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# Synthesis of selenium bridged metallacycles via oxidative addition of diaryl diselenide across Re–Re bond: Novel one-pot reaction approach

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#### ABSTRACT

One-pot synthesis of novel  $M_2E_2L_2$  type metallacycles  $[L(CO)_3Re(\mu-SeR)_2Re(CO)_3L]$  (1–5) was accomplished by oxidative addition of diaryl diselenide to low-valent transition metal carbonyl with monodentate pyridine ligands. In metallacycles 1–5, where L = pyridine ligand,  $R = C_6H_5$ ,  $CH_2C_6H_5$ , the pyridyl groups bonded to metal centres invariably adopted *cis* conformation due to  $\pi-\pi$  interaction whereas, in compounds 1a and 2a, the pyridyl ligands were oriented in *trans* conformation. When bulky phenyl groups are introduced at *para* position of pyridyl rings, as in case of metallacycle 3, the steric hindrance disrupts the soft interaction and resulted into the expansion of space in between two phenylpyridyl groups and created a void. The Metallacycles 1–5 have been characterised by elemental analysis, NMR, IR, absorption and emission spectroscopic techniques. Molecular structures of 1, 2, 2, a, 3 and 4 were determined by single crystal X-ray diffraction analysis and the structural studies of 1, 2, 3 and 4 revealed that the pyridyl groups attached to the metal centres exhibited *cis* conformation, while 1a, 2a displayed *trans* conformation.

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#### 1. Introduction

The design and study of well arranged metal-containing cyclic compounds have emerged as promising research area in modern supramolecular chemistry [1–10]. Metallacyclic compounds have a significant impact in the area of molecular sensing, catalysis, molecular electronics and hydrogen fuel technologies [11-18]. Binuclear metallacyclic structures with synthetically tailorable chemical and physical properties are potentially useful in molecular assemblies [19-23]. Earlier, sulphur bridged dinuclear rhenium and manganese complexes  $[M(CO)_4(SC_6H_5)]_2$  (M = Mn, Re) were prepared by Osborne and Stone from metal pentacarbonyl hydride with benzene thiol [24]. Liaw et al. have reported that the reaction of diphenyl diselenide with [Mn(CO)<sub>5</sub>]<sup>-</sup> proceeds to form *cis*-[Mn (CO)<sub>4</sub>(SePh)<sub>2</sub>]<sup>-</sup> via oxidative addition. Similarly, the oxidative addition reaction of diphenyl ditelluride with [Mn(CO)<sub>5</sub>]<sup>-</sup> afforded cis- $[Mn(CO)_4(TePh)_2]^-$  which further transformed into a dinuclear compound [(CO)<sub>4</sub>Mn(µ-TePh)<sub>2</sub>Mn(CO)<sub>4</sub>] [20]. Marsden and Sheldrick have reported the crystal structure of CF<sub>3</sub>Se bridged manganese compound [CF<sub>3</sub>SeMn(CO)<sub>4</sub>]<sub>2</sub> [25]. In literature, the compounds  $[M_2Br_2(CO)_6(Se_2Ph_2)]~(M\ =\ Mn,\ Re)$  containing a  $Se_2Ph_2$  unit bridging with two metal centres were reported where, the oxidative cleavage of Se-Se bond was not observed [26,27]. Dinuclear selenium bridged Re<sub>2</sub>(µ-SePh)<sub>2</sub>(CO)<sub>8</sub> compound was obtained from Re (CO)<sub>5</sub>Cl and (PhSe)<sub>2</sub> by two-step process via oxidative addition reaction and the crystal structure was reported by Liaw and coworkers [28]. The oxidative addition reaction of (PhSe)<sub>2</sub> with  $Re_2Cl_4(dppm)_2$  yielded the doubly bonded  $Re_2Cl_4(\mu$ -SePh)<sub>2</sub>( $\mu$ dppm)<sub>2</sub> with bridging SePh groups [29]. Treatment of the tetranuclear ruthenium(II) complex  $[Cp^*Ru(\mu_3-Cl)]_4$  and  $[CpRu(CH_3CN)_3]$ PF<sub>6</sub> with diphenyl diselenide afforded the benzeneselenolatebridged diruthenium complexes  $[Cp*RuCl(\mu_2-SePh)]_2$  and [CpRu(CH<sub>3</sub>CN)(µ-SePh)<sub>2</sub>(CH<sub>3</sub>CN)RuCp](PF<sub>6</sub>)<sub>2</sub> respectively [30,31]. Petillon and co-workers have reported the dinuclear molybdenum complex  $[Cp*_2Mo_2(CO)_4(\mu-SePh)_2]$  from  $[Cp*_2Mo_2(CO)_4]$  and benzene selenol [32]. Reaction of  $[\eta$ -C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>Mn $\equiv$ CC<sub>6</sub>H<sub>5</sub>]BBr<sub>4</sub> with [Et<sub>3</sub>NH] [Fe<sub>2</sub>(µ-CO)(µ-SeC<sub>6</sub>H<sub>5</sub>)(CO)<sub>6</sub>] yielded Fe–Fe bridged dinuclear complex [Fe<sub>2</sub>(µ-SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>6</sub>] [33]. Cyclopentadienyl chromium chalcogenide complex [CpCr(SePh)]<sub>2</sub>Se was obtained from the reaction of [CpCr(CO)<sub>3</sub>]<sub>2</sub> with Ph<sub>2</sub>Se<sub>2</sub> [34]. Hupp and co-workers have reported the preparation of sulphur bridged rhenium compounds  $[(CO)_4 Re(\mu-SR)]_2$  for the synthesis of thiolate bridged molecular rectangles and in the same report they have also mentioned the stepwise synthesis of selenium bridged rhenium dimers [(CO)<sub>4</sub>Re(µ-SeR)]<sub>2</sub> from selenol and Re(CO)<sub>5</sub>OTf and used as precursors for synthesising molecular rectangles [35]. Later, 2,2'bisbenzimidizolate bridged 4-Phpy containing rhenium compounds





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have been reported by Dinolfo and co-workers [36]. Recently we have accomplished the sulphur bridged dinuclear rhenium metallacycles from oxidative addition reaction of diaryl disulphides to rhenium carbonyl with monodendate pyridine ligands [37]. Herein, we report on the novel one-pot synthesis of selenium bridged neutral metallacycles  $[L(CO)_3Re(\mu-SeR)_2Re(CO)_3L]$  (L = pyridine ligand) (1–5) *via* oxidative addition of Se–Se bond across Re–Re bond by a facile reaction of rudimentary metal precursor with diaryl diselenide and monodentate pyridine ligands.

#### 2. Results and discussion

## 2.1. Synthesis of selenium bridged metallacycles **1–5** from rhenium carbonyl, diaryl diselenide and monodendate pyridine ligands

Synthesis of selenium bridged Re(I) metallacycles proceeded with *Orthogonal-bonding* approach, [38–40] i.e., simultaneous incorporation of two aryl selenolate ligands to the equatorial sites of *fac*-Re(CO)<sub>3</sub> core with substitution of CO groups by rigid monotopic N-donor ligands to the orthogonal axial site, resulting into heterotopic molecular tweezers. The formation of *cis*-[L(CO)<sub>3</sub>Re( $\mu$ -SeR)<sub>2</sub>Re (CO)<sub>3</sub>L] (1–5) was accomplished by the reaction of rhenium carbonyl with diphenyl/dibenzyl diselenides and monodentate ligands (L) like pyridine (py), 4-picoline (pic) and 4-phenylpyridine (Phpy) in mesitylene medium (Scheme 1). Synthesis of metallacycles 1 and 2 were also accompanied by the formation of trace amount of *trans* isomers 1a and 2a respectively. Metallacycles 1–5 were soluble in common organic solvents and stable at room temperature and they were characterised by spectroscopic and crystallographic techniques to arrive the structural details.

#### 2.2. Spectroscopic characterisation of compounds 1-5

The IR spectra of compounds 1-5 in CH<sub>2</sub>Cl<sub>2</sub> exhibited carbonyl stretching at the region of 2027–1897 cm<sup>-1</sup> characteristic of facial assembly of three terminal carbonyl groups (*fac*-Re(CO)<sub>3</sub>) in an octahedrally coordinated metal centre [41]. <sup>1</sup>H NMR spectra of compounds 1-5 displayed appropriate signals for the pyridine ligands and aryl groups bonded to bridging selenium and the spectral data were included in Experimental section. The <sup>1</sup>H NMR spectrum of compound 1 displayed, one doublet, two triplets for pyridyl group protons and the phenyl group protons showed one doublet and two triplets. When compared with free pyridine (8.60, 7.65 and 7.26 ppm) and diphenyl diselenide (7.61 and 7.27) ligands, the pyridyl and

phenyl group proton signals were shifted towards downfield in **1**. <sup>13</sup>C NMR of compound **1** showed signals for terminal carbonyl groups at  $\delta$  200.2 and 195.1 ppm with 1:2 ratio and the signals at around  $\delta$  157.1–126.8 ppm were attributed to pyridyl group and the phenyl group carbons resonated at  $\delta$  133.9–127.2 ppm. Similarly, <sup>1</sup>H NMR spectrum of compound **2** displayed, two doublets for pyridyl protons and methyl group protons showed a singlet. When compared to free picoline (8.39, 7.02 and 2.27) ligand, the proton signals of **2** were shifted towards downfield. <sup>1</sup>H NMR spectrum of compound **3** displayed, three doublets, one triplet and one multiplet for phenylpyridine protons and the phenyl protons of aryl selenide appeared as one doublet, one triplet and one multiplet. Compared with free phenylpyridine (8.63, 7.61, 7.48, 7.46, and 7.43) and diphenyl diselenide (7.61 and 7.27) ligands, the phenylpyridine proton signals of metallacycle were shifted towards downfield and aryl group proton signals were shifted towards upfield except one doublet. The <sup>1</sup>H NMR spectrum of compound 4 showed one doublet, one triplet, one multiplet for pyridyl group protons and the benzyl group protons appeared as one doublet, one triplet, one multiplet and a singlet for CH<sub>2</sub> group. In compound **4**, the pyridyl and aryl group proton signals were shifted towards downfield when compared with free pyridine and dibenzyl diselenide (7.29, 7.26, 7.22 and 3.83) ligands. <sup>13</sup>C NMR spectrum of compound **4** showed signals for terminal carbonyl groups at  $\delta$  202.4 and 194.0 ppm with 1:2 ratio and the signals at around  $\delta$  156.6–126.7 ppm were attributed to pyridyl group and benzyl group carbons resonated at  $\delta$  142.7–127.5 ppm and the benzyl CH<sub>2</sub> was appeared at 31.1 ppm. Likewise. <sup>1</sup>H NMR spectrum of compound **5** displayed, two doublets for picolyl group protons and two singlets for methyl and CH<sub>2</sub> group protons. When compared to uncoordinated ligand, the protons signals were shifted towards downfield. <sup>13</sup>C NMR spectrum of compound **5** exhibited signals similar to that of compound **4** in addition to the CH<sub>3</sub> group signal observed at alkyl region. The UV-Vis absorption spectra of 1-5 in CH<sub>2</sub>Cl<sub>2</sub> showed intense bands in the higher energy region at around  $\lambda_{\text{max}}$  226–275 nm, that were assigned to  $\pi - \pi^*$  transition of the ligands [18,37,42,43]. Metallacycles 1-5 upon excitation at their respective ligand centred transitions exhibited moderate emissions observed at around  $\lambda_{max}$  382–429 nm due to  $\pi - \pi^*$  excited state of the ligands [44,45].

#### 2.3. Structural characterisation of 1, 1a, 2, 2a, 3 and 4

Single crystals of compounds 1, 1a, 2, 2a and 4 were obtained by slow diffusion of hexane into concentrated solution of the



Scheme 1. Synthesis of selenium bridged dinuclear metallacycles 1-5.

compounds in dichloromethane at 5 °C. Crystals of **3** were obtained by slow cooling of warm and concentrated solution of **3** in mesitylene to room temperature. A good quality single crystals of **1**, **1a**, **2**, **2a**, **3** and **4** were subjected to single crystal X-ray diffraction studies. Details about data collection, solution and refinement were summarized for **1–4** in Table 1 and for **1a** and **2a** in Table 2, respectively. The molecular structure of **1**, **1a**, **2**, **2a**, **3** and **4** displayed a dinuclear metallacyclic structure, where each rhenium in *fac*-Re(CO)<sub>3</sub> is bonded to one pyridine ligand and two aryl selenolate groups and hence Re centres attained a distorted octahedral geometry [38,41,46–48].

Crystal structure of cis-[py(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (1) consists of Re<sub>2</sub>Se<sub>2</sub> ring that is non-coplanar with a dihedral angle of 4.34° between the Re(1)-Se(1)-Re(2) and Re(1)-Se(1)#-Re(2) planes. The Re…Re distance in Re<sub>2</sub>Se<sub>2</sub> ring is 4.024 Å. The rhenium metal centre has the bond distances of 2.6315(9) Å for Se(1)–Re(1), 2.18(1) Å for N(1)–Re(1), 1.92(1) Å for C(1)–Re(1) and 1.921(9) Å for C(2)-Re(1). The octahedral geometry is associated with the bond angles of 80.41(4)° for Se(1)-Re(1)-Se(1)#1, 84.7(2)° for N(1)-Re (1)-Se(1), 93.4(4)° for C(1)-Re(1)-C(2), 91.3(3)° for C(1)-Re(1)-Se(1), 174.7(4)° for C(1)-Re(1)-N(1), 90.4(3)° for C(2)-Re(1)-N(1) and  $173.5(3)^{\circ}$  for C(2)-Re(1)-Se(1). The two pyridyl groups were oriented in a cis conformation and stabilised by weak face-face  $\pi$ - $\pi$  stacking interaction with a distance of 3.638 Å at C(7) and C (10) carbons of two pyridyl groups (Fig. 1) [49–52]. The two phenyl groups bonded to bridging selenium are present in a plane perpendicular to that of pyridyl groups and bent away from the Re<sub>2</sub>Se<sub>2</sub> ring and pyridyl groups. Intermolecular C–H $\cdots$  $\pi$  interactions were observed in between C(6)-H(6) of pyridyl and C(11) and C(12) of phenyl selenolate group of adjacent molecules with a distance of 2.586 Å and 2.783 Å [38,53–55]. C–H…Se interactions were observed between Se(1) present in the  $Re_2Se_2$  ring and C(6)-H(6) of pyridyl ring with a distance of 3.089 Å [56–58]. C–H…O hydrogen bondings were viewed among C(8)-H(8) and C(9)-H(9) of pyridyl ligand and C(4)-O(4), C(2)-O(2) of carbonyl groups with a distance of 2.698 Å, 2.602 Å [59–61]. C–O···C (lp··· $\pi$ ) interactions were observed between C(4)–O(4) of carbonyl oxygen and C(5)carbon of pyridyl ring with a distance of 3.079 Å [62].

Table	2
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Crystallographic data and structure refinement of 1a and 2a.

Compound	1a	2a
Empirical Formula	C <sub>42</sub> H <sub>30</sub> N <sub>3</sub> O <sub>9</sub> Re <sub>3</sub> Se <sub>3</sub>	C30H24N2O6Re2Se2
Formula weight	1516.17	1038.83
Crystal system	Triclinic	Triclinic
Temperature (K)	120(2) K	120(2)
Space group	P-1	P-1
a (Å)	9.4900(8)	9.1312(4)
b (Å)	10.2246(9)	10.2140(4)
c (Å)	23.7518(13)	10.2958(4)
α (°)	95.082(6)	113.624(4)
β (°)	94.608(6)	109.647(4)
γ (°)	107.080(8)	100.546(3)
Volume (Å <sup>3</sup> )	2180.6(3)	3860.8(5)
Z	2	1
F(000)	1404	484
$D_{calc}$ (mg m <sup>-3</sup> )	2.309	2.239
$\mu (mm^{-1})$	10.867	10.257
h, k, l collected	-11,11; -11,	-10, 10; -12,
	12; -28,28	11; -12, 12
Theta range for data collection (°)	3.00-25.00	3.31-25.00
Crystal size (mm)	$0.32 \times 0.28 \times 0.22$	$0.23 \times 0.21 \times 0.17$
Reflections collected/unique	17078/7668	7146/2707
R <sub>int</sub>	0.0752	0.0164
Data/restraints/parameters	7668/0/541	2707/0/191
Final R indices	R1 = 0.0395,	R1 = 0.0147,
[I > 2 sigma(I)]	wR2 = 0.1266	wR2 = 0.0374
Goodness-of-fit on F <sup>2</sup>	1.102	1.065
R indices (all data)	R1 = 0.0603,	R1 = 0.0165,
. ,	wR2 = 0.1385	wR2 = 0.0384
Largest difference in peak and hole ( $e \text{ Å}^{-3}$ )	2.934 and -2.330	1.103 and -0.669

Molecular structure of trans-[py(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (**1a**) showed that the two pyridyl ligands bonded to two rhenium centres were oriented in a *trans* conformation. The crystal structure of **1a** consists of two sets of orientation for the phenyl selenolate groups, where one set of arrangement displays the pyridyl and phenyl selenolate groups *trans* to each other, whereas another set of arrangement exhibits both phenyl groups in a *cis* position with

#### Table 1

Crystallographic data and structure refinement of 1-4.

		2	2	
Compound	l	2	3	4
Empirical Formula	$C_{28}H_{20}N_2O_6Re_2Se_2$	C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub> Re <sub>2</sub> Se <sub>2</sub>	$C_{40}H_{28}N_2O_6Re_2Se_2$	$C_{30}H_{24}N_2O_6Re_2Se_2$
Formula weight	1010.78	1038.83	1162.96	1038.83
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Temperature (K)	150(2)	150(2)	150(2)	120(2)
Space group	P n m a	P n m a	I 2/a	P 21/n
a (Å)	23.467(2)	26.1649(10)	13.9147(11)	9.4734(2)
b (Å)	13.4773(12)	12.9805(4)	12.5534(10)	18.5774(5)
c (Å)	9.3549(10)	9.1883(4)	22.255(2)	17.9572(7)
$\alpha$ (°)	90	90	90	90
β (°)	90	90	107.737(11)	95.119(2)
γ (°)	90	90	90	90
Volume (Å <sup>3</sup> )	2958.7(5)	3120.7(2)	3702.7(6)	3147.70(16)
Z	4	4	4	4
F(000)	1872	1936	2192	1936
$D_{calc} (mg m^{-3})$	2.269	2.211	2.086	2.192
$\mu$ (mm <sup>-1</sup> )	10.679	10.128	6.424	10.041
h, k, l collected	-27, 27; -16, 15; -11, 11	-31,31; -15, 15; -10, 10	-16, 16; -14, 14; -22, 26	-11, 11; -22, 22; -21, 21
Theta range for data collection (°)	3.02-25.00	3.11-25.00	3.07-25.00	3.08-25.00
Crystal size (mm)	$0.34\times0.28\times0.22$	$0.33 \times 0.28 \times 0.21$	$0.23 \times 0.18 \times 0.14$	$0.32 \times 0.30 \times 0.27$
Reflections collected/unique	20008/2710	23724/2860	14024/3259	22017/5529
R <sub>int</sub>	0.1993	0.0509	0.1066	0.0305
Data/restraints/parameters	2710/0/196	2860/7/211	3259/0/235	5529/0/379
Final R indices [I > 2sigma(I)]	$R_1 = 0.0577$ , $wR_2 = 0.1435$	$R_1 = 0.0699$ , $wR_2 = 0.1795$	$R_1 = 0.0431$ , $wR_2 = 0.1261$	$R_1 = 0.0220$ , $wR_2 = 0.0464$
Goodness-of-fit on F <sup>2</sup>	1.040	1.157	1.211	1.016
R indices (all data)	$R_1 = 0.0634$ , $wR_2 = 0.1484$	$R_1 = 0.0738$ , $wR_2 = 0.1813$	$R_1 = 0.0597$ , $wR_2 = 0.1756$	$R_1 = 0.0303$ , $wR_2 = 0.0491$
Largest difference in peak and hole (e $Å^{-3}$ )	4.270 and -3.475	11.131 and -2.296	2.917 and -4.630	0.965 and -1.194



Fig. 1. Molecular structure of 1. The thermal ellipsoids are drawn at the 50% probability level.

the pyridyl groups occupying the trans positions (Fig. 2). The rhenium metal centre has the bond lengths of 2.650(1) Å for Re (1)-Se(1), 2.659(1) Å for Re(1)-Se(2), 2.228(8) Å for Re(1)-N(1), 1.91(1) Å for Re(1)–C(1), 1.93(1) Å for Re(1)–C(2) and 1.940(1) Å for Re(1)-C(3). The octahedral geometry is associated with the bond angles of 80.86(3)° for Se(1)–Re(1)–Se(2), 93.1(2)° for N(1)–Re (1)-Se(2), 91.9(2)° for N(1)-Re(1)-Se(1), 89.2(4)° for C(1)-Re(1)-C(3), 88.4(3)° for C(1)-Re(1)-Se(1), 178.4(4)° for C(1)-Re(1)-N(1), 88.5(3)° for C(1)-Re(1)-Se(2), 91.5(4)° for C(2)-Re(1)-C(3), 91.5  $(4)^{\circ}$  for C(2)-Re(1)-N(1) and 93.0(3)^{\circ} for C(2)-Re(1)-Se(1).  $C-H\cdots\pi$  interactions were observed in between pyridyl and phenyl selenolate group of adjacent molecules with a distance of 2.711 Å (C(7)−H(7)···C(40)), 2.697 Å (C(27)−H(27)···C(18)) and 2.803 Å (C(27)-H(27)···C(19)). C-H···O hydrogen bondings were viewed among the carbonyl groups and phenyl selenolate ligand with a distance of 2.683 Å (C(10)–H(10)···O(9)), 2.588 Å (C(11)–H(11)··· O(7)) and 2.449 Å (C(12)-H(12)···O(8)). C-H···Se interactions were observed at C(35)-H(35) and C(19)-H(19) of pyridyl group with selenium atom with a distance of 3.075 Å and 3.094 Å respectively. C–0...C (lp $\cdots \pi$ ) interactions were observed among the carbonyl and pyridine groups with the contact distances of 3.177 Å (O(5)····C(18)) and 3.215 Å (O(6)····C(6)).

Molecular structure of cis-[pic(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (2) consists of Re<sub>2</sub>Se<sub>2</sub> ring that is non-coplanar with a dihedral angle of  $4.67^{\circ}$  between the Re(1)–Se(1)–Re(2) and Re(1)–Se(1) #1-Re(2) planes. The Re…Re distance in Re<sub>2</sub>Se<sub>2</sub> ring is 3.967 Å. The rhenium metal centre has the bond lengths of 2.617(1) Å for Re (1)-Se(1), 2.22(2) Å for Re(1)-N(1), 1.61(2)Å for Re(1)-C(1) and 1.90(2) Å for Re(1)–C(2). The octahedral geometry is associated with the bond angles of  $98.39(5)^{\circ}$  for Re(1)-Se(1)-Re(2),  $81.55(6)^{\circ}$ for Se(1)-Re(1)-Se(1)#1, 85.6(4)° for N(1)-Re(1)-Se(1), 83.6(1)° for C(1)-Re(1)-C(2), 171.2(1)° for C(1)-Re(1)-N(1), 101.1(1)° for C (1)-Re(1)-Se(1), 173.4(5)° for C(2)-Re(1)-Se(1) and 90.3(6)° for C (2)-Re(1)-N(1). The two picoline groups are oriented in a *cis* conformation and stabilised by weak face-face  $\pi - \pi$  stacking interaction with a distance of 3.818 Å at C(13) and C(17) carbons of two picoline groups (Fig. 3). The two phenyl groups bonded to bridging selenium are oriented in a plane perpendicular to that of two picoline groups and bent away from the Re<sub>2</sub>Se<sub>2</sub> ring and picoline groups. The existence of C–H $\cdots$  $\pi$  interactions were found in between methyl group present in the picoline ligand and phenyl selenolate carbon with a distance of 2.898 Å (C(18)–H(18C)···C(5)), 2.860 Å (C(18)–H(18C)···C(7)), 2.836 Å (C(18)–H(18A)···C(7)) and 2.855 Å (C(18)-H(18A)····C(6)). The Re<sub>2</sub>Se<sub>2</sub> ring containing selenium atom interacted with C(16)-H(16) of picoline moiety by C-H…Se interaction with a distance of 2.989 Å. C-H…O intermolecular contacts were observed among the carbonyl groups and C(11)-H(11), C(12)-H(12) and C(14)-H(14A) of picoline ligand with a distance of 2.535 Å, 2.627 Å and 2.612 Å respectively.  $C-O\cdots C$  (lp $\cdots \pi$ ) interactions were observed between C(15) and C (16) carbons of pyridyl ring with carbonyl group oxygen by the distances of 2.992 Å and 3.158 Å.

Molecular structure of *trans*-[pic(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (**2a**) showed that the two picolyl ligands bonded to two rhenium centres are oriented in a *trans* conformation. The two phenyl selenolate groups are oriented towards two picolyl ligands. Overall, the two picoline and two phenyl groups are arranged *trans* to each other (Fig. 4). The rhenium metal centre has the bond distances of 2.6205(4) Å for Re(1)–Se(1), 2.6493(3) Å for Re(1)–Se(1)#1, 2.227 (3) Å for Re(1)–N(1), 1.910(3) Å for Re(1)–C(1), 1.910(3) Å for Re (1)–C(2) and 1.904(3) Å for Re(1)–C(3). The octahedral geometry is associated the bond angles of 99.43(1)° for Re(1)–Se(1)–Re(1)#1, 80.57(1)° for Se(1)–Re(1)–Se(1)#1, 82.21(7)° for N(1)–Re(1)–Se (1), 175.6(1)° for C(1)–Re(1)–N(1), 95.9(1)° for C(1)–Re(1)–Se(1), 92.1(1)° for C(2)–Re(1)–C(1), 91.9(1)° for C(2)–Re(1)–N(1) and 93.3(1)° for C(2)–Re(1)–Se(1). Intermolecular C–H···O contacts were observed among the carbonyl groups and picoline moiety



Fig. 2. Molecular structure of 1a. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 3. Molecular structure of 2. The thermal ellipsoids are drawn at the 50% probability level.

with a distance of 2.536 Å (C(14)–H(14)···O(1)), 2.372 Å (C(11)–H (11)···O(3)), 2.645 Å (C(7)–H(7)···O(1)) and 2.533 Å (C(13)–H (13B)···O(2)). Packing diagram of metallacycle **2a** was given in Fig. 5.

Molecular structure of *cis*-[Phpy(CO)<sub>3</sub>Re(µ-SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>Phpy] (3) consists of Re<sub>2</sub>Se<sub>2</sub> ring that is non-coplanar with a dihedral angle of 27.92° between the Re(1)–Se(1)–Re(1)#1 and Re(1)–Se(1)#1–Re (1)#1 planes and the Re…Re distance is 3.910 Å. The rhenium metal centre has the bond distances of 2.630(1) Å for Re(1)-Se(1), 2.644 (1) Å for Re(1)–Se(1)#1, 2.221(7) Å for Re(1)–N(1), 1.91(1) Å for Re (1)-C(1) and Re(1)-C(2), 1.86(1) Å for Re(1)-C(3). The octahedral geometry is associated with the bond angles of 77.35(4)° for Se(1)-Re (1)-Se(1)#1, 95.69(3)° for Re(1)-Se(1)-Re(1)#1, 84.7(2)° for N(1)-Re(1)–Se(1), 88.6(2)° for N(1)–Re(1)–Se(1)#1, 92.1(4)° for C(1)–Re (1)-N(1), 94.8(4)° for C(1)-Re(1)-Se(1), 89.2(4)° for C(2)-Re(1)-C (1),  $176.1(4)^{\circ}$  for C(2)-Re(1)-N(1),  $99.0(4)^{\circ}$  for C(2)-Re(1)-Se(1), 91.2(5)° for C(3)-Re(1)-C(1) and 92.8(4)° for C(3)-Re(1)-N(1). The crystal structure of **3** exhibits a *cis* orientation of two phenylpyridine rings with expansion of distance about 6.781 Å at C(12)-C(12)carbons of pyridyl groups (Fig. 6) Intermolecular C–H $\cdots\pi$  links were observed between phenylpyridine and phenyl selenolate groups with a distance of 2.825 Å (C(8)–H(8)···C(12)) and 2.852 Å (C(11)–H(11)··· C(5)). C–H···O hydrogen bondings were observed among the carbonyl group and C(19)-H(19), C(16)-H(16) of phenylpyridine



Fig. 4. Molecular structure of 2a. The thermal ellipsoids are drawn at the 40% probability level.

ligands with a distance of 2.684 Å and 2.551 Å. In addition, hydrogen bonding interactions were observed between C(7)–H(7) of benzyl moiety and carbonyl group with a distance of 2.491 Å. Further, C–O···C (lp··· $\pi$ ) interaction was observed between C(18) carbon of phenylpyridine ligand and oxygen atom of carbonyl group with a distance of 3.214 Å. Packing diagram of metallacycle **3** was given in Fig. 7.

While comparing the molecular structures of **1**. **2** and **3**, when the size of substituent is changed from hydrogen, methyl to bulky phenyl group at para position of the pyridine ligands, the space between two phenyl rings has been found largely increased in 3. Here, the steric hindrance imposed by phenyl groups, predominates the  $\pi - \pi$  stacking interaction and resulted in the expansion of space between phenyl rings with creation of a void in between two phenylpyridine ligands. The increase in size of void in between Phpy ligands, imparts V shape to cis-[Phpy(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re  $(CO)_3Phpy$  **(3)**. The Re…Re distance has decreased from **1** to **3** as 4.029 Å, 3.967 Å to 3.910 Å. Also, the planarity of Re<sub>2</sub>Se<sub>2</sub> metal core has been distorted and bent outwards. The dihedral angle between the planes of Re(1)-Se(1)-Re(2) and Re(1)-Se(2)-Re(2) has increased from 1 to 3 as 4.34°, 4.67° to 27.92°. In compound 3, Re (1)-Se(1)-Re(1)#1 bond angle is decreased to 95.69(3)° from  $99.56^{\circ}(3)$  as in **1** and Se(1)-Re(1)-Se(1)#1 bond angle is decreased to  $77.35(4)^{\circ}$  from  $80.41(4)^{\circ}$  as in **1**. The phenyl groups at para position of the pyridyl ring has been twisted by angle of 30.02° with respect to the pyridyl groups.

The void present in metallacycle **3** has potential to serve as a host site to exhibit molecular recognition capabilities with some planar aromatic molecules and few metal ions. The host-guest interaction studies of phenylpyridine based rhenium metallacycle have been carried out with aromatic hydrocarbons like pyrene and triphenylene using <sup>1</sup>H NMR spectroscopic technique. The chemical shift values of pyridyl protons of metallacycle 3 were shifted towards upfield on treatment with planar guest molecules such as pyrene and triphenylene. Similar upfield shifts have been observed in the binding of aromatic guests to the Pd cage, Au and Re rectangle [63]. In metallacycles 3, the pyridyl protons of Phpy are affected more than other protons, indicating that pyridyl protons are more shielded by the  $\pi$  ring of the guests. These observations reveal that the added pyrene and triphenylene interact with pyridyl protons of Phpy ligand of metallacyle **3**. The binding constants (*K*) for pyrene and triphenylene with 3 have been found as 6.8 and 10.5 M<sup>-1</sup> respectively that indicate the weak binding of metallacycle 3 with guest molecules.

structure of *cis*-[py(CO)<sub>3</sub>Re(µ-SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re Molecular (CO)<sub>3</sub>py] (4) consists of Re<sub>2</sub>Se<sub>2</sub> ring that is non-coplanar with a dihedral angle of 8.09° between the Re(1)-Se(1)-Re(2) and Re (1)-Se(2)-Re(2) planes. The Re…Re distance in Re<sub>2</sub>Se<sub>2</sub> ring is 3.954 Å. The rhenium centres has bond lengths of 2.6292(4) Å for Re(1)-Se(1), 2.6316(4) Å for Re(1)-Se(2), 2.236(3) Å for Re(1)-N(2), 1.921(5) Å for Re(1)–C(1), 1.917(5) Å for Re(1)–C(2) and 1.908 (5) Å for Re(1)-C(3). The octahedral geometry is associated with the bond angles of  $81.91(1)^{\circ}$  for Se(1)-Re(1)-Se(2),  $93.4(2)^{\circ}$  for C (1)-Re(1)-N(2), 94.0(1)° for C(1)-Re(1)-Se(1), 175.2(1)° for C(1)-Re(1)-Se(2), 91.3 (1)° for C(2)-Re(1)-N(2), 175.4 (1)° for C(2)-Re (1)–Se(1), 92.1(1)° for C(3)–Re(1)–Se(1) and 91.0(1)° for C(3)–Re (1)–Se(2). The two pyridyl groups are oriented in a *cis* conformation and stabilised by weak face–face  $\pi$ – $\pi$  stacking interaction with a distance of 3.876 Å at C(9) and C(21) carbons of two pyridine groups (Fig. 8). The two benzyl groups bonded to bridging selenium are oriented in a plane perpendicular to that of the two pyridyl groups and bent away from the Re<sub>2</sub>Se<sub>2</sub> ring and pyridine groups. The intermolecular C–H $\cdots\pi$  interactions were observed between pyridyl and benzyl selenolate groups by a distance of 2.725 Å (C(24)–H(24A)····C(15)) and 2.867 Å (C(21)–H(21)···C(15)).



Fig. 5. Packing diagram of compound 2a viewed along a axis with C-H···O hydrogen bonding interactions.

C–H···O hydrogen bonding interactions were observed between the carbonyl groups and benzyl selenolate and pyridyl moiety with a distance of 2.710 Å (C(18)–H(18)···O(5)), 2.634 Å (C(21)–H(21)··· O(2)) and 2.457 Å (C(22)–H(22)···O(4)). C–O···C (lp··· $\pi$ ) interactions were observed between C(4)–O(4), C(5)–O(5) of carbonyl oxygen and C(11) and C(7) carbons of pyridyl ring with a distance of 3.089 Å, 3.140 Å.

#### 3. Experimental

#### 3.1. Instruments and materials

All reactions were carried out under dry, oxygen-free N<sub>2</sub> atmosphere using standard schlenk techniques. The starting materials were purchased from Strem Chemicals, Inc. and Sigma–Aldrich Chemicals. Rhenium carbonyl, diphenyl diselenide, dibenzyl diselenide, 4-phenylpyridine were used as received. Pyridine, 4-picoline, mesitylene and other solvents were dried using literature procedure prior to use. IR spectra were taken on a Thermo Nicolet 6700 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Avans Bruker 400 MHz spectrometer. Absorption spectra were recorded on a Shimadzu UV-2450 UV–Vis spectrophotometer. Emission spectra were recorded on a Fluorolog Horiba jobin Yuvon SPEX-F311 spectrometer. Elemental analyses were performed using Elementar Micro Cube CHN analyzer.

#### 3.2. Synthesis of $[L(CO)_3Re(\mu-SeR)_2Re(CO)_3L]$ , general procedure

A mixture of  $\text{Re}_2(\text{CO})_{10}$  (0.6 mmol) and diaryl diselenide (0.4 mmol) were taken in a 50 ml two neck Schlenk flask and fitted with a reflux condenser. The system was evacuated and purged with N<sub>2</sub>. Monodentate pyridine ligand (L) (0.8–150 mmol) and 40–50 ml of mesitylene was added under N<sub>2</sub> atmosphere. The reaction mixture was heated to 130 °C under N<sub>2</sub> for 16–39 h and allowed to cool to room temperature. The mesitylene was removed by vacuum distillation and the solid mixture was washed with hexane, chromatographed on silica gel column using dichloromethane and



Fig. 6. Molecular structure of 3. The thermal ellipsoids are drawn at the 50% probability level.



Fig. 7. Packing diagram of 3 viewed along a axis.

hexane as eluent to gave white colour solids of  $[L(CO)_3Re(\mu-SeR)_2Re(CO)_3L]$  metallacycles.

#### 3.3. Synthesis of cis- $[py(CO)_3Re(\mu-SeC_6H_5)_2Re(CO)_3py]$ (1)

A mixture of  $Re_2(CO)_{10}$  (392 mg, 0.6 mmol) and diphenyl diselenide (124 mg, 0.4 mmol) were taken in a 50 ml two neck Schlenk



Fig. 8. Molecular structure of 4. The thermal ellipsoids are drawn at the 40% probability level.

flask and fitted with a reflux condenser. The system was evacuated and purged with N<sub>2</sub>. Freshly distilled pyridine (4 ml, 49 mmol) and mesitylene (45 ml) were added under N<sub>2</sub> atmosphere. The reaction mixture was heated to heated to 130 °C under N2 for 17 h and allowed to cool to room temperature. The solvent was removed by vacuum distillation and the reaction mixture was washed with hexane, chromatographed on silica gel column using dichloromethane and hexane as eluent (2:3) to gave white colour solid of *cis*-[py(CO)<sub>3</sub>Re(µ-SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (1). Yield: 278 mg, 56% (based on Re<sub>2</sub>(CO)<sub>10</sub>). Anal. Calcd. for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>Se<sub>2</sub>: C 33.27; H 1.99; N 2.77. Found: C 33.32; H 1.96; N 2.74%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  9.15 (d, 4H, H<sup>2</sup> (py), <sup>3</sup>J = 6.8 Hz), 8.01 (t, 2H, H<sup>4</sup>  $(py), {}^{3}J = 7.6 \text{ Hz}) 7.92 (d, 4H, H^{2} (ph), {}^{3}J = 7.2 \text{ Hz}), 7.48 (t, 4H, H^{3} (py)),$  ${}^{3}J = 6.4$  Hz), 7.35 (t, 4H, H<sup>3</sup> (ph),  ${}^{3}J = 7.4$  Hz), 7.26 (t, 2H, H<sup>4</sup> (ph),  ${}^{3}J = 7.4$  Hz).  ${}^{13}C$  NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  200.2, 195.1 (1:2, CO group), 157.1, 139.8, 126.8 (py) 133.9, 131.5, 129.5, 127.2 (ph). UV–Vis. { $\lambda_{max}^{ab}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) ( $\epsilon$ ) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>}: 227 (33550) (LIG), 267 (23550) (LIG). Emission:  $\lambda_{max}^{em}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) 406. IR  $(CH_2Cl_2)$ :  $\nu_{(CO)}$  2027 (m) 2011 (vs) 1927 (m) 1901 (vs) cm<sup>-1</sup>. The trans isomer of [py(CO)<sub>3</sub>Re(µ-Se C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (**1a**) was isolated in trace amount. IR (CH<sub>2</sub>Cl<sub>2</sub>): *v*<sub>(CO)</sub> 2013(vs), 1914(vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.95 (d, 4H, H<sup>2</sup> (py), <sup>3</sup>*J* = 6.4 Hz), 7.72 (t, 2H, H<sup>4</sup> (py), <sup>3</sup>*J* = 7.6 Hz), 7.44 (d, 4H, H<sup>3</sup> (py), <sup>3</sup>*J* = 6.4 Hz), 7.31 (t, 2H, H<sup>4</sup> (ph), <sup>3</sup>*J* = 7.2 Hz), 7.15 (t, 4H, H<sup>2</sup> (ph), <sup>3</sup>*J* = 6.8 Hz), 7.08 (t, 4H, H<sup>3</sup> (ph)).

#### 3.4. Synthesis of cis-[pic(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (**2**)

Compound **2** was prepared using  $\text{Re}_2(\text{CO})_{10}$  (392 mg, 0.6 mmol), diphenyl diselenide (124 mg, 0.4 mmol) and 4-picoline (2 ml, 20 mmol) in mesitylene (45 ml) by following the procedure adopted for **1**. It was isolated as white solid of *cis*-[picRe(CO)<sub>3</sub>( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re

(CO)<sub>3</sub>pic] (**2**). Yield: 268 mg, 55% (based on Re<sub>2</sub>(CO)<sub>10</sub>). Anal. Calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>Se<sub>2</sub>: C 34.68, H 2.32, N 2.69. Found: C 34.60, H 2.35, N 2.64%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  8.91 (d, 4H, H<sup>2</sup> (pic), <sup>3</sup>J = 6.8 Hz), 7.86 (t, 4H, H<sup>2</sup> (ph), <sup>3</sup>J = 7.2 Hz), 7.27 (t, 4H, H<sup>3</sup> (ph), <sup>3</sup>J = 7.6 Hz), 7.23 (m, 6H, H<sup>3</sup> (pic), & H<sup>4</sup> (ph)), 2.44 (s, 6H, CH<sub>3</sub>). UV–Vis. { $\lambda_{max}^{aba}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) ( $\epsilon$ ) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>}: 228 (35000) (LIG), 267 (25200) (LIG). Emission:  $\lambda_{max}^{em}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) 410. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ <sub>(CO)</sub> 2026(s), 2011(vs), 1926(m), 1900(vs) cm<sup>-1</sup>. The *trans* isomer of [picRe(CO)<sub>3</sub>(µ-SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (**2a**) was isolated in trace amount. IR(CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ <sub>(CO)</sub> 2012(vs), 1911(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.75 (d, 4H, H<sup>2</sup> (pic), <sup>3</sup>J = 6.8 Hz), 7.44 (d, 4H, H<sup>3</sup> (pic)), 7.07 (dt, 6H, H<sup>2</sup> & H<sup>4</sup> (ph)), 6.94 (d, 4H, H<sup>3</sup> (ph), <sup>3</sup>J = 6.4 Hz), 2.34 (s, 6H, CH<sub>3</sub>).

#### 3.5. Synthesis of cis-[Phpy(CO)<sub>3</sub> $Re(\mu$ -SeC<sub>6</sub> $H_5)_2Re(CO)_3Phpy$ ] (**3**)

Compound **3** was prepared using  $\text{Re}_2(\text{CO})_{10}$  (392 mg, 0.6 mmol), diphenyl diselenide (124 mg, 0.4 mmol) and 4-phenylpyridine (4 ml, 49 mmol) in mesitylene (50 ml) following the procedure adopted for 1. It was isolated as white solid of *cis*-[Phpy(CO)<sub>3</sub>Re(µ-Se C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>Phpy] (**3**). Yield: 102 mg, 30% (based on Re2(CO)10). Anal. Calcd. for C40H28N2O6Re2Se2: C 41.31, H 2.43, N 2.41. Found: C 40.97, H 2.46, N 2.44%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  9.15 (d, 4H, H<sup>2</sup> (Phpy), <sup>3</sup>J = 6.8 Hz), 7.89 (d, 4H, H<sup>2</sup> (ph),  ${}^{3}J = 8.4$  Hz), 7.68 (d, 4H, H $^{3}$  (Phpy),  ${}^{3}J = 6.8$  Hz), 7.58 (d, 4H, H $^{2\prime}$ (Phpy),  ${}^{3}J = 8.4$  Hz), 7.40 (t, 2H, H<sup>4</sup> (ph),  ${}^{3}J = 7.4$  Hz), 7.32 (m, 8H, H<sup>3</sup> (ph) & H<sup>3</sup>' (Phpy)), 7.22 (t, 2H, H<sup>4</sup>' (Phpy),  ${}^{3}J = 7.8$  Hz). UV–Vis. { $\lambda_{max}^{ab}$  $(CH_2Cl_2)/(nm)(\epsilon) dm^3 mol^{-1} cm^{-1}$ ; 226 (36550) (LIG), 266 (43650) (LIG). Emission:  $\lambda_{max}^{em}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) 405 and 428. IR(CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu_{(CO)}$ 2026(s), 2011(vs), 1927(m), 1901(vs) cm<sup>-1</sup>. The trans isomer of  $[Phpy(CO)_3Re(\mu-Se\ C_6H_5)_2Re(CO)_3Phpy]$  was isolated in trace amount. IR(CH<sub>2</sub>Cl<sub>2</sub>) :  $\nu$ <sub>(CO)</sub> 2012(vs), 1912(s) cm<sup>-1</sup>.

Molecular recognition properties of *cis*-[Phpy(CO)<sub>3</sub>Re( $\mu$ -SeC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>Phpy] (**3**) with pyrene and triphenylene have been studied using <sup>1</sup>H NMR spectroscopic technique by keeping the host (**3**) concentration (0.46 × 10<sup>-3</sup> M) as constant and increasing the guest (pyrene) concentration (35.7 × 10<sup>-4</sup>–38.0 × 10<sup>-3</sup> M) and (triphenylene) (6.9 × 10<sup>-3</sup>–36.8 × 10<sup>-3</sup> M) respectively in CDCl<sub>3</sub>. The chemical shift values of pyridyl protons of metallacycle **3** have been found to be shifted towards upfield by adding pyrene and triphenylene. The binding constant (*K*) (pyrene, *K* = 6.8 M<sup>-1</sup>; triphenylene, *K* = 10.5 M<sup>-1</sup>) for these host–guest interactions were evaluated on the basis of Benesi–Hildebrand relationship by using curve fitting method [63].

#### 3.6. Synthesis of cis-[ $py(CO)_3Re(\mu$ -SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (**4**)

Compound **4** was prepared using  $\text{Re}_2(\text{CO})_{10}$  (392 mg, 0.6 mmol), dibenzyl diselenide (136 mg, 0.4 mmol) and pyridine (12 ml, 150 mmol) in mesitylene (40 ml) by following the procedure adopted for **1**. It was isolated as white solid of *cis*-[pyRe(CO)<sub>3</sub>(µ-Se CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>py] (**4**). Yield: 149 mg, 69% (based on Re<sub>2</sub>(CO)<sub>10</sub>). Anal. Calcd. for C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>Se<sub>2</sub>: C 34.69, H 2.33, N 2.70. Found: C 34.78, H 2.31, N 2.74%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  8.82 (d, 4H, H<sup>2</sup> (pp), <sup>3</sup>*J* = 6.4 Hz), 7.86 (t, 4H, H<sup>3</sup> (py), <sup>3</sup>*J* = 7.6 Hz), 7.51 (d, 4H, H<sup>2</sup> (ph), <sup>3</sup>*J* = 8.4 Hz), 7.32 (m, 8H, H<sup>3</sup> (py & ph)), 7.25 (t, 2H, H<sup>4</sup> (ph), <sup>3</sup>*J* = 7.2 Hz), 4.46 (s, 4H, CH<sub>2</sub> (benz)). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, ppm):  $\delta$  202.4, 194.0 (1:2, CO group), 156.6, 139.4, 126.7 (py) 142.7, 129.6, 129.5, 127.5 (ph), 31.1 CH<sub>2</sub> (benz). UV–Vis. { $\lambda max$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) ( $\epsilon$ ) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>}: 227 (36950) (LIG), 272 (16850) (LIG). Emission:  $\lambda max$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) 382. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{(CO)}$  2017(m), 2000 (vs), 1917(m), 1902(s) cm<sup>-1</sup>.

#### 3.7. Synthesis of cis-[pic(CO)<sub>3</sub>Re( $\mu$ -SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (**5**)

Compound **5** was prepared using Re<sub>2</sub>(CO)<sub>10</sub> (392 mg, 0.6 mmol), dibenzyl diselenide (136 mg, 0.4 mmol) and 4-picoline (1 ml, 10 mmol) in mesitylene (50 ml) by following the procedure adopted for **1**. It was isolated as pale yellow colour solid of *cis*-[picRe (CO)<sub>3</sub>( $\mu$ -SeCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Re(CO)<sub>3</sub>pic] (**5**). Yield: 16 mg, 9% (based on Re<sub>2</sub>(CO)<sub>10</sub>). Anal. Calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>Re<sub>2</sub>Se<sub>2</sub>: C 36.02, H 2.64, N 2.62. Found: C 36.13, H 2.59, N 2.64%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.59 (d, 4H, H<sup>2</sup> (pic), <sup>3</sup>J = 6.4 Hz), 7.48 (d, 4H, H<sup>2</sup> (ph), <sup>3</sup>J = 6.8 Hz), 7.31 (t, 4H, H<sup>3</sup> (pic), <sup>3</sup>J = 6.4 Hz), 7.25 (t, 2H, H<sup>2</sup> (ph), <sup>3</sup>J = 7.2 Hz), 6.82 (d, 4H, H<sup>3</sup> (pic), <sup>3</sup>J = 6.4 Hz), 4.43 (s, 4H, CH<sub>2</sub> (benz)), 2.30 (s, 6H, CH<sub>3</sub> (pic)). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  201.0, 193.4 (1:2, CO group), 155.6, 149.2, 125.8, 21.2 (pic) 142.1, 129.0, 128.7, 126.7 (ph) 30.8 CH<sub>2</sub> (benz). UV–Vis. { $\lambda_{max}^{ab}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) ( $\varepsilon$ ) dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>}: 227 (39550), 275 (16550). Emission:  $\lambda_{max}^{em}$  (CH<sub>2</sub>Cl<sub>2</sub>)/(nm) 429. IR(CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{(CO)}$  2019(m), 2004(vs), 1915 (m), 1897(s) cm<sup>-1</sup>.

#### 3.8. Crystal structure determinations

Crystals of 1, 1a, 2, 2a and 4 suitable for single crystal X-ray crystallography were obtained by slow diffusion of hexane into CH<sub>2</sub>Cl<sub>2</sub> solution. Crystals of **3** were grown from mesitylene solution. Single crystal X-ray structural studies were performed on Oxford Diffraction XCALIBUR-S CCD equipped diffractometer with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K using graphite-monochromated Mo Ka radiation ( $\lambda_{\alpha}$  = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan' techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97 [64], refining on  $F^2$ . The positions on all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2  $\times$  U<sub>eq</sub> of their parent atoms.

#### 4. Conclusion

In conclusion, we have demonstrated the spontaneous association of six components into a metallacycle containing pyridyl ligands, *via* the tandem addition of Se–Se bond across Re–Re bond. The molecular structure of compounds **1**, **1a**, **2**, **2a**, **3** and **4** have been elucidated by single crystal X-ray diffraction analysis. Studies towards the change of substituents at *para* position of pyridyl ring, by bulky phenyl groups pursues disruption of soft interaction leading to the expansion of void in compound **3**. We have concluded that this methodology is an effective and comparatively expedient route the class of compounds and the novel metallacycle having a shape of a molecular tweezer exhibit molecular recognition properties. The one-pot synthetic methodology paves strategy for the design and synthesis of novel metallacyclophanes, when multidentate pyridine ligands are used and the research works in this direction are in progress.

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#### Appendix A. Supplementary material

CCDC 745187, 745188, 745189, 745190, 745191 and 763990 contain supplementary crystallographic data for 1, 1a, 2, 2a, 3 and 4 respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif.

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