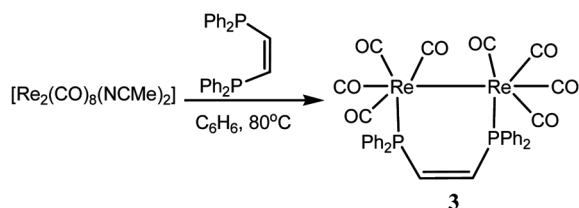


The structure consists of a dirhenium core with an axially coordinated *cis*-Ph₂PCH=CHPh₂P(O) ligand linked to a Re atom through PPh₂ group in a monodentate fashion. The P(2)–O(11) distance of 1.345(7) Å is significantly shorter than the P–O bond distance of 1.432(16) Å in [Re₂(CO)₉(κ¹-dppf(O))]. The overall structures of **1** and **2** are similar to that of *ax*-[Re₂(CO)₉{κ¹-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 [Re₂(CO)₉{κ¹-Ph₂P(CH₂)_nPPh₂}]^(Ref. 24) (n = 1–6), [Re₂(CO)₉{κ¹-(*o*-anisyl)₂P(CH₂)₃PPh₂}]^(Ref. 25) and [Re₂(CO)₉{κ¹-dppf(O)}],^(Ref. 23) indicating that they have similar distribution of the carbonyl groups.¹⁴ The ³¹P{¹H} 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 {Re₂(CO)₉} moiety, while the higher-field resonance is due to the uncoordinated phosphorus atom. The ³¹P{¹H} NMR resonances of **1** are comparable to those reported for [Re₂(CO)₉{κ¹-(*o*-anisyl)₂P(CH₂)₃PPh₂}]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 ¹H NMR spectrum shows multiplets ranging from δ 7.7–7.1 (integrated to 22H) due to phenyl and olefinic proton resonances of Ph₂PCH=CHPPh₂ and Ph₂PCH=CHPh₂P(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 [Re₂(CO)₈(MeCN)₂] with *cis*-Ph₂PCH=CHPPh₂

Reaction of [Re₂(CO)₈(MeCN)₂] with *cis*-Ph₂PCH=CHPPh₂ in boiling benzene led to the isolation of the close-bridged compound *eq*-[Re₂(CO)₈(μ-κ²-*cis*-Ph₂PCH=CHPPh₂)] (**3**) in 38% yield (Scheme 2).



Scheme 2 — Reaction of [Re₂(CO)₈(MeCN)₂] with *cis*-Ph₂PCH=CHPPh₂ at 80 °C

The compound has been fully characterized by elemental analysis, IR, ¹H NMR, ³¹P{¹H} 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*-Ph₂PCH=CHPPh₂ 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 [Re₂(CO)₈(μ-κ²-dppb)] but is marginally shorter than the Re–Re bond distance of 3.1075(3) Å in [Re₂(CO)₈(μ-κ²-dppp)].^(Ref. 24) The *cis*-Ph₂PCH=CHPPh₂ 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 [Re₂(CO)₆(μ-κ²:κ²-C₂S₂O₂) (Ph₂PCH=CHPPh₂)] (av. 2.519 Å), [Re₂(CO)₆(μ-κ²:κ²-C₂O₄) (Ph₂PCH=CHPPh₂)] (av. 2.502 Å) and [(μ-κ²:κ²-C₂S₄) (Ph₂PCH=CHPPh₂)]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 structure of *eq*-[Re₂(CO)₈(μ-κ²-*cis*-Ph₂PCH=CHPPh₂)] (**3**) showing 50% probability thermal ellipsoids

for $[\text{Re}_2(\text{CO})_8\{\mu\text{-}\kappa^2\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}]^{(\text{Ref. } 24)}$ ($n = 1\text{--}4$) indicating that they have similar distribution of the carbonyl ligands. The $^{31}\text{P}\{^1\text{H}\}$ 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*-Ph₂PCH=CHP ligand.

Conclusions

In summary, it has been shown in this work that the monoacetonitrile compound $[\text{Re}_2(\text{CO})_9(\text{NCMe})]$ reacts with *cis*-Ph₂PCH=CHPPh₂ to provide a mixture of mono substituted κ^1 -phosphinated compounds *ax*- $[\text{Re}_2(\text{CO})_9(\kappa^1\text{-cis-Ph}_2\text{PCH=CHPPh}_2)]$ (**1**) and *ax*- $[\text{Re}_2(\text{CO})_9\{\kappa^1\text{-cis-Ph}_2\text{PCH=CHPPh}_2\text{P(O)}\}]$ (**2**) by elimination of the acetonitrile ligand which co-crystallized within a single space group. The bis(acetonitrile) compound $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$ on the contrary, reacts with *cis*-Ph₂PCH=CHPPh₂ to afford the close-bridged compound *eq*- $[\text{Re}_2(\text{CO})_8(\mu\text{-}\kappa^2\text{-cis-Ph}_2\text{PCH=CHPPh}_2)]$ (**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](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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