Structural studies of phosphor-1,1-diselenoato Mn(I) and Re(I) complexes

Ching-Shiang Fang, Yao-Jheng Huang, Bijay Sarkar, C.W. Liu *

Department of Chemistry, National Dong Hwa University, Hualien 97401, Taiwan

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ABSTRACT

Mononuclear complexes of the type, M(CO)$_4$[Se$_2$P(OR)$_2$] (M = Mn, R = ^{i}Pr, **1a**; Et, **1b**; M = Re, R = ^{i}Pr, **3a**; Et, **3b**) can be prepared from either [-Se(Se)P(O^{i}Pr)$_2$]$_2$ (**A**) or [Se{-Se(Se)P(OEt)$_2$}$_2$] (**B**) with M(CO)$_5$Br. *O,O′*-dialkyl diselenophosphate ([(RO)$_2$PSe$_2$]$^-$, abbreviated as dsep) ligands generated from **A** and **B** act as a chelating ligand in these complexes. Upon refluxing in acetonitrile, these mononuclear complexes yield dinuclear complexes with a general formula of [M$_2$(CO)$_6${Se$_2$P(OR)$_2$}$_2$] (M = Mn, R = ^{i}Pr, **2a**; Et, **2b**; M = Re, R = ^{i}Pr, **4a**; Et, **4b**). Dsep ligands display a triconnective, bimetallic bonding mode in the dinuclear compounds and this kind of connective pattern has never been identified in any phosphor-1,1-diselenoato metal complexes. Compounds **2b**, **3b**, and **4** are structurally characterized. Compounds **2b** and **3b** display weak, secondary Se···Se interactions in their lattices.

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1. Introduction

Several metal complexes of organophosphorus dichalcogenides have been reported where these ligands coordinate to the metal center through their P or chalcogen (S, Se) atoms to form mono- or multinuclear metal complexes [1–3]. Although a handful of Mn(I) [4–7] and Re(I) [8–12] complexes of dithiophosphinate [R$_2$PS$_2$]$^-$ ligands can be identified in the literature, yet those of their selenium analog, namely Mn/Re complexes of diselenophosphinate [R$_2$PSe$_2$]$^-$ have not been reported. However, some Mn and Re metallacycles formed by the chelating, selenoimidodiphosphinate ligand, N(SePPh$_2$)$_2$, are known [13–16].

Surprisingly, Mn and Re complexes involving a diselenophosphate (abbreviated as dsep) ligand have never been reported. Dsep ligands are known to coordinate to various metal atoms through their Se atoms and lead to the formation of complexes with a variety of nuclearities [1,17–20]. This group reported mononuclear, trischelated compounds such as In{Se$_2$P(O^{i}Pr)$_2$}$_3$ [17], Sb{Se$_2$P(O^{i}Pr)$_2$}$_3$ [18], and Bi{Se$_2$P(O^{i}Pr)$_2$}$_3$ [19] which display a loosely bound dimeric unit via intermolecular Se···Se interactions. In addition, some of these complexes are excellent single-source precursors for the fabrication of metal selenide or phosphate nanomaterials [18,19]. On the other hand Cu(I) and Ag(I) form high nuclearity complexes with an interstitial selenide anion, of which some of them display intriguing photoluminescent properties [20].

Dsep ligands are known to adopt several coordination patterns in their metal complexes as represented in Scheme 1. Surprisingly the bimetallic–triconnective pattern (**f**) has never been reported.

Herein, we report the first synthesis of mononuclear and dinuclear Re(I) and Mn(I) complexes of isopropyl and ethyl homolog of dsep **1**–**4** and structural elucidation of a mononuclear compound **3b** and three dinuclear compounds **2b**, **4a** and **4b**. While the dsep ligand shows a simple, chelating pattern in **1** and **3**, a triconnective–bimetallic coordination mode is observed in **2** and **4** for the first time in the reported metal complexes bearing a diselenophosphate ligand [1].

2. Results and discussion

Mononuclear manganese complexes Mn(CO)$_4$[Se$_2$P(OR)$_2$] (R = ^{i}Pr, **1a**; Et, **1b**) are synthesized from either [−Se(Se)P(O^{i}Pr)$_2$]$_2$ (**A**) or [Se{-Se(Se)P(OEt)$_2$}$_2$] (**B**) with equimolar amount of Mn(CO)$_5$Br in acetone at room temperature for 24 h in 60.6% and 72.3% yield, respectively (Scheme 2). However, the corresponding Re complexes Re(CO)$_4$[Se$_2$P(OR)$_2$] (R = ^{i}Pr, **3a**; Et,**3b**) are obtained by refluxing either [−Se(Se)P(O^{i}Pr)$_2$]$_2$ or [Se{-Se(Se)P(OEt)$_2$}$_2$] with Re(CO)$_5$Br in 1:2 molar ratio in toluene for an hour in 58.4% and 52.1% yield, respectively. The higher temperature is required for the generation of **3a**–**b**, compared to that of **1a**–**b**, attributable to the higher stability of Re(CO)$_5$Br over its Mn analog and the similar phenomenon was observed by Villarreal et al. during the formation of {Re(CO)$_4$[Ph$_2$P(Se)NP(Se)Ph$_2$]} [15]. Dinuclear compounds Mn$_2$(CO)$_6$[Se$_2$P(OR)$_2$]$_2$ (R = ^{i}Pr, **2a**; Et, **2b**) could be generated by refluxing mononuclear Mn complexes **1a**–**b** in acetonitrile for an hour. Both di-rhenium complexes Re$_2$(CO)$_6$[Se$_2$P(OR)$_2$]$_2$ (R = ^{i}Pr, **4a**; Et, **4b**) can also be obtained by refluxing the corresponding mononuclear rhenium compound (**3a**–**b**) in acetonitrile for 1 h.

Efforts have been made to yield the mononuclear complexes **1** and **3** directly by stirring or refluxing M(CO)$_5$Br (M = Mn, Re) with

* Corresponding author.
 E-mail address: chenwei@mail.ndhu.edu.tw (C.W. Liu).

dsep ligands in solution, but to no avail. Certainly the reduction of the ligands **A** and **B** that yield dsep ligand during the complexation process plays a crucial role in knocking out a CO from the metal ion precursor. Most probably the reduction of the ligands takes place at the cost of oxidation of CO, which eventually was released from the coordination sphere of metal center.

2.1. NMR spectroscopy

All of the mononuclear compounds, **1a–b** and **3a–b,** show a single peak flanked with a pair of Se satellites in ^{31}P NMR spectrum. Also a singlet with a set of Se satellites observed in ^{31}P NMR spectrum of the dinuclear Mn complexes **2a–b** indicates some dynamic
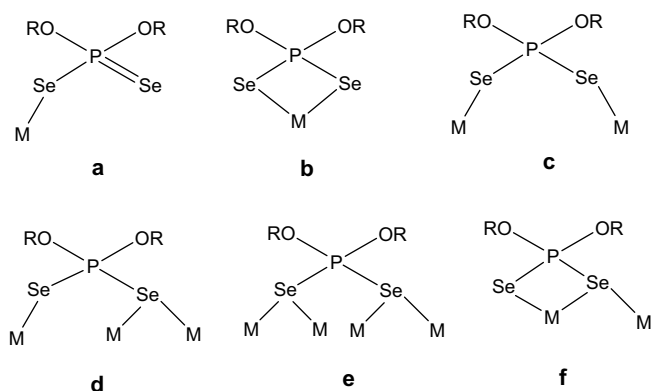
equilibrium could be attained in solution within the NMR time-scale so that only an averaged selenium satellite is identified despite of the presence of two, non-equivalent Se nuclei in each dsep unit of the complexes (vide infra.). However dinuclear Re complexes **4a–b** do show a singlet flanked with two pair of satellites in ^{31}P NMR spectrum. Unlike a set of satellite is depicted in **2a–b**, two $^{31}P–^{77}Se$ coupling constants in the range of 577–610 Hz in **4a–b** must have been originated from the coupling by two, non-equivalent ^{77}Se nuclei in solution. All the $^{31}P–^{77}Se$ coupling constants observed in compounds **1–4** suggest the P–Se bond order remains in between 1 and 2 [21]. The coupling constants observed in ^{31}P NMR spectra are also comparable with those from ^{77}Se NMR spectra for these compounds. Unfortunately, ^{77}Se NMR data of the dinuclear compounds **2a–b** and **4a–b** are not available. On the other hand, that the similar type of protons in a particular complex resonating at the same field in ^{1}H NMR spectrum for all compounds suggests similar environment around pendant isopropyl and ethyl protons in solution phase. For example all the methyl and methine protons of **4a** resonate at 1.39 and 4.80 ppm, even though the ^{31}P NMR spectrum suggested the inner core of the complex may contain non-equivalent Se atoms.

2.2. IR spectroscopy

IR spectra of the compounds **1a–b** and **3a–b** are very similar, all these four compounds exhibit four bands in the carbonyl stretching frequency region. Four CO groups attached to a six-coordinate metal center where all carbonyl groups are in *cis-* disposition to form a C_{2v} local symmetry corresponding to $2A_1 + B_1 + B_2$ vibrational modes give rise to such an infrared pattern [22]. On the other hand, the $\nu(CO)$ region in the IR spectra (KBr) of each of
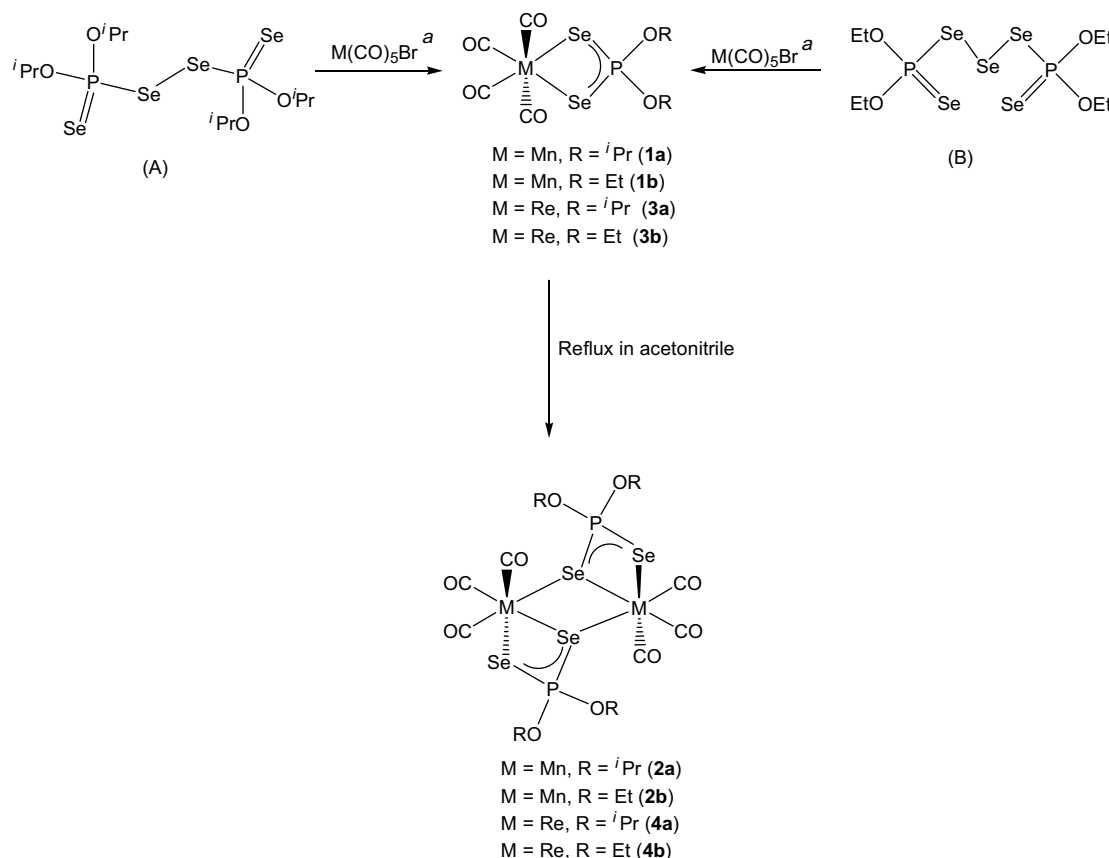
Scheme 1.

Scheme 2. [a]Acetone as solvent and stirring at RT for Mn complexes (**1a–b**); toluene as solvent and stirring with reflux for Re complexes (**3a–b**).

Table 1
Bond lengths and angles in **2b**, **3b**, **4a** and **4b** with esds in parentheses.

2b

Se(1)–P(1) 2.186(2)	Se(1)–Mn(1) 2.5560(15)	Se(1)–Mn(1A) 2.560(1)
Se(2)–P(1A) 2.151(2)	Se(2)–Mn(1) 2.5837(16)	Mn(1)–C(7) 1.790(9)
Mn(1)–C(5) 1.799(10)	Mn(1)–C(6) 1.819(8)	
P(1)–Se(1)–Mn(1) 103.49(7)	P(1)–Se(1)–Mn(1A) 80.53(7)	Mn(1)–Se(1)–Mn(1A) 95.69(4)
P(1) Se(2) Mn(1A) 80.61(7)	C(7)–Mn(1)–C(5) 87.9(4)	C(7)–Mn(1)–C(6) 89.8(4)
C(5)–Mn(1)–C(6) 91.6(4)	C(7)–Mn(1)–Se(1) 172.5(3)	C(5)–Mn(1)–Se(1) 99.6(3)
C(6)–Mn(1)–Se(1) 90.2(3)	C(7)–Mn(1)–Se(1A) 95.6(3)	C(5)–Mn(1)–Se(1A) 90.2(3)
C(6)–Mn(1)–Se(1A) 174.4(3)	Se(1)–Mn(1)–Se(1A) 84.31(4)	C(7)–Mn(1)–Se(2) 89.1(3)
C(5)–Mn(1)–Se(2) 173.8(3)	C(6)–Mn(1)–Se(2) 93.8(3)	Se(1)–Mn(1)–Se(2) 83.44(5)
Se(1A)–Mn(1)–Se(2) 84.75(4)	Se(2A)–P(1)–Se(1) 106.15(10)	O(3)–C(5)–Mn(1) 175.4(8)
O(4)–C(6)–Mn(1) 177.7(8)	O(5)–C(7)–Mn(1) 175.7(8)	

3b

Re(1)–C(6) 1.913(6)	Re(1)–C(7) 1.920(5)	Re(1)–C(5) 2.002(5)
Re(1)–C(8) 2.009(6)	Re(1)–Se(2) 2.6457(7)	Re(1)–Se(1) 2.6462(7)
Se(2)–P(1) 2.1606(14)	Se(1)–P(1) 2.1580(15)	
C(6)–Re(1)–C(7) 91.6(2)	C(6)–Re(1)–C(5) 89.1(2)	C(7)–Re(1)–C(5) 90.9(2)
C(6)–Re(1)–C(8) 91.9(2)	C(7)–Re(1)–C(8) 92.2(2)	C(5)–Re(1)–C(8) 176.68(19)
C(6)–Re(1)–Se(2) 94.93(17)	C(7)–Re(1)–Se(2) 173.44(18)	C(5)–Re(1)–Se(2) 89.70(14)
C(8)–Re(1)–Se(2) 87.04(15)	C(6)–Re(1)–Se(1) 175.34(15)	C(7)–Re(1)–Se(1) 92.33(18)
C(5)–Re(1)–Se(1) 88.35(15)	C(8)–Re(1)–Se(1) 90.48(18)	Se(2)–Re(1)–Se(1) 81.16(2)
P(1)–Se(2)–Re(1) 86.54(4)	P(1)–Se(1)–Re(1) 86.58(4)	Se(1)–P(1)–Se(2) 105.71(6)
O(3)–C(5)–Re(1) 179.9(6)	O(4)–C(6)–Re(1) 178.1(5)	O(5)–C(7)–Re(1) 178.7(6)

4a

Re(1)–C(7) 1.902(5)	Re(1)–C(8) 1.909(5)	Re(1)–C(9) 1.924(5)
Re(1)–Se(2) 2.6660(6)	Re(1A)–Se(2) 2.6685(6)	Re(1)–Se(1) 2.6693(6)
Se(1)–P(1) 2.1445(13)	Se(2)–P(1) 2.2057(13)	
C(7)–Re(1)–C(8) 87.1(2)	C(7)–Re(1)–C(9) 87.9(2)	C(8)–Re(1)–C(9) 90.9(2)
C(7)–Re(1)–Se((2) 96.04(17)	C(8)–Re(1)–Se(2) 174.76(17)	C(9)–Re(1)–Se(2) 93.41(17)
C(7)–Re(1)–Se(2A) 172.86(16)	C(8)–Re(1)–Se(2A) 93.52(17)	C(9)–Re(1)–Se(2A) 99.20(17)
Se(2)–Re(1)–Se(2A) 82.88(2)	C(7)–Re(1)–Se(1) 92.20(16)	C(8)–Re(1)–Se(1) 94.93(16)
C(9)–Re(1)–Se(1) 174.15(17)	Se(2)–Re(1)–Se(1) 80.77(2)	Se(2A)–Re(1)–Se(1) 80.66(2)
P(1)–Se(1)–Re(1) 82.55(4)	P(1)–Se(2)–Re(1) 81.53(3)	P(1)–Se(2)–Re(1A) 103.07(4)
Re(1)–Se(2)–Re(1A) 97.12(2)	Se(1)–P(1)–Se(2) 105.23(5)	O(3)–C(7)–Re(1) 176.7(5)
O(5)–C(9)–Re(1) 176.9(5)	O(4)–C(8)–Re(1) 177.3(5)	

4b

Re(1)–C(5) 1.902(17)	Re(1)–C(7) 1.917(13)	Re(1)–C(6) 1.918(15)
Re(1A)–Se(2) 2.6630(15)	Re(1)–Se(2) 2.6655(15)	Re(1)–Se(1) 2.6775(16)
Se(2)–P(1) 2.191(4)	Se(1)–(P1) 2.148(4)	
C(5)–Re(1)–C(7) 87.8(6)	C(5)–Re(1)–C(6) 87.6(6)	C(7)–Re(1)–C(6) 89.4(6)
C(5)–Re(1)–Se(2A) 171.7(5)	C(7)–Re(1)–Se(2) 92.8(4)	C(6)–Re(1)–Se(2) 100.7(4)
C(5)–Re(1)–Se(2) 96.7(4)	C(7)–Re(1)–Se(2A) 175.1(4)	C(6)–Re(1)–Se(2A) 92.6(5)
Se(2)–Re(1)–Se(2A) 82.45(5)	C(5)–Re(1)–Se(1) 89.9(5)	C(7)–Re(1)–Se(1) 96.9(4)
C(6)–Re(1)–Se(1) 173.1(5)	Se(2A)–Re(1)–Se(1) 81.78(5)	Se(2)–Re(1)–Se(1) 81.27(4)
P(1)–Se(2)–Re(1A) 103.57(10)	P(1)–Se(2)–Re(1) 81.18(10)	Re(1)–Se(2)–Re(1A) 97.55(5)
P(1)–Se(1)–Re(1) 81.67(10)	Se(1)–P(1)–Se(2) 106.64(15)	O(4)–C(6)–Re(1) 176.8(14)
O(3)–C(5)–Re(1) 178.6(14)	O(5)–C(7)–Re(1) 177.6(14)	

the four dinuclear species **2a–b** and **4a–b** exhibits two strong bands (**2a**, 2014, 1920; **2b**, 2004, 1927; **4a**, 2016, 1918; **4b**, 2021, 1903) which point to a facial assembly of three carbonyl ligands in an octahedrally coordinated metal center [22,23].

2.3. Structural studies

2.3.1. Compound **2b**

Selected angles and bond lengths are presented in Table 1. A perspective view is presented in Fig. 1a for the compound **2b**, a dinuclear Mn complex which crystallizes in triclinic $P\bar{1}$ space group. Each of the Mn atoms are slightly distorted octahedrally coordinated by three carbonyl carbon, one terminal selenium Se2 and two bridging Se1 atoms in the dinuclear complex. Three carbonyl carbons attached to the Mn atom show *facial* conformation. One of the Se atoms (Se2) is connected to the Mn1 in terminal fashion whereas the other Se (Se1) atom is connected to both Mn atoms. Each PSe₂ fragment of two dsep and two Mn atoms form a fused eight-membered tricyclic ring which remains in chair form.

The central ring formed by two Mn and two bridging Se1 atoms displays a planar parallelogram with consecutive Se1–Mn1 distances of 2.5560(15) and 2.5600(14) Å. The other manganese–selenium (Mn–Se2) distances are 2.5837(16) Å. The Mn–Se distances are comparable to that observed in the Mn[Ph₂P(Se)NP(Se)Ph₂]₂ (2.5344(11) and 2.5691(11) Å) [13] and are indicative of their covalent nature [24]. The P–Se lengths [2.186(2) and 2.151(2) Å] are slightly longer than that in isopropyl homolog of ammonium salt of dsep ligand NH₄Se₂P(O^{i}Pr)₂ [2.1414(8) and 2.1249(8) Å] [21]. Intermolecular Se···Se interactions form 1D network (Fig. 1b) as evidenced from the Se1···Se1 distances of 3.795 Å which are in the range of reported distances having Se···Se nonbonding secondary interaction [25].

2.3.2. Compound **3b**

The compound crystallizes in $P\bar{1}$ where the dsep ligand is chelated through two of its Se to the Re atom. The angles around the Re are in the range of 81.16(2)–176.68(19)°, indicating slightly distorted octahedral geometry around the rhenium atom. The
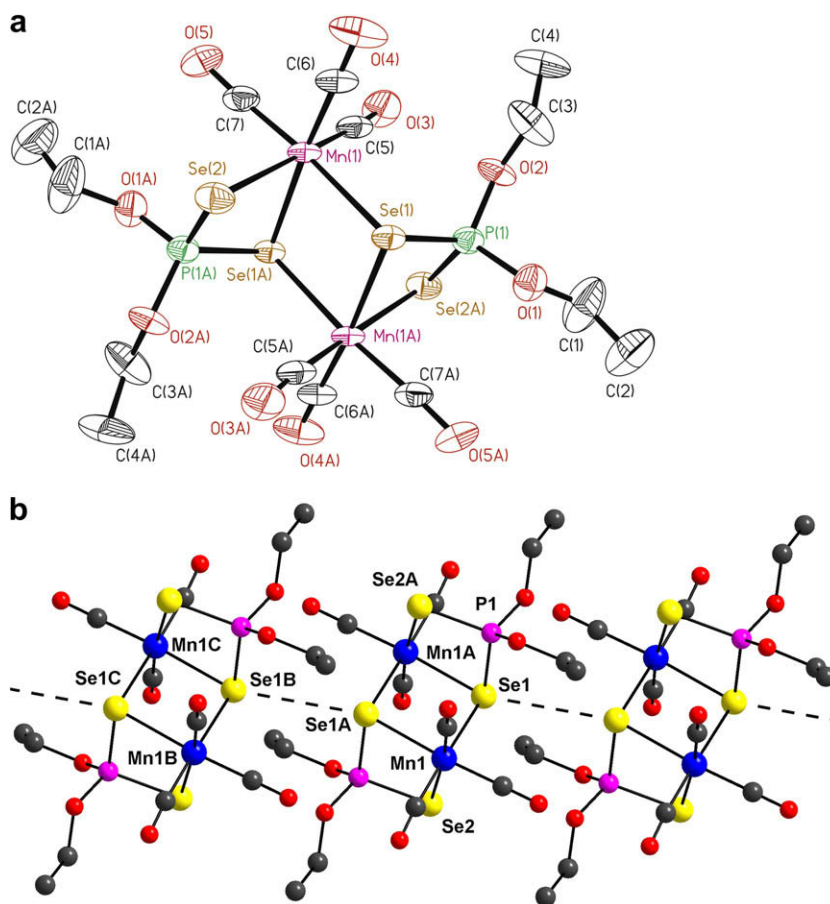
Fig. 1. (a) Perspective view of Mn$_2$(CO)$_6$[Se$_2$P(OEt)$_2$]$_2$, **2b**. (b) 1D network formed by Se$\cdots$Se interaction along a-axis in the lattice of **2b**. (Symmetry codes: A = $-x$, $1 - y$, $-z$; B = $-1 + x$, y, z; C = $-1 - x$, $1 - y$, $-z$).

bite angle of the dsep, Se1–P1–Se2, is 105.71(6)°. The Re atom is only 0.031 Å out of the Se1P1Se2 plane. The metal center is further attached to four carbonyl carbon besides aforementioned two Se atoms. The Re–Se distances [2.6457(7), 2.6462(7) Å] are slightly longer than those observed in [Re(CO)$_3$(PPh$_3$){Ph$_2$P(Se)NP(Se)Ph$_2$-κ^{2}Se}] [2.6382(6), 2.6277(6) Å] [16]. These fall below the cut off length (2.76 Å) for Re–Se single bond [16]. Intermolecular Se$\cdots$Se interaction also generates a supramolecular dimeric structure (Fig. 2) where the Se2$\cdots$Se2 non-bonding distance is 3.771 Å.

2.3.3. Compound 4a

A perspective view of the molecule is presented in Fig. 3. The compound is iso-structural with its Mn analog **2b**. In the dinuclear Re structure, dsep ligands adopted a triconective–bimetallic coordination mode where Se2 acts as a bridging atom between two Re centers and Se1 attached to one Re atom in a terminal fashion. The angle of Se1–P1–Se2 is 105.23(5)°. Thus both Re atoms attached to two bridging Se, a terminal Se and three CO through their carbon atoms. The geometry around Re atoms are slightly distorted octahedral as evident from the bond angles around the Re [174.76(17)–80.66(1)°]. The CO groups attached to Re are in a *facial* manner. The molecule also contains a center of inversion. Two PSe$_2$ fragments of dsep and two Re atoms assemble into an eight-membered tricylic ring, which is composed of three, fused four-membered rings and forms a chair-like conformation. The central ring formed by two Re and two bridging Se2 atoms is a perfect planar parallelogram where two Re–Se2 distances are almost equal [2.6660(6) and 2.6685(6) Å]. The Re–Se1 bond distance is 2.6693(6) Å.
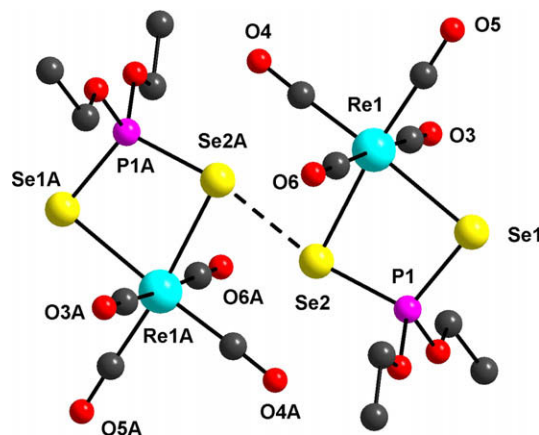
Fig. 2. Se$\cdots$Se interaction forms a dimer in lattice of **3b**. (Symmetry code for A = $-x$, $-y$, $-z$).

2.3.4. Compound 4b

A perspective view of the molecule is presented in Fig. 4. The **4b** is isostructural with its isopropyl homolog **4a**. The dinuclear species contains two Re atoms while each of them coordinated by a terminal Se, two bridging Se atoms and three carbonyl carbons. The central parallelogram of the stairwise structure, formed by two Re and two Se, involves two Re1–Se2 distances 2.6630(15) and 2.6655(15) Å. The Re(1)–Se(1) 2.6775(16) is slightly longer.
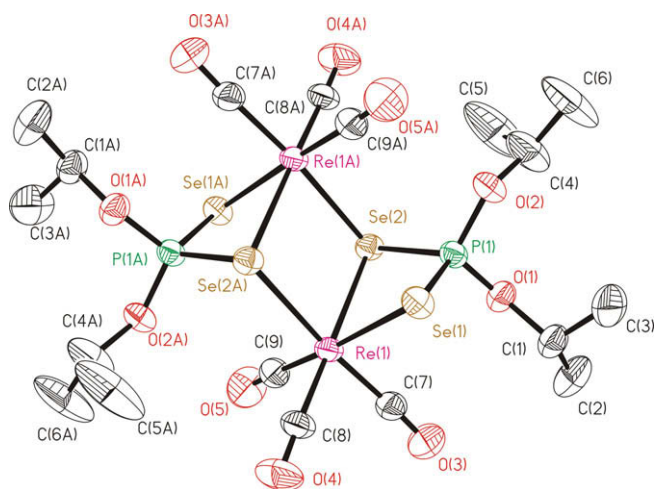
Fig. 3. Perspective view of Re$_2$(CO)$_6$[Se$_2$P(O^{i}Pr)$_2$]$_2$, **4a**.
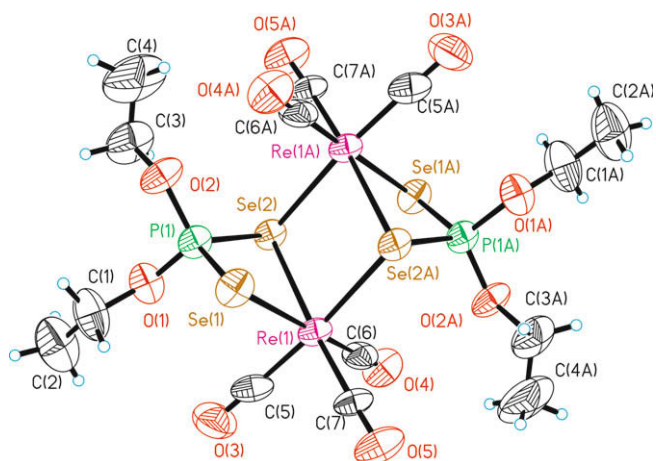
Fig. 4. Perspective view of Re$_2$(CO)$_6$[Se$_2$P(OEt)$_2$]$_2$, **4b**.

3. Conclusion

Syntheses of four mononuclear Mn(I) and Re(I) complexes (**1a–b**, **3a–b**) containing dsep [(OR)$_2$PSe$_2$]$^-$ ligand, by the reaction of oxidized derivative of dsep [(OR)$_2$P(Se)Se$_n$P(Se)(OR)$_2$]$^-$ (where n = 2, 3) and M(CO)$_5$Br, are demonstrated. As expected Mn complexes could be synthesized at ambient temperature whereas Re compounds required 110 °C (refluxing toluene) for the reaction. As the metal ions retain their +1 oxidation state, so most probably reduction of the ligands took place during the reaction, at the cost of the oxidation of the CO and subsequent release of them creates a vacant coordination site on the metal atom. In this situation, formation of highly stable chelating complexes was the driving force for the formation of mononuclear complexes **1** and **3**. In addition simple and straightforward dimerization of these mononuclear complexes to form compounds with a general formula of M$_2$(CO)$_6$[Se$_2$P(OR)$_2$]$_2$ (**2a–b**, **4a–b**) have also been achieved. Among these, one mononuclear compounds **3b**, and three dinuclear compounds, **2b**, **4a–b**, are structurally characterized. These are the first examples of manganese and rhenium complexes incorporating phosphor-1,1-diselenoates. In the mononuclear structure **3b**, the dsep ligands acts as a chelating ligand; however the same ligand shows a bimetallic-triconnective binding mode in the dinuclear compounds (**2** and **4**) due to the presence of one more vacant coor-

dination site on the metal center upon knocking out one CO during the formation of dinuclear species.

4. Experimental

4.1. Materials and Instruments

All chemicals and reagents obtained from commercial sources were purified/dried and used as received. Commercial Hexane, diethyl ether, and toluene were distilled from Na. ROH (R = Et, ^{i}Pr), were distilled from Mg. Acetonitrile and acetone were distilled from P$_2$O$_5$. All the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting materials, Mn(CO)$_5$Br and Re(CO)$_5$Br, were purchased from Strem Chemicals. The [−Se(Se)P(O^{i}Pr)$_2$]$_2$ and Se[-(Se)SeP(OEt)$_2$]$_2$ were prepared by modified methods reported in literature [26]. The elemental analyses were done using a Heraeus CHN-O-PAPID Element Analyzer (CHN) and Tacussel Coulomax 78 automatic cautometeric titritior (Cl, S). ^{1}H, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker Advance-300 MHz Fourier transform spectrometers. The ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR are referenced externally against 85% H$_3$PO$_4$ (δ = 0) and PhSeSePh (δ = 463 ppm), respectively. All infrared spectra were recorded on a JASCO FT-IR 401 spectrometer at 25 °C using KBr plates. Melting points were measured by using Fargo melting point apparatus, MP-2D.

4.2. Synthesis of Mn(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$], **1a**

To a 50 mL acetone solution of [-Se(Se)P(O^{i}Pr)$_2$]$_2$ (0.500 g, 0.82 mmol) in a 100 mL Schlenk flask, Mn(CO)$_5$Br (0.225 g, 0.82 mmol) was added. The mixture was stirred at room temperature for 24 h. The residue was filtered off and the filtrate was evaporated to dryness under vacuum to get product. The product was purified by column chromatography over silica gel using ethyl acetate/hexane (1:200) as the eluent. The first band eluted out was dried under vacuum to get Mn(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$] as a yellow solid.

Yield: 0.235 g (60.6%). M.p.: 54 °C. Anal. Calc. for C$_{10}$H$_{14}$MnO$_6$PSe$_2$: C, 25.30; H, 2.98. Found: C, 24.90; H, 3.09%. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.36 (d, $^3J_{HH}$ = 6 Hz, 12H, -CH(CH$_3$)$_2$), 4.86 (m, 2H, -CH(CH$_3$)$_2$); ^{31}P NMR (121.5 MHz, CDCl$_3$, δ, ppm): 42.4 ($^1J_{PSe}$ = 612 Hz); ^{77}Se NMR (57.2 MHz, CDCl$_3$, δ, ppm): -223.2 (d, $^1J_{SeP}$ = 614 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2080, 2006, 1944, 1923.

4.3. Synthesis of Mn(CO)$_4$[Se$_2$P(OEt)$_2$], **1b**

The method is the same as for compound **1a** but used the ligand [Se{-Se(Se)P(OEt)$_2$}$_2$] instead of [−Se(Se)P(O^{i}Pr)$_2$]$_2$. The color of the product is yellow. Yield: 0.252 g (72.3%). M.p.: 63 °C. Anal. Calc. for C$_8$H$_{10}$MnO$_6$PSe$_2$: C, 21.54; H, 2.26. Found: C, 21.70; H, 2.59%. ^{1}H NMR (300 MHz, acetone-d$_6$, δ, ppm): 1.39 (t, $^3J_{HH}$ = 14 Hz, 6H, -CH$_2$CH$_3$), 4.20 (m, 4H, -CH$_2$CH$_3$); ^{31}P NMR (121.5 MHz, acetone-d$_6$, δ, ppm): 47.0 ($^1J_{PSe}$ = 618 Hz); ^{77}Se NMR (57.2 MHz, acetone-d$_6$, δ, ppm): −255.4 (d, $^1J_{SeP}$ = 621 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2079, 2004, 1987, 1955.

4.4. Synthesis of Mn$_2$(CO)$_6$[Se$_2$P(O^{i}Pr)$_2$]$_2$, **2a**

Mn(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$], **1a** (0.21 g, 0.45 mmol) was dissolved in 50 mL of acetonitrile in a 100 mL Schlenk flask. It was then refluxed for 1 h under a nitrogen atmosphere. The residues were filtered off and the filtrate was evaporated to dryness under vacuum to get the crude product. The crude product was washed with n-hexane to obtain pure Mn$_2$(CO)$_6$[Se$_2$P(O^{i}Pr)$_2$]$_2$ as a yellow solid. Yield: 0.044 g (22.1%). M.p.: 106 °C. Anal. Calc. for C$_{18}$H$_{28}$Mn$_2$O$_{10}$P$_2$Se$_4$: C, 24.23; H, 3.16. Found: C, 23.94; H, 2.88%. ^{1}H NMR (300 MHz,

acetone-d_6, δ, ppm): 1.39 (d, $^3J_{HH}$ = 6 Hz, 12H, -CH(CH$_3$)$_2$), 4.79 (m, 2H, -CH(CH$_3$)$_2$); ^{31}P NMR (121.5 MHz, acetone-d_6, δ, ppm): 50.9 ($^1J_{PSe}$ = 652 Hz). IR (KBr, ν_{CO}, cm^{-1}): 2014, 1920.

4.5. Synthesis of Mn$_2$(CO)$_6$[Se$_2$P(OEt)$_2$]$_2$, 2b

This was synthesized in a similar procedure adopted for the compound 2a while Mn(CO)$_4$[Se$_2$P(OEt)$_2$], 1b (0.20 g, 0.45 mmol) was used instead of 1a. The single crystal suitable for X-ray crystallography was obtained by slow evaporation of acetone solution of the compound. Yield: 0.068 g (36.4%). M.p.: 128 °C. Anal. Calc. for C$_{14}$H$_{20}$Mn$_2$O$_{10}$P$_2$Se$_4$: C, 20.11; H, 2.41. Found: C, 19.82; H, 2.28%. ^{1}H NMR (300 MHz, acetone-d_6, δ, ppm): 1.31 (t, $^3J_{HH}$ = 18 Hz, 12H, -CH$_2$CH$_3$), 4.14 (m, 8H, -CH$_2$CH$_3$); ^{31}P NMR (121.5 MHz, acetone-d_6, δ, ppm): 57.1 ($^1J_{PSe}$ = 650 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2004, 1927.

4.6. Synthesis of Re(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$], 3a

To a 50 mL toluene solution of [−Se(Se)P(O^{i}Pr)$_2$]$_2$ (0.076 g, 0.124 mmol) in a 100 mL Schlenk flask Re(CO)$_5$Br (0.100 g, 0.246 mmol) was added. The mixture was refluxed for 1 h. It was then filtered and the filtrate was evaporated to dryness under vacuum to get the crude product. The crude product was washed with hexane to obtain Re(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$] as a dark brown solid. Yield: 0.087 g (58.4%). M.p.: 60 °C. Anal. Calc. for C$_{10}$H$_{14}$ReO$_6$PSe$_2$: C 19.84; H 2.21. Found: C 20.14; H 2.33%. ^{1}H NMR (300 MHz, toluene-d_8, δ, ppm): 1.11 (d, $^3J_{HH}$ = 13 Hz, 12H, -CH(CH$_3$)$_2$), 4.57 (m, 2H, -CH(CH$_3$)$_2$); ^{31}P NMR (121.5 MHz, toluene-d_8, δ, ppm): 58.5 ($^1J_{PSe}$ = 573.6 Hz); ^{77}Se NMR (57.2 MHz, toluene-d_8, δ, ppm): −185.0 (d, $^1J_{SeP}$ = 572.3 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2103, 1981, 1934, 1920. FAB-MS (m/z): 605.3 [M$^+$].

4.7. Synthesis of Re(CO)$_4$[Se$_2$P(OEt)$_2$], 3b

The method of synthesis of 3b is same as 3a using the ligand [Se{-Se(Se)P(OEt)$_2$}$_2$] instead of [−Se(Se)P(O^{i}Pr)$_2$]$_2$. The crude product was washed with hexane and acetonitrile as well. The color of the product was dark brown. The single crystal obtained by diffusing hexane into toluene solution of the compound. Yield: 0.074 g (52.1%). M.p.: 71 °C. Anal. Calc. for C$_8$H$_{10}$ReO$_6$PSe$_2$·CH$_3$CN: C, 19.42; H, 2.12. Found: C, 19.69; H, 2.07%. ^{1}H NMR (300 MHz, toluene-d_8, δ, ppm): 0.97 (t, $^3J_{HH}$ = 15 Hz, 6H, -CH$_2$CH$_3$), 3.83 (m, 4H, -CH$_2$CH$_3$); ^{31}P NMR (121.5 MHz, toluene-d_8, δ, ppm): 64.7

($^1J_{PSe}$ = 584 Hz); ^{77}Se NMR (57.2 MHz, toluene-d_8, δ, ppm): −210.4 (d, $^1J_{SeP}$ = 581 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2098, 2008, 1977, 1945; FAB-MS (m/z): 577.3 [M$^+$].

4.8. Synthesis of Re$_2$(CO)$_6$[Se$_2$P(O^{i}Pr)$_2$]$_2$, 4a

[Re(CO)$_4$[Se$_2$P(O^{i}Pr)$_2$], 3a (0.087 g, 0.144 mmol) was refluxed in 50 mL of acetonitrile in a 100 mL Schlenk flask for 1 h. The residue was filtered off and the filtrate was evaporated to dryness under low pressure to get dark brown solid which was washed with ether and the powdery solid was dried under vacuum to get Re$_2$(CO)$_6$[Se$_2$P(O^{i}Pr)$_2$]$_2$. The single crystal obtained by diffusing hexane into toluene solution of the compound. Yield: 0.042 g (50.3%). M.p.: 140 °C. Anal. Calc. for C$_{18}$H$_{28}$Re$_2$O$_{10}$P$_2$Se$_4$: C, 18.72; H, 2.44. Found: C, 18.68; H, 2.44%. ^{1}H NMR (300 MHz, toluene-d_8, δ, ppm): 1.39 (d, $^3J_{HH}$ = 6.2 Hz, 12H, -CH(CH$_3$)$_2$), 4.80 (m, 2H, -CH(CH$_3$)$_2$); ^{31}P NMR (121.5 MHz, toluene-d_8, δ, ppm): 65.3 ($^1J_{PSe}$ = 577.2, 596.9 Hz). IR (KBr, ν_{CO}, cm^{-1}): 2016, 1918.

4.9. Synthesis of Re$_2$(CO)$_6$[Se$_2$P(OEt)$_2$]$_2$, 4b

The method is same as for compound 4a but used Re(CO)$_4$[Se$_2$P(OEt)$_2$], 3b (0.074 g, 0.128 mmol) instead of 3a. The color of the product was dark brown. The single crystal suitable for X-ray crystallography was obtained by diffusing hexane into toluene solution of the compound. Yield: 0.029 g (41.2%). M.p.: 187 °C. Anal. Calc. for C$_{14}$H$_{20}$Re$_2$O$_{10}$P$_2$Se$_4$: C, 15.31; H, 1.84. Found: C, 15.22; H, 1.91%. ^{1}H NMR (300 MHz, toluene-d_8, δ, ppm): 1.36 (t, $^3J_{HH}$ = 15 Hz, 12H, -CH(CH$_3$)$_2$), 4.02 (m, 8H, -CH(CH$_3$)$_2$); ^{31}P NMR (121.5 MHz, toluene-d_8, δ, ppm): 69.8 ($^1J_{PSe}$ = 581.8, 610.6 Hz); IR (KBr, ν_{CO}, cm^{-1}): 2021, 1903. FAB-MS (m/z): 1098.5 (M$^+$).

4.10. X-ray structure determination

The single crystals were mounted on the tip of glass fiber with epoxy resin and the data were collected on APEX II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073Å). Data reduction was performed with SAINT [27], which corrects for Lorentz and polarization effects. A multi-scan absorption correction based on SADABS was applied. The structure was solved by the use of direct methods, and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package [28], incorporated in SHELXTL/PC V5.10 [29]. Several ghost peaks around the Re atom in 4b are identified. H-atoms were added in

Table 2
Crystal data and structure refinement details for 2b, 3b, 4a, and 4b.

	2b	3b	4a	4b
Formula	C$_7$H$_{10}$MnO$_5$PSe$_2$	C$_8$H$_{10}$ReO$_6$PSe$_2$	C$_9$H$_{14}$O$_5$PReSe$_2$	C$_7$H$_{10}$ReO$_5$PSe$_2$
Fw	417.98	577.25	577.29	549.24
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.1225(19)	6.5797(12)	8.3418(11)	7.207(2)
b (Å)	9.846(3)	10.1814(18)	9.9199(14)	9.855(3)
c (Å)	10.585(3)	11.987(2)	11.1915(14)	10.503(4)
α (deg)	80.804(8)	104.969(4)	115.404(2)	70.613(7)
β (deg)	73.996(6)	97.485(4)	105.808(3)	75.296(7)
γ (deg)	69.226(6)	94.398(4)	95.267(3)	85.410(7)
V (Å^3)	665.6(3)	764.0(2)	781.37(18)	680.6(4)
Z	2	2	2	2
ρ_{calc}, g cm^{-3}	2.086	2.509	2.454	2.680
μ, mm^{-1}	6.580	12.833	12.543	14.393
T, K	298(2)	273(2)	298(2)	273(2)
Independent reflections	3360	3791	3858	3115
Reflections collected	7360 (R_{int} = 0.0736)	10781 (R_{int} = 0.0376)	11862 (R_{int} = 0.0326)	6761 (R_{int} = 0.0518)
goodness of fit on F^2	0.939	1.015	1.059	0.981
R indices (all data)	R_1 = 0.1303 wR_2 = 0.1744	R_1 = 0.0368 wR_2 = 0.0830	R_1 = 0.0326 wR_2 = 0.0773	R_1 = 0.0859 wR_2 = 0.1734
Final R indices (I > 2σ(I))	R_1 = 0.0695 wR_2 = 0.1554	R_1 = 0.0301 wR_2 = 0.0796	R_1 = 0.0289 wR_2 = 0.0756	R_1 = 0.0655, wR_2 = 0.1618
Largest difference in peak and hole, e/Å^3	1.682 and −1.298	1.400 and −1.275	2.232 and −0.761	4.016 and −3.523

idealized positions. The crystallographic data are presented in Table 2.

Acknowledgements

Appendix A. Supplementary material

CCDC 702593–702596 contain the supplementary crystallographic data for compounds **2b**, **3b**, **4a**, and **4b**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.011.

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