Dirhenium carbonyl compounds bearing *cis*-1,2-bis(diphenylphosphino)ethylene and *cis*-1,2-bis(diphenylphosphino)ethylene oxide ligands

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Reaction of $[Re_2(CO)_9(MeCN)]$ with *cis*-1,2-bis(diphenylphosphino)ethylene (*cis*-$Ph_2PCH=CHPPh_2$) in boiling benzene (80 °C) afforded two compounds, *ax*-$[Re_2(CO)_9(\kappa^1$-*cis*-$Ph_2PCH=CHPPh_2)]$ (**1**) and *ax*-$[Re_2(CO)_9\{\kappa^1$-*cis*-$Ph_2PCH=CHPh_2P(O)\}]$ (**2**) where the ligand is axially coordinated in a κ^1 monodentate fashion through phosphorus. The close-bridged compound *eq*-$[Re_2(CO)_8(\mu$-κ^2-*cis*-$Ph_2PCH=CHPPh_2)]$ (**3**) is obtained from a similar reaction of the same ligand with $[Re_2(CO)_8(NCMe)_2]$ in refluxing benzene. In this case the diphosphine is equatorially coordinated to two Re atoms in a symmetrical bridging fashion. Compounds **1**−**3** have been characterized by IR, ^1H NMR, $^{31}P\{^1H\}$ NMR spectroscopy and single crystal X−ray diffraction analyses.

Keywords: Rhenium carbonyl, Diphosphine, Close-bridged, Phosphine oxide, X−ray structures

The coordination chemistry of diphosphine ligands such as bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)methane (dmpm), bis(diphenylphosphino)ethane (dppe) and analogous ligands has been extensively studied since they are readily available, robust, and their properties can be fine-tuned through the modification of the methylene chain between phosphorus atoms.[1–13] It has been observed that the archetypal examples of dppm include chelate compounds where the four membered metallacyclic ring so formed is under tremendous ring strain. Therefore, the ligand prefers to form κ^1 compounds in many cases or bridge two metal atoms resulting in a variety of coordination geometries.[14–16] There are ample examples of the formation of chelate or bridged compounds by these ligands, however, except for dppm,[17–22] other examples containing κ^1 coordinated diphosphine ligands are limited in the literature. Few structures are shown in Fig. 1. In 1991, in the development of dppf [dppf = 1,1-bis(diphenylphosphino)ferrocene] coordination chemistry, Hor *et al*. reported the mono coordinated dppf compound $[Re_2(CO)_9(\kappa^1$-dppf)] from the Me_3NO assisted reaction with $[Re_2(CO)_{10}]$, which on oxidation with H_2O_2 in CH_3CN afforded the phosphine-oxide compound $[Re_2(CO)_9\{\kappa^1$-dppf(O)\}].[23] The Leong group reported that the reactions of $[Re_2(CO)_{10}]$ with $[Ph_2P(CH_2)_nPPh_2]$ (n = 1–6) initiated by Me_3NO afforded the monophosphine compounds $[Re_2(CO)_9(\kappa^1$-$Ph_2P(CH_2)_nPPh_2)]$ (n = 1–6) which on further

reaction with Me_3NO furnished the close-bridged compounds $[Re_2(CO)_8(\mu,\kappa^2$-$Ph_2PP(CH_2)_nPPh_2)]$ and phosphine-oxide compounds $[Re_2(CO)_9\{\kappa^1$-$Ph_2P(CH_2)_nPh_2P(O)\}]$ (n = 1–6).[24] Some of these compounds were isolated as either equatorial or axial isomers, or a mixture of both.

In comparison to a fairly good number of known $[Re_2(CO)_9(\kappa^1$-diphosphine)], $[\{Re_2(CO)_9\}_2(\mu,\kappa^2$-diphosphine)] and $[Re_2(CO)_8(\mu,\kappa^2$-diphosphine)] compounds containing diphosphines with saturated carbon backbone of varying lengths, to the best of our knowledge, only one example of a structurally characterized diphosphine derivative, *eq*-$[Re_2(CO)_9(\kappa^1$-*trans*-$Ph_2PCH=CHPPh_2)]$ possessing an unsaturated carbon backbone is reported by Yan and coworkers.[25] They also described the phosphine-oxide compound *eq*-$[Re_2(CO)_9\{\kappa^1$-*trans*-$PPh_2CH=CHPh_2P(O)\}]$ and an unusual close-bridged compound, $[Re_2(CO)_8(\mu,\kappa^1(O),\kappa^1(P)$-$OPPh_2CH=CHPPh_2)$ by the Me_3NO assisted reaction of *eq*-$[Re_2(CO)_9(\kappa^1$-*trans*-$Ph_2PCH=CHPPh_2)]$ with Me_3NO. In this paper, we report the synthesis and crystallographic characterization of *ax*-$[Re_2(CO)_9(\kappa^1$-*ax*-$Ph_2PCH=CHPPh_2)]$, *ax*-$[Re_2(CO)_9\{\kappa^1$-*cis*-$Ph_2PCH=CHPh_2P(O)\}]$ and *eq*-$[Re_2(CO)_8(\mu$-κ^2-*cis*-$Ph_2PCH=CHPPh_2)]$.

Materials and Methods

Unless otherwise stated, all reactions were performed under a nitrogen atmosphere using
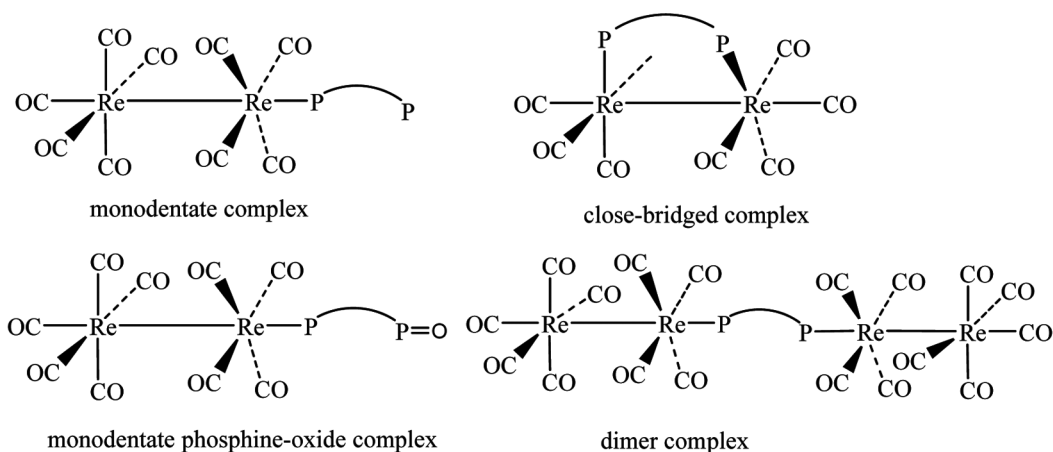
Fig. 1 — Skeletal structures of dinuclear monodentate, close-bridged, monodentate phosphine-oxide and dimer compounds bearing diphosphine ligands

standard Schlenk techniques. Reagent grade solvents were dried using the standard methods and were freshly distilled prior to use. $[Re_2(CO)_{10}]$ was purchased from Strem Chemicals, Inc. and used without further purification. *cis*-$Ph_2PCH=CHPPh_2$ was purchased from Sigma-Aldrich and used as received. The starting compounds $[Re_2(CO)_9(NCMe)]$ and $[Re_2(CO)_8(NCMe)_2]$ were prepared according to the literature procedures.[26,27] Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. NMR spectra were recorded on a BrukerAvance III HD (400 MHz) instrument. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvents (^{1}H) and to external 85% H_3PO_4 (^{31}P). Elemental analyses were performed by the Microanalytical Laboratories of the Wazed Miah Science Research Centre at Jahangirnagar University. Products were separated in the air by TLC plates coated with 0.25 mm of silica gel (HF254-type 60, E. Merck, Germany).

Reaction of [Re₂(CO)₉(MeCN)] with *cis*-Ph₂PCH=CHPPh₂

A solution of $[Re_2(CO)_9(MeCN)]$ (82 mg, 0.123 mmol) and *cis*-$Ph_2PCH=CHPPh_2$ (48.8 mg, 0.123 mmol) in 30 mL of benzene was heated to reflux for 3.3 h. The colour of the reaction mixture changed from light yellow to brown. The solvent was removed under reduced pressure and the residue chromatographed by TLC silica gel. Elution with cyclohexane/CH_2Cl_2 (7:3, v/v) gave two bands. The faster moving band afforded a mixture of *ax*-$[Re_2(CO)_9(\kappa^1$-*cis*-$Ph_2PCH=CHPPh_2)]$ (1) (40 mg, 32%) and *ax*-$[\{Re_2(CO)_9\{\kappa^1$-*cis*-

$Ph_2PCH=CHPh_2P(O)\}]$ (2) (34.5 mg, 27%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. Spectroscopic data for 1 and 2: Anal. Calc. (%) for $C_{35}H_{22}O_9P_2Re_2$: C, 41.18; H, 2.17. Found (%): C, 39.42; H, 2.3. IR (νCO, CH_2Cl_2): 2104 m, 2034 m, 1995 vs, 1922 w, 1934 w cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): δ 7.7–7.1 (m, 22H). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): compound 1, δ −3.8 (d, J = 32.4 Hz, 1P), −32.5 (d, J = 32.4 Hz, 1P); compound 2: δ 14.9 (d, J = 14.2 Hz, 1P), 1.1 (d, J = 14.2 Hz, 1P); 1:2;60:40.

Reaction of [Re₂(CO)₈(MeCN)₂] with *cis*-Ph₂PCH=CHPPh₂

To a benzene solution (25 mL) of $[Re_2(CO)_8(MeCN)_2]$ (100 mg, 0.147 mmol) was added *cis*-1,2-bis(diphenylphosphino)ethylene (73 mg, 0.184 mmol) in a three-necked flask. The reaction mixture was heated to reflux for 3.5 h. The color changed from pale yellow to brown. The solvent was evaporated to dryness, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (7:3, v/v) afforded unconsumed $[Re_2(CO)_8(MeCN)_2]$ (trace) and *eq*-$[Re_2(CO)_8(\mu$-κ^2-$Ph_2PCH=CHPPh_2)]$ (3) (0.055 g, 38%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at 4 °C. Spectroscopic data for 3: Anal. Calc. (%) for $C_{34}O_8P_2H_{22}Re_2$: C, 41.13; H, 2.23. Found: C, 41.35; H, 2.48. IR (νCO, CH_2Cl_2): 2071 s, 2019 s, 1979 vs, 1956 sh, 1915 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–7.39 (m, 20H), 6.98 (m, 2H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 10.0 (s).

Crystallography

Yellow crystals of 1, 2 and 3 suitable for X-ray diffraction analysis were grown by slow diffusion

of hexane into a CH_2Cl_2 solution containing each compound at 4 °C. X-ray intensity data were collected on a Bruker D8 Venture diffractometer equipped with a PHOTON II CPAD detector or on an Agilent Super Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) using a Nylon loop and Paratone oil, and the diffraction data were collected at low temperatures using Mo-Kα radiation (λ= 0.71073). Data reduction and integration were carried out with SAINT PLUS[28] and absorption corrections were applied using the program SADABS.[29] The structures were solved with the SHELXS[30] structure solution program by direct methods and refined by full-matrix least-squares based on F^2 using XL[30] within the OLEX2[31] graphical user interface. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included using a riding model. Details of data collection and pertinent crystallographic parameters are collected in Table 1.

Results and Discussion

Reaction of [Re$_2$(CO)$_9$(MeCN)] with *cis*-Ph$_2$PCH=CHPPh$_2$

Heating a benzene solution of [Re$_2$(CO)$_9$(MeCN)] and *cis*-Ph$_2$PCH=CHPPh$_2$ at 80 °C afforded a mixture of *ax*-[Re$_2$(CO)$_9$(κ^1-*cis*-Ph$_2$PCH=CHPPh$_2$)] (**1**) and the phosphine oxide compound *ax*-[Re$_2$(CO)$_9${κ^1-*cis*-Ph$_2$PCH=CHPh$_2$P(O)}] (**2**) in ca. 59% yield, after usual work up, chromatographic separation and recrystallization (Scheme 1). The compounds have been fully characterized by elemental analysis, IR, ^{1}H NMR and ^{31}P{^{1}H} NMR spectroscopy together with single crystal X-ray diffraction analyses. Several attempts to separate the compounds by preparative thin layer chromatography and recrystallization were, however, unsuccessful. Single crystal X-ray diffraction analyses using more than one crystal confirmed that both **1** and **2** co-crystallized within the same space group and are present in the crystal lattice in a ratio of about 60:40. This was consistent with the ^{31}P NMR data. The data was refined considering that the diphosphine ligand had been partially oxidized. The oxygen atom of the phosphine oxide was refined

with 40% occupancy. The positions of the phosphorus and carbon atoms of the ligands were common in both the phosphine and the phosphine oxide.

The solid-state molecular structure of **1** is depicted in Fig. 2 and selected bond distances and angles are presented in Table 2. The structure consists of a dirhenium core with nine terminal carbonyl ligands

Table 1 — Crystallographic data and structure refinement details for **1**, **2** and **3**		
Compound	**1, 2**	**3**
Empirical formula	C$_{35}$H$_{22}$O$_{9.4}$P$_2$Re$_2$	C$_{34}$H$_{22}$O$_8$P$_2$Re$_2$
Formula weight	1027.26	992.85
Temperature (K)	150(1)	217.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a (Å)	11.6822(3)	11.353(3)
b (Å)	12.0917(4)	12.069(3)
c (Å)	15.5639(4)	13.646(4)
α (°)	92.818(2)	65.457(11)
β (°)	110.440(3)	89.760(10)
γ (°)	118.047(3)	72.860(11)
Volume (Å^3)	1756.62(10)	1610.3(7)
Z	2	2
ρ$_{calc}$ (g/cm^3)	1.942	2.048
μ (mm^{-1})	7.030	7.661
F(000)	974.0	940.0
Crystal size/mm^3	0.24 × 0.2 × 0.18	0.152 × 0.103 × 0.077
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range (°)	5.58 to 59	3.79 to 54.46
Index ranges	−15 ≤ h ≤ 15, −16 ≤ k ≤ 16, −20 ≤ l ≤ 21	−14 ≤ h ≤ 14, −15 ≤ k ≤ 15, −17 ≤ l ≤ 17
Reflections collected	28390	57573
Independent reflections	8664 [R$_{int}$ = 0.0435, R$_{sigma}$ = 0.0474]	7146 [R$_{int}$ = 0.0383, R$_{sigma}$ = 0.0183]
Data/restraints/parameters	8664/0/443	7146/0/416
Goodness-of-fit on F^2	1.131	1.085
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0301, wR$_2$ = 0.0511	R$_1$ = 0.0148, wR$_2$ = 0.0339
Final R indexes [all data]	R$_1$ = 0.0424, wR$_2$ = 0.0556	R$_1$ = 0.0189, wR$_2$ = 0.0353
Largest diff. peak/hole / e (Å^{-3})	1.99/−1.37	0.73/−0.67
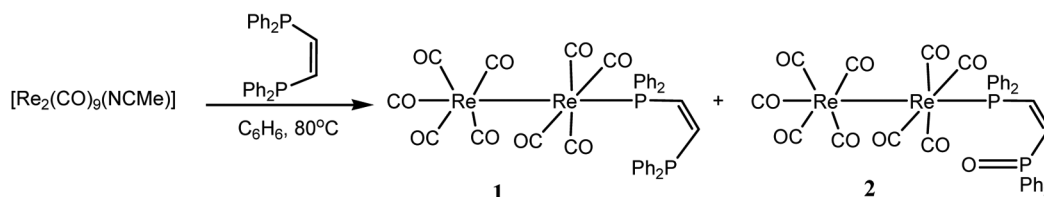
Scheme 1 — Reaction of [Re$_2$(CO)$_9$(MeCN)] with *cis*-Ph$_2$PCH=CHPPh$_2$ at 80 °C

and a *cis*-Ph₂PCH=CHPPh₂ ligand. The structure confirms substitution of the acetonitrile ligand by the *cis*-Ph₂PCH=CHPPh₂ ligand. The Re–Re bond distance of 3.0317(2) Å is very similar to those observed for *ax*-[Re₂(CO)₉{κ¹-dppf(O)}] [3.049(1) Å][Ref. 23] and *eq*-[Re₂(CO)₉(PPh₂H)] [3.0526(7) Å][Ref. 32] but is shorter than that reported for *eq*-[Re₂(CO)₉(κ¹-*trans*-PPh₂CH=CHPPh₂)] [3.1077(2) Å][Ref. 25]. The latter was reported from the Me₃NO initiated reaction of [Re₂(CO)₁₀] with *trans*-Ph₂PCH=CHPPh₂ and authors very briefly mentioned that heating the equatorial isomer at 110 °C gave the axial isomer.

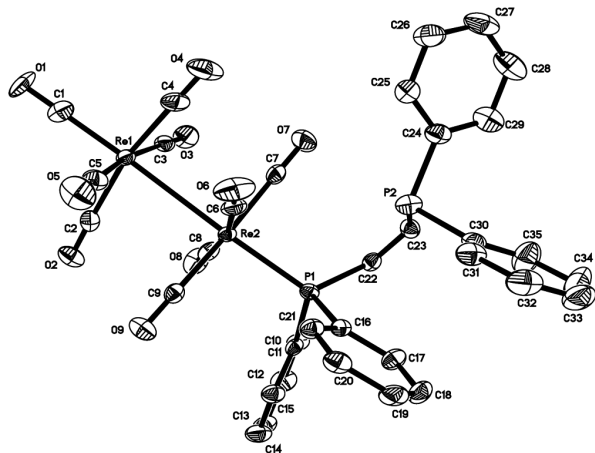The cis-Ph₂PCH=CHPPh₂ ligand in **2** is coordinated axially to Re(2) via P(1) atom and the Re(2)–P(1) bond distance of 2.3724 (10) Å is comparable to the Re–P bond distance in *ax*-[Re₂(CO)₉{κ¹-dppf(O)}] [2.390(5)Å].[23] This is in contrast to that reported for *eq*-[Re₂(CO)₉(κ¹-*trans*-PPh₂CH=CHPPh₂)] in which the dangling *trans*-PPh₂CH=CHPPh₂ ligand is equatorially coordinated to a Re atom.[22] The solid-state molecular structure of **2** is depicted in Fig. 3.
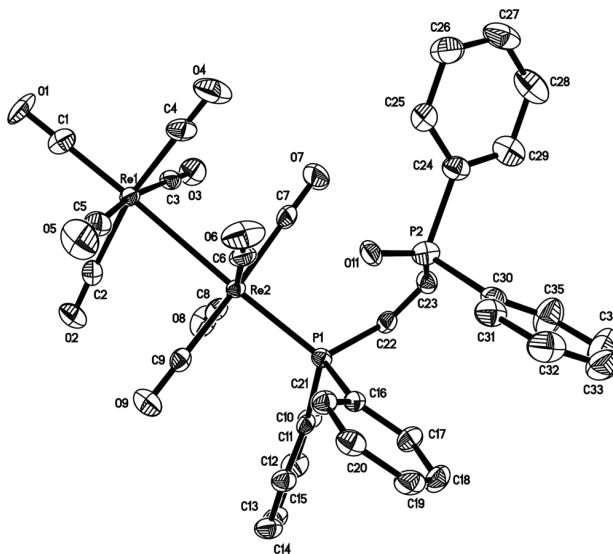

Fig. 2 — The solid-state molecular structure of *ax*-[Re₂(CO)₉(κ¹-*cis*-Ph₂PCH=CHPPh₂)] (**1**) showing 50% probability thermal ellipsoids

Fig. 3 — The solid-state molecular structure of *eq*-[Re₂(CO)₈(μ-κ²-*cis*-Ph₂PCH=CHPPh₂)] (**3**) showing 50% probability thermal ellipsoids

Table 2 — Selected bond distances and angles for **1–3**		
Compound	Bond distances (Å)	Bond angles (°)
	Re(1)–Re(2) 3.0317(2)	Re(1)–Re(2)–P(1) 174.60(3)
1, **2**	Re(2)–P(1) 2.3724(10)	Re(2)–P(1)–C(22) 114.08(12)
	P(1)– C(22) 1.818(4)	P(1)–C(22)– C(23) 126.4(3)
	C(22)–C(23) 1.332(5)	C(22)–C(23)–P(2) 123.0(3)
	P(2)–C(23) 1.816(4)	O(11)–P(2)–C(23) 122.2(3)
	P(2)–O(11) 1.345(7)	P(1)–Re(2)–C(7) 90.81(12)
		P(1)–Re(2)–C(9) 91.54(11)
		P(1)–Re(2)–C(8) 92.01(12)
	Re(1)–Re(2) 3.0676(6)	Re(1)–Re(2)–P(2) 93.71(2)
3	Re(1)–P(1) 2.4197(8)	Re(2)–Re(1)–P(1) 94.18(3)
	Re(2)–P(2) 2.4314(8)	Re(1)–P(1)–C(22) 122.22(8)
	P(1)– C(22) 1.810(2)	Re(2)–P(2)–C(21) 123.85(8)
	P(2)–C(21) 1.819(2)	P(1)–C(22)–C(21) 132.39(18)
		P(2)–C(21)–C(22) 132.58(18)
		Re(1)–C(1)–O(1) 179.0(2)
		Re(1)–C(2)–O(2) 178.0(2)
		Re(1)–C(3)–O(3) 179.5(3)
		Re(1)–C(4)–O(4) 179.7(3)
		Re(2)–C(5)–O(5) 178.8(2)
		Re(2)–C(6)–O(6) 177.5(2)
		Re(2)–C(7)–O(7) 178.9(2)
		Re(2)–C(8)–O(8) 176.1(2)

The structure consists of a dirhenium core with an axially coordinated *cis*-Ph$_2$PCH=CHPh$_2$P(O) ligand linked to a Re atom through PPh$_2$ group in a monodentate fashion. The P(2)–O(11) distance of 1.345(7) Å is significantly shorter than the P–O bond distance of 1.432(16) Å in [Re$_2$(CO)$_9$(κ^1-dppf(O)]. The overall structures of **1** and **2** are similar to that of *ax*-[Re$_2$(CO)$_9${κ^1-dppf(O)}].[23]

The IR spectrum of **1**, **2** shows five terminal ν(CO) bands in the region 2104–1934 cm^{-1}. The pattern of the IR spectrum is very similar to that observed for [Re$_2$(CO)$_9${κ^1-Ph$_2$P(CH$_2$)$_n$PPh$_2$}][(Ref. 24)] (n = 1–6), [Re$_2$(CO)$_9${κ^1-(*o*-anisyl)$_2$P(CH$_2$)$_3$PPh$_2$}][(Ref. 25)] and [Re$_2$(CO)$_9$ {κ^1–dppf(O)}], [(Ref. 23)] indicating that they have similar distribution of the carbonyl groups.[14] The ^{31}P{^{1}H} NMR spectra of **1** and **2** display two sets of four doublets at δ –3.8 (J 32.4 Hz), –32.5 (J 32.4 Hz) and δ 14.9 (J 14.4 Hz), 1.05 (J 14.4 Hz) with a relative ratio of 6:4; the former pair of resonances is assigned for compound **1** while the latter pair is valid for **2**. For each compound, the lower-field signal is assigned to the phosphorus atom bonded to the {Re$_2$(CO)$_9$} moiety, while the higher-field resonance is due to the uncoordinated phosphorus atom. The ^{31}P{^{1}H} NMR resonances of **1** are comparable to those reported for [Re$_2$(CO)$_9${κ^1-(*o*-anisyl)$_2$P(CH$_2$)$_3$PPh$_2$}][25] (δ –16.7 and –37.1) which clearly supports the fact that although compounds **1** and **2** co-crystallized within the same space group in solid-state but they show individual identity in solution. The ^{1}H NMR spectrum shows multiplets ranging from δ 7.7–7.1 (integrated to 22H) due to phenyl and olefinic proton resonances of Ph$_2$PCH=CHPPh$_2$ and Ph$_2$PCH=CHPh$_2$P(O) ligands of **1** and **2**. The resonances for the two olefinic protons of the two diphosphine ligands are overlapped with phenyl proton resonances.

Reaction of [Re$_2$(CO)$_8$(MeCN)$_2$] with *cis*-Ph$_2$PCH=CHPPh$_2$

Reaction of [Re$_2$(CO)$_8$(MeCN)$_2$] with *cis*-Ph$_2$PCH=CHPPh$_2$ in boiling benzene led to the isolation of the close-bridged compound *eq*-[Re$_2$(CO)$_8$(μ-κ^2-*cis*-Ph$_2$PCH=CHPPh$_2$)] (**3**) in 38% yield (Scheme 2).
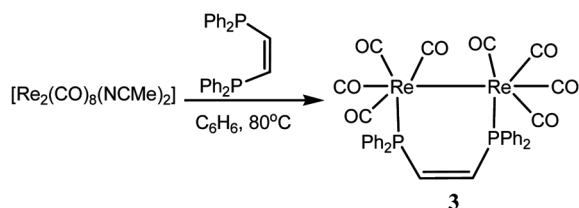
Scheme 2 — Reaction of [Re$_2$(CO)$_8$(MeCN)$_2$] with *cis*-Ph$_2$PCH=CHPPh$_2$ at 80 °C

The compound has been fully characterized by elemental analysis, IR, ^{1}H NMR, ^{31}P{^{1}H} NMR and single crystal X-ray diffraction analyses.

The solid-state molecular structure of **3** is depicted in Fig. 4 and the selected bond distances and bond angles are provided in Table 2. The structure consists of two mutually bonded rhenium atoms with a bridging *cis*-Ph$_2$PCH=CHPPh$_2$ ligand and eight terminal CO ligands, four bonded to each of Re(1) and Re(2). The Re(1)–Re(2) bond length at 3.0676(6) Å, is significantly shorter than the Re–Re bond distance of 3.1791(2) in [Re$_2$(CO)$_8$(μ-κ^2-dppb)] but is marginally shorter than the Re–Re bond distance of 3.1075(3) Å in [Re$_2$(CO)$_8$(μ-κ^2-dppp)].[(Ref. 24)] The *cis*-Ph$_2$PCH=CHPPh$_2$ ligand is linked to the dirhenium core in such a way that P(1) is bonded to Re(1) and P(2) is coordinated to Re(2) both equatorially. The Re–P bond distances [Re(1)–P(1) 2.4197, Re(2)–P(2) 2.4314(8)] are significantly shorter than those found in [Re$_2$(CO)$_6$(μ-κ^2:κ^2-C$_2$S$_2$O$_2$) (Ph$_2$PCH=CHPPh$_2$)] (av. 2.519 Å), [Re$_2$(CO)$_6$(μ-κ^2:κ^2-C$_2$O$_4$) (Ph$_2$PCH=CHPPh$_2$)] (av. 2.502 Å) and [(μ-κ^2:κ^2-C$_2$S$_4$) (Ph$_2$PCH=CHPPh$_2$)][7] (av. 2.525 Å). The coordination geometry about the Re atoms in **3** is best described as distorted from the ideal octahedral geometry, as evidenced from the Re centered bond angles (Table 2).

Spectroscopic data of **3** are in accord with the X-ray determined structure. The pattern of the ν(CO) absorption spectrum is similar to that reported
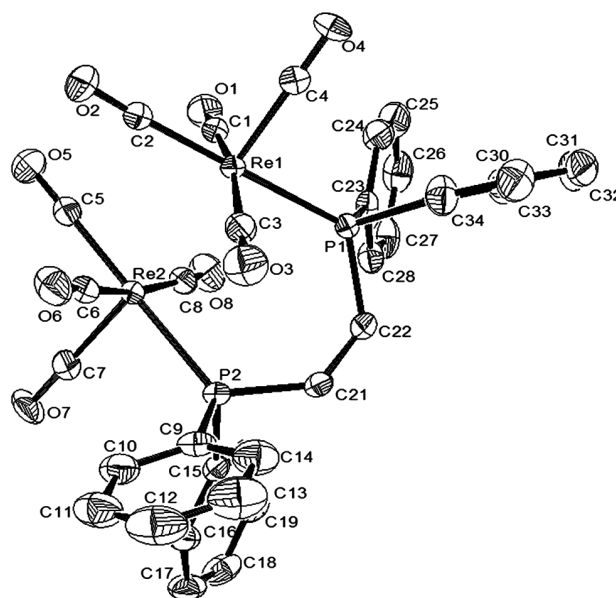
Fig. 4 — The solid-state molecular str6ucture of *eq*-[Re$_2$(CO)$_8$(μ-κ^2-*cis*-Ph$_2$PCH=CHPPh$_2$)] (**3**) showing 50% probability thermal ellipsoids

for $[Re_2(CO)_8\{\mu\text{-}\kappa^2\text{-}Ph_2P(CH_2)_nPPh_2\}]$[Ref. 24] (n = 1–4) indicating that they have similar distribution of the carbonyl ligands. The $^{31}P\{^1H\}$ NMR spectrum of **3** displays a singlet at δ 10.0, reflecting a symmetrical close-bridged coordination mode of the diphosphine. The ^1H NMR spectrum contains a series of multiplets in the region δ 7.48–7.39 (integrated for 20H) attributed to the phenyl hydrogens and a multiplet at 6.98 (integrated for 2H) of aliphatic–CH=CH protons of the *cis*-Ph$_2$PCH=CHP ligand.

Conclusions

In summary, it has been shown in this work that the monoacetonitrile compound $[Re_2(CO)_9(NCMe)]$ reacts with *cis*-Ph$_2$PCH=CHPPh$_2$ to provide a mixture of mono substituted κ^1-phosphinated compounds *ax*-$[Re_2(CO)_9(\kappa^1\text{-}cis\text{-}Ph_2PCH=CHPPh_2)]$ (**1**) and *ax*-$[Re_2(CO)_9\{\kappa^1\text{-}cis\text{-}Ph_2PCH=CHPh_2P(O)\}]$ (**2**) by elimination of the acetonitrile ligand which co-crystallized within a single space group. The bis(acetonitrile) compound $[Re_2(CO)_8(NCMe)_2]$ on the contrary, reacts with *cis*-Ph$_2$PCH=CHPPh$_2$ to afford the close-bridged compound *eq*-$[Re_2(CO)_8(\mu\text{-}\kappa^2\text{-}cis\text{-}Ph_2PCH=CHPPh_2)]$ (**3**) by the loss of two acetonitrile ligands. All of the three new compounds have been structurally characterized.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://www.nopr.niscair.res.in/jinfo/ijca/IJCA_60A(10) 1289-1295_SupplData.pdf. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary material. CCDC 2103253 (for **1** and **2**), CCDC 2103252 (for **3**). Copies of the data can be obtained free of charge on application to CCDC, http://www.ccdc.cam.ac.uk).

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