C(4)C(14)-Re(1)-C(12) 89.3(2) C(24)-Re(2)-C(23) 98.1(2) C(14)-Re(1)-C(13)97.0(2) C(22)-Re(2)-C(23) 89.1(2) C(12)-Re(1)-C(13) 87.0(2) C(21)-Re(2)-C(23) 165.8(2) C(14)-Re(1)-C(11) 94.4(2) C(24)-Re(2)-P(2) 86.0(1) C(12)-Re(1)-C(11) C(22)-Re(2)-P(2) 174.4(1)89.9(2) C(13)-Re(1)-C(11)168.2(2)C(21)-Re(2)-P(2)91.6(1) C(14)-Re(1)-P(1)84.8(1) C(23)-Re(2)-P(2) 90.1(1) C(12)-Re(1)-P(1) 172.8(2) C(24)-Re(2)-Re(1) 167.3(1) C(13)-Re(1)-P(1)97.7(1) C(22)-Re(2)-Re(1)78.8(1) 82.8(1) C(11)-Re(1)-P(1)86.5(1)C(21)-Re(2)-Re(1) C(14)-Re(1)-Re(2)171.5(1)C(23)-Re(2)-Re(1)83.2(1) C(12)-Re(1)-Re(2) 82.4(2) P(2)-Re(2)-Re(1) 106.6(3) C(13)-Re(1)-Re(2) 84.7(1) C(4)-P(2)-Re(2)121.0(2) 83.7(1) 126.9(2) C(11)-Re(1)-Re(2)C(1)-P(1)-Re(1)P(1)-Re(1)-Re(2)103.3(3)C(2)-C(1)-P(1)114.0(3)C(24)-Re(1)-C(22) 88.6(2) C(3)-C(2)-C(1) 113.9(4) C(24)-Re(2)-C(21) 96.1(2) C(2)-C(3)-C(4)112.7(4) C(22)-Re(2)-C(21) 90.6(2) C(3)-C(4)-P(2) 119.2(3)

for an axial phosphorus atom can be expected to be around +24 ppm by comparison with ax-[Re<sub>2</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)] ( $\Delta \delta = +23.9$  ppm) [12] and ax-[Re<sub>2</sub>(CO)<sub>9</sub>( $\eta^1$ -dppf)] ( $\Delta \delta = +22.9$  ppm) [3]. The equatorial isomers can be converted to the axial isomers by refluxing in toluene for 10 min. At room temperature, isomerization is complete within a week. Unlike the monophosphine complexes [Re<sub>2</sub>(CO)<sub>9</sub>(PR<sub>3</sub>)] [PR<sub>3</sub> = PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, P(O-*o*-tol)<sub>3</sub>, PPh<sub>3</sub>, P(CH<sub>2</sub>Ph)<sub>3</sub>] [11], where complete isomerization is not always observed, complete isomerization is always obtained in the monodentate diphosphine complexes.

In general, yields of the monodentate complexes were relatively low and very dependent on the exact reaction conditions, except for the dppm complex, the yield of which was consistently reproducible (Table 1). The low yield may be attributed to the fact that the monodentate complexes have a tendency to be irreversibly adsorbed on the silica TLC plates. The variation of the yield may reflect the high reactivity of the monodentate complexes with the [Re<sub>2</sub>(CO)<sub>9</sub>(solvent)] intermediate to form the dimer complexes. This is supported by the observation that a relatively low yield of the monodentate complex is always accompanied by a relatively high yield of the dimer complex, and vice versa.

The relatively high and constant yield of the dppm monodentate complex may be attributed to the reluctance of this metalloligand complex to coordinate to another  $[\text{Re}_2(\text{CO})_9]$  fragment, which in turn can be attributed to the unfavourable steric interactions that would occur between the two  $[\text{Re}_2(\text{CO})_9(\text{PPh}_2)]$  fragments held in close proximity by the methylene bridge [13-15].

# 3.2. Reactions of the complexes $[Re_2(CO)_9(\eta^1-P-P)]$ $(P-P=Ph_2P(CH_2)_nPPh_2, n = 1-6)$ with $Me_3NO$

Generally, reactions of  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$  with Me<sub>3</sub>NO proceeded readily at room temperature. Two major products, the close-bridged complex 1,2-dieq- $[\text{Re}_2(\text{CO})_8(\mu\text{-}P\text{-}P)]$  and the phosphine oxide complex  $[\text{Re}_2(\text{CO})_9\{\text{P}\text{-}P(\text{O})\}]$ , were isolated by TLC using an eluant of acetone-hexane (1:3) mixture. The formation of phosphine oxide complexes is unexpected and the mechanism for their formation will be discussed in an-other paper. Suffice it to say here that the phosphine oxide complexes result from the reaction of Me<sub>3</sub>NO with  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$ , and that this reaction was not

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Table 11 Crystallographic data for [ $\{cis-\text{ReCl}(\text{CO})_4\}_2(\mu-\text{dpph})$ ] (3)

Empirical formula	$C_{20}H_{17}Cl_4O_4PRe$	
Formula weight	680.31	
Temperature (K)	293(2)	
Wavelength (Å)	0.71073	
Crystal system	triclinic	
Space group	$P\overline{1}$	
Unit cell dimensions		
a (Å)	8.9488(3)	
b (Å)	11.6877(4)	
c (Å)	12.9457(5)	
α (°)	98.043(1)	
β(°)	102.155(1)	
γ (°)	103.28(1)	
$V(Å^3)$	1262.79(8)	
Z	2	
$D_{\text{(calc)}}$ (Mg/m <sup>3</sup> )	1.789	
Absorption coefficient (mm <sup>-1</sup> )	5.320	
F(000)	654	
Crystal size (mm <sup>3</sup> )	0.56  imes 0.48  imes 0.26	
$\theta$ range for data collection (°)	2.20-29.29	
Index ranges	$-12 \leqslant h \leqslant 11, -16 \leqslant k \leqslant 15,$	
	$0 \leq l \leq 17$	
Reflections collected	9371	
Independent reflections $(R_{int})$	5868 [0.0289]	
Completeness to $\theta = 29.29^{\circ}$	85.1%	
Absorption correction	SADABS	
Maximum and minimum	0.189197 and 0.030441	
transmission		
Refinement method	full-matrix least-squares on $F^2$	
Data/restraints/parameters	5868/0/271	
Goodness-of-fit on $F^2$	1.065	
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0365, wR_2 = 0.0922$	
<i>R</i> indices (all data)	$R_1 = 0.0405, wR2_{-}0.0973$	
Largest differential peak	1.287  and  -1.494	
and hole (e $Å^{-3}$ )		

Table 12

Selected bond lengths (Å) and angles (°) for  $[{cis-ReCl(CO)_4}_2(\mu-dpph)]$  (3)

Re(1)-C(13)	1.911(6)	Re(1)-Cl(1)	2.480(2)
Re(1)-C(11)	1.981(7)	P(1)–C(1)	1.833(5)
Re(1)-C(14)	1.998(6)	C(1)–C(2)	1.529(7)
Re(1)-C(12)	2.015(6)	C(2) - C(3)	1.514(7)
Re(1) - P(1)	2.476(1)	C(3)–C(3a)	1.57(1)
C(13) - Re(1) - C(11)	90.6(3)	C(14) - Re(1) - Cl(1)	91.4(2)
C(13)-Re(1)-C(14)	92.3(2)	C(12)-Re(1)-Cl(1)	84.8(2)
C(11)-Re(1)-C(14)	89.0(3)	P(1)-Re(1)-Cl(1)	89.2(5)
C(13)-Re(1)-C(12)	91.5(3)	C(121)–P(1)–C(111)	102.1(2)
C(11)-Re(1)-C(12)	91.9(3)	C(121)–P(1)–C(1)	104.6(2)
C(14)-Re(1)-C(12)	176.1(2)	C(111)-P(1)-C(1)	104.2(3)
C(13)-Re(1)-P(1)	91.5(2)	C(121)-P(1)-Re(1)	111.3(2)
C(11)-Re(1)-P(1)	177.5(2)	C(111)-P(1)-Re(1)	117.3(2)
C(14)-Re(1)-P(1)	89.6(2)	C(1)-P(1)-Re(1)	115.8(2)
C(12)-Re(1)-P(1)	89.4(2)	C(2)-C(1)-P(1)	113.9(4)
C(13)-Re(1)-Cl(1)	176.3(2)	C(3)-C(2)-C(1)	110.5(4)
C(11)-Re(1)-Cl(1)	88.8(2)	C(2)-C(3)-C(3a)	112.5(6)

observed in the synthesis of  $[\text{Re}_2(\text{CO})_9(\eta^1\text{-}P\text{-}P)]$  since in the latter Me<sub>3</sub>NO was reacted with  $[\text{Re}_2(\text{CO})_{10}]$  prior to the addition of the diphosphines.



Fig. 4. Equatorial and axial positions of dirhenium carbonyl complexes.

In principle, the oxidative decarbonylation of the  $[\text{Re}_2(\text{CO})_9(\eta^1-P-P)]$  complexes by Me<sub>3</sub>NO can give rise to either chelate  $[(CO)_5Re-Re(CO)_3(\eta^2-P-P)]$  or closebridged  $[Re_2(CO)_8(\mu-P-P)]$  complexes. The presence of only one signal in the <sup>31</sup>P NMR spectra could reflect either a 1,2-diequatorial (closed-bridge) or 1,1-diequatorial (chelate) coordination mode of the diphosphine. One major evidence for the formation of only closebridged products and not chelate products comes from the expected difference in IR spectra of the two types of products in the carbonyl stretching region. The major difference between their v(CO) spectra relates to the highest-frequency absorptions of the [Re(CO)<sub>5</sub>] and [Re(CO)<sub>4</sub>] units. The [Re(CO)<sub>5</sub>] unit would show the highest absorption band at around 2105 cm<sup>-1</sup> while the [Re(CO)<sub>4</sub>] unit would exhibit the highest absorption peak in the range of 2065–2072 cm<sup>-1</sup> [16,17]. All the  $[Re_2(CO)_8(P-P)]$  complexes isolated have their highest v(CO) peak occurring within the latter range, confirming the absence of [Re(CO)<sub>5</sub>] units.

Site selectivity studies on substitution reactions of  $[\text{Re}_2(\text{CO})_9\text{L}]$  by Ingham and Coville [16] showed that when  $L = P(\text{O-}o\text{-tol})_3$  or  $P(\text{CH}_2\text{Ph})_3$ , reaction of  $[\text{Re}_2(\text{CO})_9\text{L}]$  with Me<sub>3</sub>NO and a second ligand L' (L' = RCN) only yields products in which the two substituents are coordinated to different Re atoms. The authors argued that the initially attached P-donor ligand plays a major role in the Me<sub>3</sub>NO reaction, directing reactivity to only the second metal center. The formation of close-bridged complexes here further confirms their results.

It is interesting to note that in the reactions of the dppm, dppe and dppp monodentate complexes, the phosphorus atoms of the close-bridged products are both coordinated equatorially, while in the reactions of the dppb, dpppe and dpph monodentate complexes, the <sup>31</sup>P NMR data suggest that ax-eq or even ax-ax products were isolated first, which then isomerized to the eq-eq products. This difference may be due to the different lengths of the carbon chains of the diphosphines. In the dppm, dppe and dppp complexes, the carbon chains are too short to allow the P atoms to coordinate in the ax-eq or ax-ax fashion. In the dppb and dpppe complexes, however, the carbon chains are long enough for one P atom to be coordinated

equatorially to one Re atom and the other coordinated axially to the other Re atom. Lastly, the carbon chain in the dpph complex is so long that even the ax-ax product can be formed.

The effect of increase in the length of the carbon chain between the two phosphorus atoms on the formation of close-bridged complexes is also reflected in the yields (Table 4). The yields decrease with the increase in the length of the carbon chain. This is consistent with the increase in steric strain that accompanies the increase in length of the diphosphine chain that needs to be accommodated between two mutually-bonded Re atoms.

It is also observed that, for the monodentate complexes which can be isolated in both equatorial and axial forms, the yields of  $[\text{Re}_2(\text{CO})_8(\mu-\text{P}-\text{P})]$  complexes from equatorial isomers are always higher than those from the axial isomers. Unreacted axial monodentate complexes were also isolated at the end of the reactions of these complexes with Me<sub>3</sub>NO. This suggests that the *ax*- $[\text{Re}_2(\text{CO})_9(\eta^1-\text{P}-\text{P})]$  complexes are less reactive than their equatorial isomers towards Me<sub>3</sub>NO.

The length of the carbon chain of the diphosphine also appears to affect the yield of the phosphine oxide complexes. The formation of the phosphine oxide complex is apparently inhibited when the carbon chain is either too short (dppm) or too long (dpph) (Table 4).

# 3.3. Crystal structures of $[Re_2(CO)_8(\mu\text{-}dppp)]$ (1) and $[Re_2(CO)_8(\mu\text{-}dppb)]$ (2)

In view of the lack of structural data for close-bridged complexes, X-ray crystallographic analyses for complexes 1 and 2 were carried out.

The molecule of 1 (Fig. 5) possesses a crystallographic  $C_2$  axis which joins C(2) of the propylene group and the middle of the Re–Re bond. The geometry about each rhenium is best described as distorted octahedral, and the two Re octahedra are staggered, being rotated by 40.1° from the C(13)–C(13a) eclipsed position and exhibiting a P–Re–Re–P torsional angle of 46.2°. The P...P axis makes a projection of 26.4° onto the Re–Re bond, and the P...P distance (4.176 Å) is much larger than the Re–Re bond length of 3.1075(3) Å.

The accommodation of the dppp chain between two mutually bonded Re atoms creates significant strain on the molecule, as shown by the obtuse P–Re–Re angle [96.87(2)°] and an elongation of the Re–Re bond compared to that in  $[\text{Re}_2(\text{CO})_{10}]$  [3.041(1) Å] [18]. The strain is also evident from the very large C(1)–P(1)–Re(1), C(2)–C(1)–P(1) and C(1)–C(2)–C(1a) bond angles involving the dppp bridge.

The two Re octahedra in the molecule of 2 (Fig. 6) are also staggered, being rotated by 47.2° from the C(12)–C(22) eclipsed position, and exhibiting a P–Re– Re-P torsional angle of 53.1°. These angles are much larger than the corresponding angles in complex 1, reflecting the larger steric demand of the dppb ligand compared to dppp. Although the P...P distance (4.968 A) is much longer than that in the dppp analogue, the projection of the P...P axis makes a similar angle of  $26.0^{\circ}$  with the Re–Re bond in **2**. The molecule of **2** also shows much distortion due to the presence of the long dppb bridge. For example, the P-Re-Re angles [average 104.93(3)°] and the Re–Re bond distance [3.1791(2) A] are much larger than those of 1  $[96.87(2)^{\circ}$  and 3.1075(3) A]. The elongated Re-P bond distances [average 2.508(1) A] and decreased Re-Re-C(axial) bond angles [average 169.4(1)°] compared to those of 1  $[2.4811(9) \text{ Å and } 174.3(1)^{\circ}]$  are also indicative of the increased steric strain when dppp is replaced by dppb. Within the dppb backbone, the strain is reflected in the large bond angles, especially the C(3)-C(4)-P(2) angle [119.2(3)°].

# 3.4. Formation and crystal structure of [{cis-ReCl- $(CO)_4$ }\_2( $\mu$ -dpph)] (3)



Fig. 5. Crystal structure of  $[Re_2(CO)_8(\mu-dppp)]$  (1).

Several attempts were made to grow single crystals of  $[Re_2(CO)_8(\mu\text{-}dpph)]$  by slow evaporation of  $CH_2Cl_2-$ 



Fig. 6. Crystal structure of  $[Re_2(CO)_8(\mu-dppb)]$  (2).

hexane solutions of the complex. These attempts resulted in either powdery solids or polycrystalline material. Good crystals were obtained when  $CH_2Cl_2$  was replaced by  $CDCl_3$ , but the crystals were of the complex [{*cis*-ReCl(CO)<sub>4</sub>}<sub>2</sub>(µ-dpph)] (**3**) and not [Re<sub>2</sub>(CO)<sub>8</sub>-(µ-dpph)]. Complex **3** probably resulted from the oxidative chlorination of [Re<sub>2</sub>(CO)<sub>8</sub>(µ-dpph)] by chloroform in the presence of light. A possible reason for the easy oxidation may be that the breaking of the Re– Re bond results in a substantial relief of the immense steric strain originating from the accommodation of the long dpph chain between two mutually-bonded Re atoms.

The <sup>31</sup>P NMR spectrum of **3** shows only one signal at 0.7 ppm. This reflects the symmetrical bridging mode of dpph. The solution IR spectrum of **3** (in CH<sub>2</sub>Cl<sub>2</sub>) exhibits a different v(CO) pattern from those of the [Re<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -P-P)] complexes. Four bands [2110w, 2020s(sh), 2005s, 1943m] were observed in the carbonyl-stretching region. This (3A' + A") pattern is similar to those of other octahedral *cis*-[ReX(CO)<sub>4</sub>L] complexes (L = neutral donor, X = halide) [17,19].

The molecule of **3** (Fig. 7) consists of two octahedral rhenium centers singly-bridged by a dpph ligand. Each rhenium atom is coordinated to four carbonyl ligands, one chloro ligand, and one phosphino group which is *cis* to the chloro ligand. The dpph chain is fully extended and not coiled, thus maximising the distance between the [ReCl(CO)<sub>4</sub>] units. Interestingly, the C(1)–C(2) bond is *anti* to the phenyl group C(121)–C(126) rather than the apparently more sterically demanding [ReCl(CO)<sub>4</sub>] group. The molecule possesses a crystallographic inversion center at the midpoint of the C(3)–C(3a) bond of the hexylene bridge. Thus only one half of the molecule is crystallographically unique.

The strongest Re–CO linkage occurs in the carbonyl group *trans* to the  $\pi$ -donating chloro ligand, the Re–C(13) bond [1.911(6) Å] being much shorter than the



Fig. 7. Crystal structure of  $[{cis-ReCl(CO)_4}_2(\mu-dpph)]$  (3).

other Re–C bonds [1.981(7), 1.998(6) and 2.015(6) A]. This phenomenon is also observed in the complex *cis*-[ReCl(CO)<sub>4</sub>(PPh<sub>2</sub>H)] [19].

# 3.5. Trends in <sup>31</sup>P chemical shifts of $[Re_2(CO)_8(\mu-P-P)]$ complexes

Compounds of phosphorus with transition metals have been intensively studied by <sup>31</sup>P NMR spectroscopy [20–24]. Generally, the  $\delta_p$  values for metal complexes with alkylphosphine or arylphosphine ligands can be approximately predicted using empirical relationships of the type indicated in Eq. (1), which states that the coordination shift  $\Delta \delta$  is a linear function of the  $\delta_p$  value of the free ligand [24].

$$\Delta \delta = \delta_{p}(\text{complex}) - \delta_{p}(\text{free ligand})$$
$$= A[\delta_{p}(\text{free ligand})] + B. \tag{1}$$

The constants A and B depend on the metal, the type of complex and the other ligands present.

For complexes with chelating ligands, the expression for the coordination shift should be modified by adding a ring contribution  $\Delta R$  [24]. The ring contribution is the difference between the coordination shifts for complexes with chelating ligands (e.g., dppe) and those in which the bidentate ligand is replaced by two similar, but monodentate ligands (e.g., PMePh<sub>2</sub>). Although the theoretical explanations of  $\Delta R$  are not well-developed, the knowledge of its contribution to the  $\delta_p$  value is useful for structure determination and assignment of <sup>31</sup>P resonances.

There is no study, to our knowledge, reported for ring contributions of close-bridged transition metal complexes with diphosphines. The <sup>31</sup>P data for the closebridged dirhenium complexes with Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (n = 1-6) are therefore inspected to see if any noteworthy features are observed. The  $\delta_P$  values for the close-bridged complexes are compared with those for the free phosphines in Table 13, and a plot of  $\Delta\delta$  against  $\delta_P$  (free) is given in Fig. 8. It can be seen that the  $\Delta\delta$ value for the dppp complex is much smaller than those

Table 13		
<sup>31</sup> P NMR data for	1,2-dieq-[Re2(CO)8(µ-P-P)]	and free phosphines

P–P	$\delta_p$ (free) <sup>a</sup>	[Re <sub>2</sub> (CO) <sub>8</sub> (µ-P–P)]	
		$\delta_{\rm p}{}^{\rm b}$	$\Delta\delta$
dppm	-25.0	0.3	+25.3
dppe	-14.7	4.2	+18.9
dppp	-17.8°	-17.5	+0.3
dppb	-17.8	-1.0	+16.8
dpppe	-18.3	-1.0	+17.3
dpph	-18.2	-1.0	+17.2

<sup>a</sup> In THF.

<sup>b</sup> In CDCl<sub>3</sub>.

<sup>c</sup> In toluene.



Fig. 8. Plot of  $\Delta\delta$  against  $\delta_P$ (free) for [Re<sub>2</sub>(CO)<sub>8</sub>( $\mu$ -P–P)] complexes (P–P = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>, n = 1-6).

of the other diphosphine complexes, suggesting the presence of a ring contribution. It would be of interest to extend this study to other close-bridged [Re<sub>2</sub>(CO)<sub>8</sub>-( $\mu$ -P–P)] complexes with diphosphines containing propylene backbones, to see if they also exhibit small  $\Delta\delta$  values.

#### 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC 214442 (for 1), 214443 (for 2), and 214444 (for 3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam ac.uk or http://www.ccdc.cam.ac.uk).

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