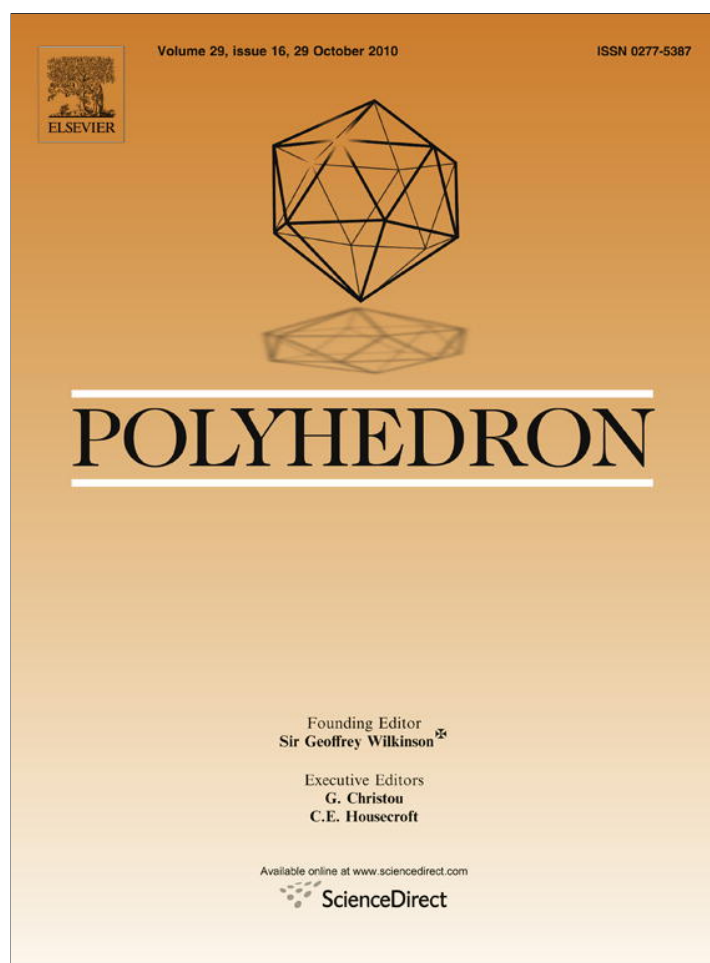


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Formation of carbonylrhenium cryptates with alkali metal cations: Coordination chemistry studies of $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$, E = O, S, Se towards $\text{ReBr}(\text{CO})_5$

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ABSTRACT

Reaction of $\text{ReBr}(\text{CO})_5$ with $\text{Li}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ afforded the cryptate $\text{Li}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_3]$; whereas $\text{K}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ reacted with $\text{ReBr}(\text{CO})_5$ to give $\text{K}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_2]$. Other chalcogen ligands' salts $\text{M}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, E = Se and S, M = K and Li gave dirhenium carbonyls with bromido and $\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2$, E = Se or S bridges upon reaction with $\text{ReBr}(\text{CO})_5$.

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1. Introduction

The anions $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$, E = O, S and Se have been studied for some years [1–3]; however, it is only since the 1990s that most of their coordination chemistry, both to transition and representative elements, has been explored as evidenced by a large number of reports on complexes containing these ligands [4]. The ability of the $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$, (E = O, S and Se) anions to ligate in diverse fashions and to take on several ring conformations is one of the reasons why these ligands have been extensively studied; their potential applications in photonic devices and sensors [5], biological activity [6], and recently as potential biomolecule labels in luminescent bioassays or materials for laser systems [7] (particularly some imidodiphosphate, $[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]^-$, complexes with long-lived near-infrared luminescent properties) have further contributed to increase the interest in compounds containing these so-called inorganic (no carbon atoms in the backbone) ligands.

We have systematically been developing the reaction chemistry of the tetraphenyldichalcogenoimidodiphosphate anions, $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$, E = O, S and Se toward group 7 carbonyls specifically Mn and Re [8]. We found that upon reaction of the rhenium precursors $\text{ReBr}(\text{CO})_5$, $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{THF})_2$, and $\text{ReOTf}(\text{CO})_5$ with $\text{Na}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ a spontaneous assembly of the cryptate

$\text{Na}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_3]$ occurred in high yields [9]. Cryptate reaction yield was virtually quantitative when $\text{ReBr}(\text{CO})_5$ was used as starting material (Scheme 1). In order to broaden the scope of this research we directed our attention to Li and K cations; in addition, we turned our efforts to study the reaction chemistry of the salts $\text{M}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, E = Se and S, M = Li and K towards $\text{ReBr}(\text{CO})_5$ with the aim of preparing the corresponding Se and S cryptates.

2. Results and discussion

The cryptate $\text{Li}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_3]$, **1** was formed upon reaction of $\text{ReBr}(\text{CO})_5$ with $\text{Li}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ in boiling toluene for 4 h in an 84% yield (Scheme 2).

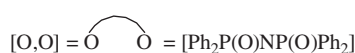
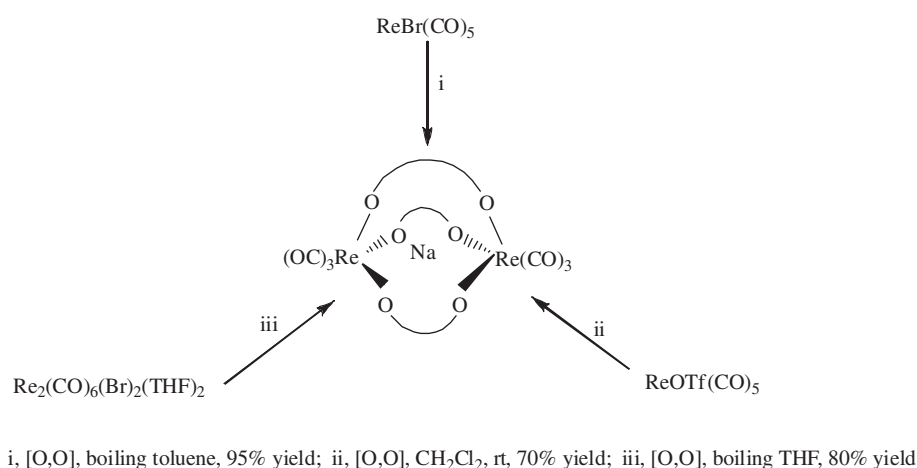
Analytical and spectroscopic data showed that **1** is a dinuclear rhenate(I) carbonyl complex. It is stable in the solid state for months in air, but it decomposes in hours in halogen solvents. Complex **1** is insoluble in nonpolar hydrocarbons.

The KBr IR spectrum of **1** consisted of two bands in the $\nu(\text{CO})$ region: 2020 s and 1895 vs cm^{-1} ; in toluene, the IR spectrum showed three strong bands at 2023, 1925, and 1900 cm^{-1} , all of the bands arise from terminal CO's. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in solution showed one singlet at 30.3 ppm (the $^{31}\text{P}\{^1\text{H}\}$ NMR signal of $\text{Li}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ appears at 19.1 ppm [10]) due to three symmetrically bound $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligands.

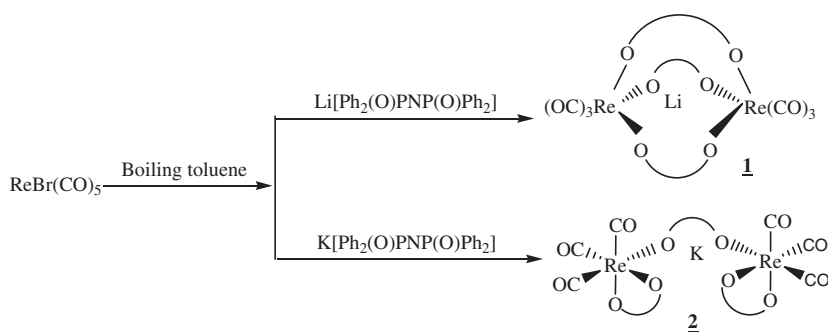
An X-ray analysis was performed on single crystals of **1** and its structure is shown in Fig. 1 together with some selected bond distances and angles. The structure of complex **1** is similar to that

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Scheme 1.



Scheme 2.

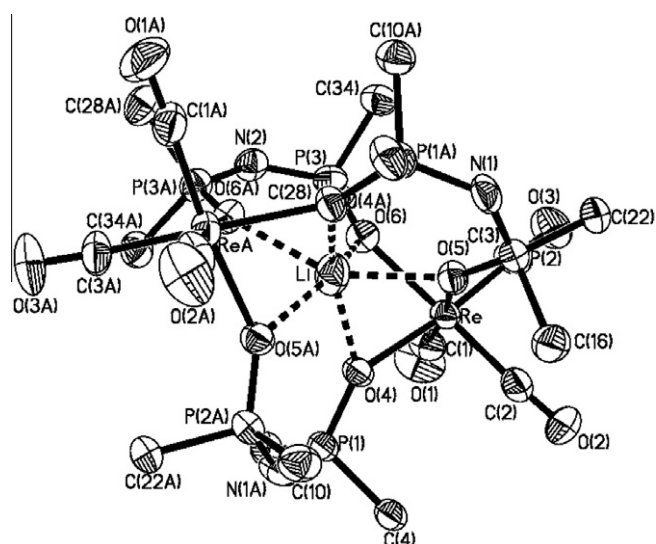


Fig. 1. Molecular structure of **1** including the atom numbering scheme. Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles [°]: Re–O(4) 2.171(4), Re–O(5) 2.159(4), Re–O(6) 2.162(4), Li–O(4) 2.159(5), Li–O(5) 2.165(8), Li–O(6) 2.142(12), P(1)–O(4) 1.525(4), P(2)–O(5) 1.531(4), P(3)–O(6) 1.513(4), P(2)–N(1)–P(1A) 133.5(3), P(3)–N(2)–P(3A) 133.8(5), P(1)–N(1A)–P(2A) 133.5(3), C(1)–Re–O(5) 172.9(2), C(2)–Re–O(6) 171.6(2), C(3)–Re–O(4) 174.2(2), O(4)–Re–O(5) 76.3(1), O(4)–Re–O(6) 76.0(1), O(5)–Re–O(6) 75.7(1).

of the cryptate Na[Re₂(CO)₆{μ-Ph₂P(O)NP(O)Ph₂-κ²O,O'}₃] [9]: it consists of two -Re(CO)₃ fragments united by three end bound Ph₂P(O)NP(O)Ph₂ ligands that make up an organometallic cryptate [11] wherein the Li cation is encased. The coordination geometry around both rhenium centers is pseudooctahedral. There are six O–Li interactions that render the coordination geometry around the lithium cation a trigonal antiprism. The PNP angles of the bridging ligands Ph₂P(O)NP(O)Ph₂ are all equal within experimental error (ca. 133°).

Reaction of the K[Ph₂P(O)NP(O)Ph₂] salt with ReBr(CO)₅ in boiling toluene for 2 h afforded complex **2** in 92% yield as depicted in Scheme 2.

Analytical and spectroscopic data showed that the **2**, just like **1**, is a dinuclear rhenate(I) carbonyl complex. It is stable in the solid state in air for months, insoluble in nonpolar organic solvents and, in contrast to **1**, it is stable in low polarity halogen solvents.

The IR spectrum of **2** showed two bands in the ν(CO) region: 2019 s and 1888 vs cm⁻¹ in KBr and 2022 and 1900 cm⁻¹ in CH₂Cl₂. It can be inferred that the negative charge in rhenates **1** and **2** is concentrated on the oxygen atoms of [Re₂(CO)₆{μ-Ph₂P(O)NP(O)Ph₂-κ²O,O'}₃]⁻ and [Re₂(CO)₆{μ-Ph₂P(O)NP(O)Ph₂-κ²O,O'}₃]{Ph₂P(O)NP(O)Ph₂-κ²O,O'}₂]⁻, respectively, that interact with the cation; since, it is known that carbonyl metallates give rise to carbonyl bands in the range 1600–2000 cm⁻¹ for terminal carbonyls in solution; whereas the IR ν(CO) bands of **1** and **2** lie within the range for neutral metal carbonyls (1900–2200 cm⁻¹) [12].

The ^{31}P NMR $\{^1\text{H}\}$ spectrum of **2** showed two singlets: one at 28.5 ppm and the other at 26.8 ppm due to the inequivalence of the $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligands (see below).

The structure of **2** (determined by a single crystal X-ray analysis, Fig. 2) shows two $-\text{Re}(\text{CO})_3$ moieties linked by two oxygen atoms of a $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligand. The other two $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligands function in a chelating capacity at each rhenium center of both $-\text{Re}(\text{CO})_3$ fragments. The K cation engages in four interactions with the oxygen atoms of the $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligands rendering it tetracoordinated.

The coordination geometry around each rhenium center in **2** is pseudooctahedral, whereas the coordination geometry around the potassium atom cannot be described in terms of a regular polyhedron: the oxygen atoms O(7), O(9), O(10), O(12) and the alkali metal K(1) lie nearly on a plane (with mean deviations of -0.1249 , 0.1078 , -0.1346 , 0.0549 and 0.0968 Å, resp.). There are no metallophilic interactions between the rhenium and the potassium ions. The OPNPO backbone is renowned for its flexibility, e.g., in compound $\text{HN}(\text{OPPh}_2)_2$ the PNP angle measures 180° [13]. In the present case the PNP angle of the bridging $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligand in **2** measures $135.7(3)^\circ$; in comparison, the PNP angles of the $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ chelators measure $125.9(3)^\circ$ and $124.5(3)^\circ$. It is apparent that formation of **2** with only one bridging $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ is due to the larger K cation (1.51 Å) as compared to Li (0.9 Å) [14].

It is well known that most reported transition metalcryptates of alkali metal cations are composed of arene ligands that, on the one hand, bind the 'hard' alkali cations (in the sense of Pearson's 'soft-hard' acid-base model) with N or O atoms and, on the other hand, ligate transition metals by a relatively 'soft' atom, e.g. phosphorus. In the present case the oxygen atoms of the $\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2$ ligands in complex **1** bind both transition and alkali metals. Unlike their organic counterparts, multinuclear heterometallic cryptates are capable of binding metal ions either through metallophilic interactions between the metal capping groups and the guest ion or, as in the present case, through strong Lewis base interactions of the donor groups of the ligands [15]. In general heteronuclear complexes have been extensively studied due to their application in molecular magnetism and nonlinear optics [16], among other areas; in particular the syn-

thesis of heterometallic cryptates of transition and alkali metals is significant as these cryptates have proven adequate for multifunctional catalytic systems and electro- and photochemical devices [17].

We explored the reaction chemistry of $\text{M}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, $\text{E} = \text{Se}$ and S ; $\text{M} = \text{Li}$ and K towards $\text{ReBr}(\text{CO})_5$ with a view to construct chalcogen cryptates analogous to $\text{M}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_3]$, $\text{M} = \text{Li}$ and Na . Reaction of $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, $\text{E} = \text{Se}$, S with $\text{ReBr}(\text{CO})_5$ under toluene reflux in a molar ratio 2:1 ($\text{ReBr}(\text{CO})_5/\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$) gave complexes **3** and **4** respectively in good yields according to Scheme 3(a).

Complexes **3** and **4** are partially soluble in chlororganic solvents and insoluble in hexane. When exposed to air **3** and **4** are stable as solids for months; in solution they decompose within ca. a month. Under a nitrogen atmosphere these complexes can be stored as solids indefinitely at low temperature.

The IR spectra of complexes **3** and **4** show two strong bands (2024, 1930 and 2028, 1935 cm^{-1} , resp. in CH_2Cl_2) indicative of a *fac* disposition of the three carbonyl groups at each metal center (an eclipsed conformation with a D_{3h} local symmetry of the $(\text{CO})_3\text{Re}-\text{Re}(\text{CO})_3$ carbonyl groups along the Re-Re axis, see below).¹ The ^{31}P NMR $\{^1\text{H}\}$ spectra showed only one signal, at 28 and 41 ppm for **3** and **4** respectively, consistent with a symmetrical ligation of the imidodichalcogenophosphinato ligand.

The structures of **3** and **4**, shown in Fig. 3 and 4 resp., were determined by single crystal X-ray diffraction analyses.

The unit cell of complex **4** contains two chemically identical but crystallographically independent molecules. The structures show that the metal centers are linked by two bridges: one bromido and one $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, $\text{E} = \text{Se}$ for **3** and $\text{E} = \text{S}$ for **4** bound in a bimetallic tetraconnective fashion. The distance between the rhenium centers (3.571 and 3.515 Å resp. for **3** and **4**) indicates no bonding interaction in both complexes (the Re-Re bonding distance in $(\text{OC})_5\text{Re}-\text{Re}(\text{CO})_5$ is 3.0413(11) Å [18]). The metal centers in **3** and **4** display distorted octahedral geometry. The Re-Br-Re angle in **3**, $83.56(2)^\circ$, is somewhat larger than in **4**, $82.05(3)^\circ$, such flexibility of the bromido bridge Re-Br-Re is well known, e.g., in the complex $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{PhCH}_2\text{SeSeCH}_2\text{Ph})$ the Re-Br-Re angle measures 94.6° [19]. The Re-Re nonbonding distance in **3** is longer than in **4**. The difference in angle size and Re-Re nonbonding distance in **3** compared to **4** are clearly due to the chalcogen size (Se versus S, resp.). The dihedral angle between the $\text{Re}(1)-\text{E}(1)-\text{E}(2)$ and $\text{Re}(2)-\text{E}(1)-\text{E}(2)$ planes measures 128.8° for $\text{E} = \text{Se}$ (complex **3**) and 132.6° for $\text{E} = \text{S}$ (complex **4**); this is a reflection of the longer rhenium-chalcogen distance in **3** as compared to **4**. The E-P-N-P-E, $\text{E} = \text{Se}$, S fragment in both molecules is essentially planar (with a mean plane deviation of 0.03 and 0.029 Å for **3** and **4**, resp.). The Re-E, $\text{E} = \text{Se}$ or S distances in **3** and **4** are similar (see Figs. 3 and 4) indicating a symmetrical coordination of the inorganic ligands to both $-\text{Re}(\text{CO})_3$ fragments.

IR reaction monitoring for formation of **3** showed the presence of mononuclear complex $\text{Re}(\text{CO})_4[\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2\text{-}\kappa^2\text{Se},\text{Se}']$ **5** (2098 m, 2005 s, 1984 s, 1941 cm^{-1} in toluene [8a]) as a reaction intermediate; so, we decided to prepare dinuclear complexes **3** and **4** starting from $\text{Re}(\text{CO})_4[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}\kappa^2\text{S},\text{S}']$, $\text{E} = \text{Se}$ and S respectively and $\text{ReBr}(\text{CO})_5$ according to Scheme 3(b). Mononuclear complexes $\text{Re}(\text{CO})_4[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2\text{-}\kappa^2\text{E},\text{E}']$, $\text{E} = \text{Se}$ **5** [8a] and $\text{E} = \text{S}$ **6** were readily available upon reaction of $\text{ReBr}(\text{CO})_5$ with the corresponding $\text{K}[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$ salt as shown in Eq. (1).

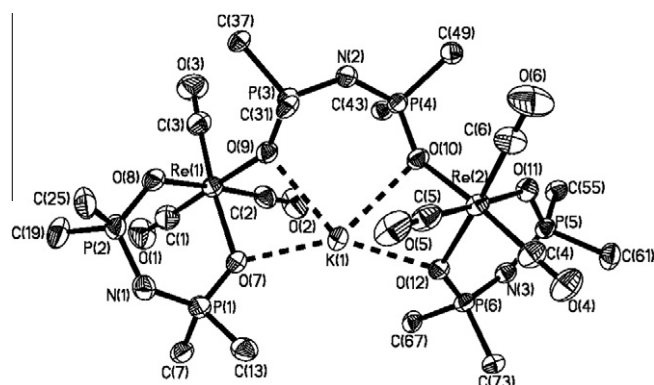
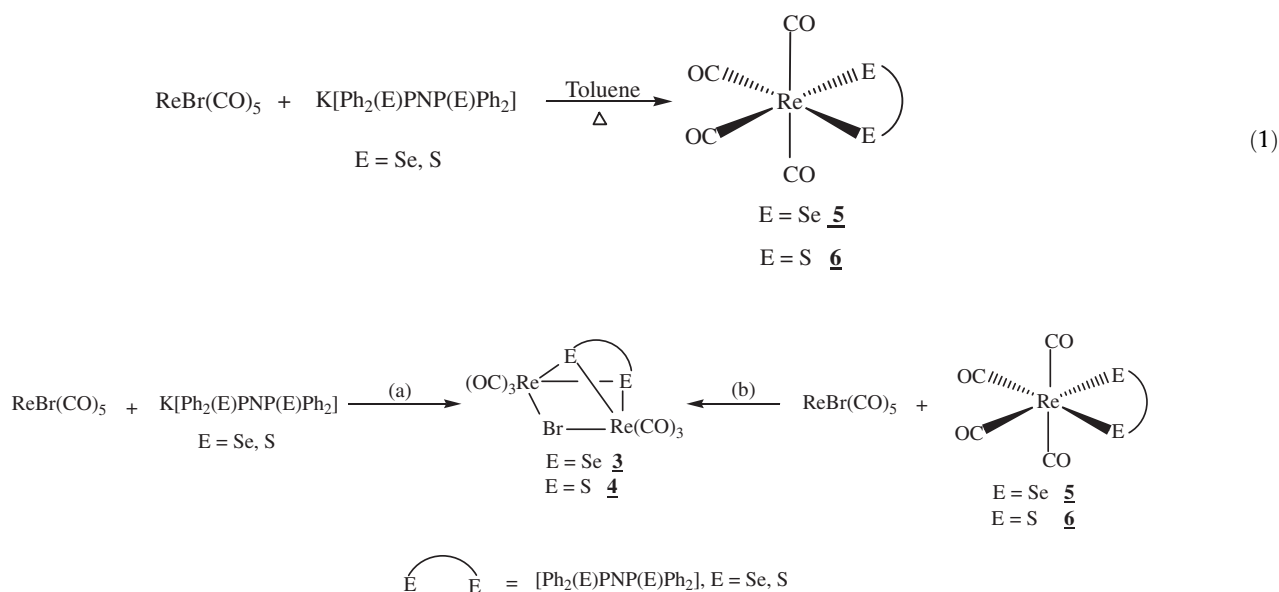


Fig. 2. Molecular structure of **2** including the atom numbering scheme. Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles $^\circ$: $\text{Re}(1)-\text{O}(7)$ 2.180(3), $\text{Re}(1)-\text{O}(8)$ 2.152(3), $\text{Re}(1)-\text{O}(9)$ 2.158(3), $\text{K}(1)-\text{O}(7)$ 2.572(4), $\text{K}(1)-\text{O}(9)$ 2.709(3), $\text{K}(1)-\text{O}(10)$ 2.746(4), $\text{K}(1)-\text{O}(12)$ 2.565(3), $\text{P}(1)-\text{O}(7)$ 1.518(4), $\text{P}(2)-\text{O}(8)$ 1.522(4), $\text{P}(3)-\text{O}(9)$ 1.521(3), $\text{P}(4)-\text{O}(10)$ 1.516(3), $\text{P}(5)-\text{O}(11)$ 1.519(3), $\text{P}(6)-\text{O}(12)$ 1.527(3), $\text{P}(2)-\text{N}(1)-\text{P}(1)$ 125.9(3), $\text{P}(3)-\text{N}(2)-\text{P}(4)$ 135.7(3), $\text{P}(6)-\text{N}(3)-\text{P}(5)$ 124.5(3), $\text{C}(1)-\text{Re}(1)-\text{O}(9)$ 177.6(2), $\text{C}(2)-\text{Re}(1)-\text{O}(8)$ 173.0(2), $\text{C}(3)-\text{Re}(1)-\text{O}(7)$ 175.0(2), $\text{C}(4)-\text{Re}(2)-\text{O}(10)$ 174.2(2), $\text{C}(5)-\text{Re}(2)-\text{O}(11)$ 176.8(2), $\text{C}(6)-\text{Re}(2)-\text{O}(12)$ 176.1(2), $\text{O}(7)-\text{Re}(1)-\text{O}(8)$ 83.4(1), $\text{O}(7)-\text{Re}(1)-\text{O}(9)$ 80.9(1), $\text{O}(8)-\text{Re}(1)-\text{O}(9)$ 80.9(1), $\text{O}(10)-\text{Re}(2)-\text{O}(11)$ 81.9(1), $\text{O}(10)-\text{Re}(2)-\text{O}(12)$ 78.3(1).

¹ Another possible symmetry group for **3** and **4** could be D_{3d} with the $\text{Re}(\text{CO})_3-\text{Re}(\text{CO})_3$ carbonyls staggered along the Re-Re axis; notwithstanding, the bonding fashion of the ligands $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]$, $\text{E} = \text{Se}$, S compels the carbonyls to adopt an eclipsed conformation as attested by the X-ray diffraction analysis.



Scheme 3.

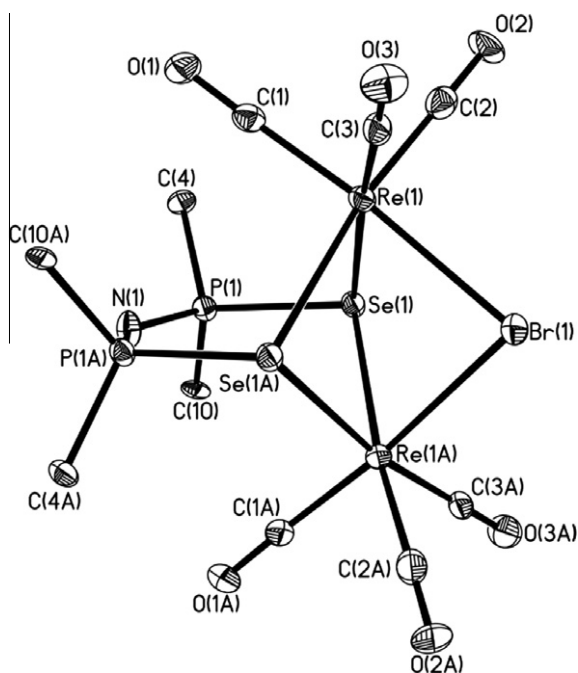


Fig. 3. Molecular structure of **3** including the atom numbering scheme. Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles [°]: Re(1)–Se(1) 2.6313(5), Re(1)–Se(1A) 2.6356(5), Re(1)–Br(1) 2.6800(6), Re(1)–Br(1)–Re(1A) 83.56(2), P(1)–N(1)–P(1A) 138.8(4), Se(1)–Re(1)–Se(1A) 83.58(2), C(1)–Re(1)–Br(1) 174.8(2), C(2)–Re(1)–Se(1) 171.8(2), C(3)–Re(1)–Se(1A) 171.4(2), Se(1)–Re(1)–Br(1) 77.30(1), Se(1A)–Re(1)–Br(1) 77.22(1).

The new complex **6** was prepared upon reaction of equimolar amounts of ReBr(CO)_5 and the $\text{K[Ph}_2\text{P(S)NP(S)Ph}_2\text{]}$ salt in hot toluene (see Experimental). It is an off-white material soluble in dichloromethane, partially soluble in toluene and insoluble in non-polar organic solvents. In the solid state **6** is stable in air for several days; however, in solution it decomposes within hours giving a yellow solution of unidentified products. The IR spectrum of **6** shows four bands in the carbonyl stretching region. The disposition of the carbonyl groups gives rise to a C_{2v} local symmetry corresponding with the $2A_1 + B_1 + B_2$ vibration modes [12]. The struc-

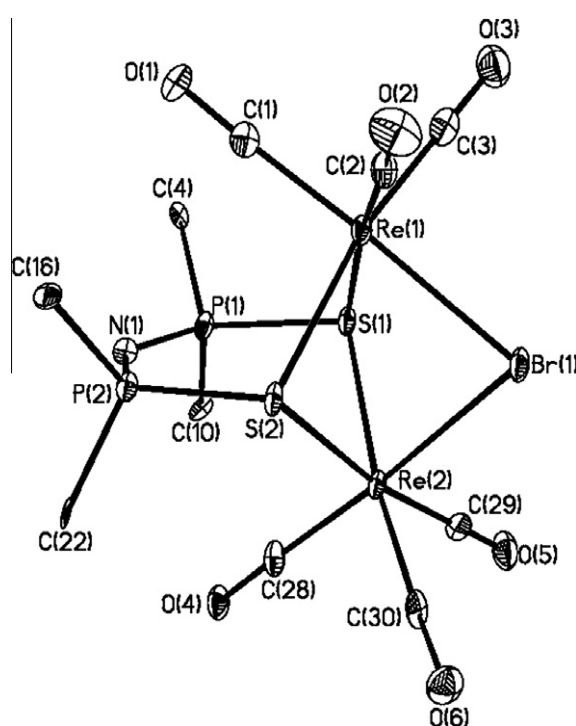


Fig. 4. Molecular structure of **4** including the atom numbering scheme. Only phenyl *ipso* carbon atoms are shown for clarity. Partial occupancy of crystallization solvent is not shown. Selected bond lengths [Å] and angles [°]: Re(1)–S(1) 2.526(2), Re(1)–S(2) 2.548(2), Re(2)–S(1) 2.538(2), Re(2)–S(2) 2.543(2), Re(1)–Br(1) 2.673(1), Re(2)–Br(1) 2.683(1), Re(1)–Br(1)–Re(2) 82.05(3), P(1)–N(1)–P(2) 134.8(5), S(1)–Re(1)–S(2) 81.32(7), C(1)–Re(1)–Br(1) 177.1(3), C(2)–Re(1)–S(1) 171.7(3), C(3)–Re(1)–S(2) 169.1(3), C(28)–Re(2)–Br(1) 175.8(3), C(29)–Re(2)–S(2) 171.7(3), C(30)–Re(2)–S(1) 171.6(3), S(1)–Re(1)–Br(1) 77.87(5), S(2)–Re(1)–Br(1) 76.96(5), S(1)–Re(2)–Br(1) 77.48(5), S(2)–Re(2)–Br(1) 76.87(5).

ture of **6** was determined by an X-ray analysis and can be described as a regular octahedron wherein the inorganic ligand $\text{Ph}_2\text{P(S)NP(S)Ph}_2$ is bound to the metal center in a monometallic biconnective fashion that renders a six membered metallo-ring with a twist boat conformation; see Fig. 5 for selected bond lengths and angles.

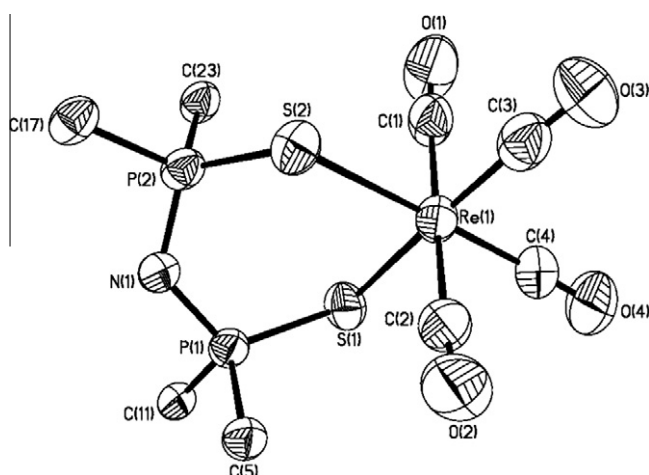


Fig. 5. Molecular structure of **6** including the atom numbering scheme. Only phenyl *ipso* carbon atoms are shown for clarity. Selected bond lengths [Å] and angles [°]: Re(1)–S(1) 2.522(1), Re(1)–S(2) 2.540(1), P–S_{av} 2.015(2), P–N_{av} 1.590(3), P(1)–N(1)–P(2) 127.3(2), S(1)–Re(1)–S(2) 97.44(4), S(1)–P(1)–N(1) 117.7(1), P(1)–S(1)–Re(1) 108.21(6), C(2)–Re(1)–C(1) 177.4(2), C(3)–Re(1)–S(1) 173.5(2), C(4)–Re(1)–S(2) 175.8(2).

The difference between both Re–S bond lengths is small (0.018(1) Å); so, it can be stated that the tetraphenylimidodithiophosphinate coordination is symmetrical: the ³¹P{¹H} NMR spectrum of **6** in solution shows one signal at 37.0 ppm for both phosphorus atoms of the coordinated ligand. The P–S (P–S_{av} 2.015(2) Å) and P–N (P–N_{av} 1.590(3) Å) bond lengths are equal and lie within P–S and P–N simple and double bonds (P–S 2.057(1) and P=S 1.945(1) Å; P–N 1.612(3) and P=N 1.557(3) Å in [2-(Me₂NCH₂)C₆H₄]Te–S–PPh₂=N–PPh₂=S [20]). The flexibility of the PNP fragment is apparent from the PNP angle in **6** (127.3(2)°) compared with the PNP angle in **4** (134.8(5)°).

In order to investigate the difference in the reaction chemistry of ReBr(CO)₅ towards the oxygen salts M[Ph₂P(O)NP(O)Ph₂], M = Li and K on the one hand, and the selenium and sulfur salts K[Ph₂P(E)NP(E)Ph₂] on the other hand, we conducted an IR monitoring experiment of the assembling process of **1** in the ν(CO) region at 85–90° C for 16 h (Fig. 6).

We detected reaction intermediates that could not be isolated; however, we could propose band assignments by comparison with analogous complexes: the band at 2006 cm⁻¹ was tentatively assigned to the oxygen analogous of **6**, Re(CO)₄[Ph₂P(S)NP(S)Ph₂-κ²S,S'] (step 1, Scheme 4). The band at 1939 cm⁻¹ was assigned to Re₂(CO)₆[μ-Br][μ-Ph₂P(O)NP(O)Ph₂-κ²O,O'] (the oxygen analogous of **3** and **4**, step 2 Scheme 4). At 1858 cm⁻¹ appears a band that we assigned to the complex Re₂(CO)₆[μ-Ph₂P(O)NP(O)Ph₂-κ²O,O']₂, the oxygen analogous of **C** (step 3, Scheme 4). The bands at 2023, 1925, and 1900 cm⁻¹ arise from CO's vibrations of **1**. Band overlap precluded detection of the expected number of bands in all intermediates.

The report that carbonylrhenium complexes with bromido bridges undergo nucleophilic attack by MER (M = Na, Li; E = S, Se, Te; R = organic substituent) to give the corresponding chalcogenido bridged dirhenium complexes [21] encouraged us to attempt the substitution of the [Ph₂P(Se)NP(Se)Ph₂] ligand for the bromido bridge in **4** in order to move one step further to cryptate assembly (step 3, Scheme 4). Reaction of **4** and K[Ph₂P(Se)NP(Se)Ph₂] with a 1:2 molar ratio resp. under toluene reflux resulted in an off-white poorly soluble material in all standard organic solvents.² The lack of solubility precluded a sound characterization, however, with

² We also tested reactions of both K[Ph₂P(E)NP(E)Ph₂] E = Se and S toward **3** and K[Ph₂P(S)NP(S)Ph₂] toward **4**: all of them led to insoluble materials.

the spectroscopic data available we may infer this material to be complex **7** as shown in Scheme 4.

3. Conclusions

Self-assembly of an Li organometallic cryptate was achieved upon reaction of Li[Ph₂P(O)NP(O)Ph₂] salt with ReBr(CO)₅. Coordination of three Ph₂P(O)NP(O)Ph₂ ligands' oxygen atoms in a bridging capacity rendered cryptate formation possible. This coordination fashion can be realized due to the well known flexibility of the OPNP backbone of the imidodiphosphinate ligand; however, when K, a larger cation, was tried to be placed in the cryptand's cavity a complex of identical Li cryptate stoichiometry, but different spatial arrangement was formed. Organometallic cryptates of other imidodichalcogenophosphinate ligands were elusive; however, their reaction chemistry towards ReBr(CO)₅ contributed to our understanding of the assembly process of the organometallic-imidodiphosphinate cryptates. It is apparent that the length of the Ph₂P(O)NP(O)Ph₂ ligand is not adequate to encase a K atom; notwithstanding, K coordination can still be achieved. The assembly of organometallic cryptates of imidodiphosphinate ligands with longer backbones to encase atomic or molecular cations remains a promising research area due to their potential applications in multifunctional catalytic systems, electro- and photochemical devices, and biological processes as well.

4. Experimental

4.1. General details

All preparations were conducted under an atmosphere of nitrogen using standard Schlenk techniques with Schlenk-type glassware on a dual-manifold vacuum line. All solvents were distilled over standard drying agents under an inert atmosphere directly before use and deoxygenated. ReBr(CO)₅, chlorodiphenylphosphine, hexamethyldisilazane, and potassium *tert*-butoxide were acquired from Strem Chemicals, Inc. and used with no further purification except for chlorodiphenylphosphine, which was distilled under vacuum (102 °C, 1 mmHg). *n*-BuLi was acquired from Aldrich Chemical Co. Gray selenium was acquired from Fisher Reagents Scientific Company. HN(PPh₂)₂, HN(EPh₂)₂, E = O, S, and Se; and M[(EPh₂)₂N], E = O, M = Li; E = O, S and Se, M = K [3] and Re₂(CO)₆Br₂(THF)₂ [22] were prepared according to literature procedures. Details concerning crystal data and refinement are given in Table 1. Reactions were monitored by IR spectroscopy in the characteristic region for carbonyl stretching vibrations, ν(CO). All ORTEP drawings for reported structures depict 50% probability ellipsoids.

IR spectra were obtained in solution (4000–580 cm⁻¹) using a Nicolet FT-IR 55X spectrometer and in KBr disk (4000–200 cm⁻¹) in a Perkin Elmer 283B spectrometer. NMR spectra were obtained at room temperature on Varian Unity 300, Perkin Elmer 283B, and Jeol GX300 spectrometers. ¹H NMR spectra were referenced to residual solvent peaks with chemical shifts (δ) reported in ppm downfield of tetramethylsilane. ³¹P{¹H} NMR spectra were externally referenced to 85% H₃PO₄. FAB(+) mass spectra were recorded on a JEOL SX-102A instrument.

4.1.1. Synthetic procedure for **1** and **2**

ReBr(CO)₅ was added to a solution of M[Ph₂P(O)NP(O)Ph₂], M = Li, **1** and M = K, **2** in 100 mL of dry degassed toluene. The reaction mixture was refluxed and then cooled to room temperature. The solids were filtered out and toluene was removed under reduced pressure leaving behind a solid. The solid was washed with 3 × 10 mL portions of hot toluene and the product extracted with 3 × 10 mL of dichloromethane at room temperature and dried under vacuum.

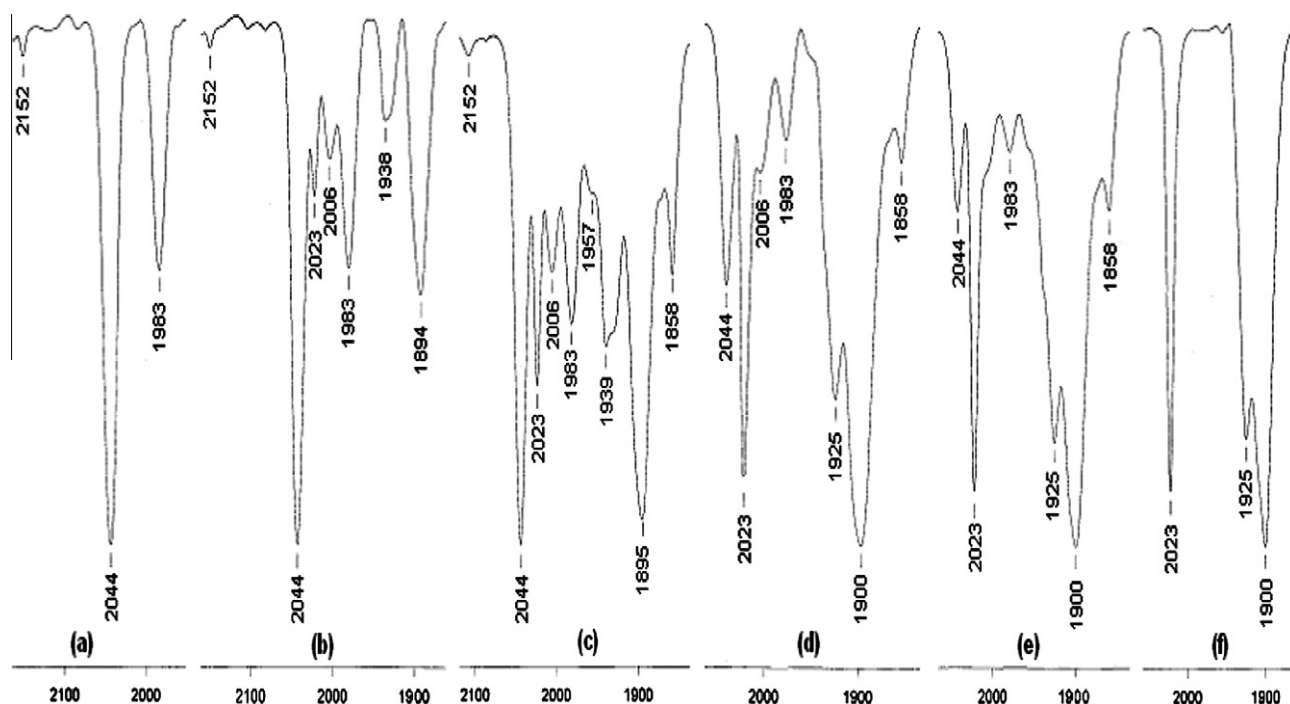
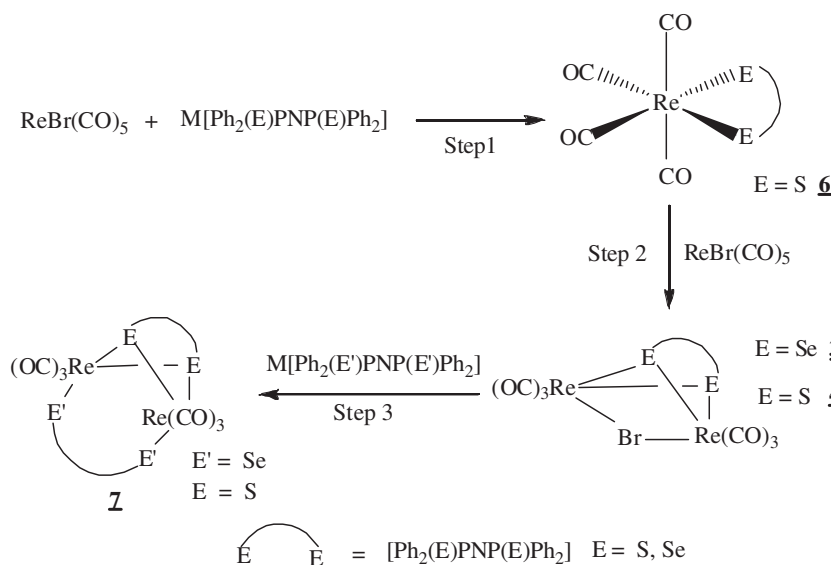


Fig. 6. Self-assemblage IR monitoring of **1** in toluene (85–90 °C). (a) Time 0; (b) 1 h; (c) 4 h; (d) 8 h; (e) 12 h; and (f) 16 h.



Scheme 4.

4.1.2. $\text{Li}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_3]$, lithium [(hexacarbonyl)tris-(μ -tetraphenylimidodiphosphinato- $\kappa^2\text{O},\text{O}'$)dirhenate] (**1**)

Reaction time: 4 h. 0.063 g (0.15 mmol) $\text{Li}[\text{N}(\text{OPPh}_2)_2]$ and 0.03 g (0.074 mmol) $\text{ReBr}(\text{CO})_5$. Molar ratio: 2:1 ($\text{Li}[\text{N}(\text{OPPh}_2)_2]$, $\text{ReBr}(\text{CO})_5$; resp.) Product: off-white solid, (0.057 g, 84%), mp 265–270 °C (from dichloromethane). (Anal. Calc. for $\text{C}_{78}\text{H}_{60}\text{LiN}_3\text{O}_{12}\text{P}_6\text{Re}_2$: C, 52.15; H, 3.37. Found: C, 51.86; H, 3.59%). $\nu_{\text{max}}(\text{KBr}) \text{ cm}^{-1}$ 2020 s, 1895 vs (CO), 1226 s $\nu(\text{P}_2\text{N})$. $\nu_{\text{max}}(\text{Toluene}) \text{ cm}^{-1}$ 2023 s, 1925 s, and 1900 s (CO). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ/ppm : 7.64 [dd, H_o , $^3J_{\text{H}_o\text{-P}} = 12 \text{ Hz}$, H_o , $^3J_{\text{H}_o\text{-H}_m} = 7 \text{ Hz}$], 7.3–6.8 [m, H_m and H_p]. $^{31}\text{P NMR}\{^1\text{H}\}$ (CDCl_3 , 121.7 MHz): δ/ppm : 30.3 [s(broad), $\text{Ph}_2\text{P}=\text{O}$], MS (m/e): 1796, $[\text{M}+1]$, $\text{Li}[\text{Re}_2(\text{CO})_6\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}_3]^+$; 1453, $[\text{Re}_2(\text{CO})_5\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}_2\text{-OPNP}(\text{O})\text{Ph}_2]^+$; 873, $[\text{Re}_2(\text{CO})_3\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}_2]^+$; 687, $[\text{Re}(\text{CO})_3\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}]^+$; 659, $[\text{Re}(\text{CO})_2\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}]^+$; 424, $\text{Li}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]^+$. Suitable crystals for an X-ray analysis were obtained from a 2:1 mixture of chloroform–hexane, respectively, at 4 °C for several days.

$\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]^+$; 424, $\text{Li}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]^+$. Suitable crystals for an X-ray analysis were obtained from a 2:1 mixture of chloroform–hexane, respectively, at 4 °C for several days.

4.1.3. $\text{K}[\text{Re}_2(\text{CO})_6\{\mu\text{-Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_2\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\text{-}\kappa^2\text{O},\text{O}'\}_2]$, potassium [(hexa-carbonyl) (μ -tetraphenylimidodiphosphinato- $\kappa^2\text{O},\text{O}'$)bis(tetraphenylimidodiphosphinato- $\kappa^2\text{O},\text{O}'$)dirhenate] (**2**)

Reaction time: 2 h. 0.2 g (0.44 mmol) $\text{K}[\text{N}(\text{OPPh}_2)_2]$ and 0.09 g (0.22 mmol) $\text{ReBr}(\text{CO})_5$. Molar ratio: 2:1 ($\text{K}[\text{N}(\text{OPPh}_2)_2]$, $\text{ReBr}(\text{CO})_5$; resp.) Product: off-white solid (0.185 g, 92%), mp 285–290 °C (from dichloromethane). (Anal. Calc. for $\text{C}_{78}\text{H}_{60}\text{KN}_3\text{O}_{12}\text{P}_6\text{Re}_2$: C, 51.23; H, 3.31. Found: C, 50.95; H, 3.28%). $\nu_{\text{max}}(\text{KBr}) \text{ cm}^{-1}$: 2019 s, 1888 vs (CO); 1217 m (P_2N). $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2) \text{ cm}^{-1}$ 2022 vs, 1900 vs (CO). $^{31}\text{P NMR}\{^1\text{H}\}$ (CDCl_3 , 121.7 MHz): δ/ppm : 28.5 [s, $\text{Ph}_2\text{P}=\text{O}$] 26.8

Table 1
Crystal data for **1**, **2**, **3**, **4**, and **6**.

	1	2	3	4	6
Chemical formula	C ₇₈ H ₆₀ LiN ₃ O ₁₂ P ₆ Re ₂ ·2CHCl ₃	C ₇₈ H ₆₀ KN ₃ O ₁₂ P ₆ Re ₂ ·3C ₆ H ₁₄	C ₃₀ H ₂₀ BrNO ₆ P ₂ Re ₂ Se ₂ ·2CHCl ₃	C ₃₀ H ₂₀ BrNO ₆ P ₂ Re ₂ Se ₂ ·1.5CH ₂ Cl ₂	C ₂₈ H ₂₀ NO ₄ P ₂ ReS ₂
Formula weight	2035.19	2087.13	1401.38	2392.46	746.71
T (K)	298(2)	173(2)	100(2)	100(2)	293(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	P1	C2/c	C2/c	P1
a (Å)	24.6612(11)	14.3420(10)	26.677(3)	42.079(6)	9.058(1)
b (Å)	13.9224(6)	18.2436(13)	10.0201(10)	9.7175(14)	12.530(1)
c (Å)	25.6469(12)	20.8643(15)	18.0301(18)	18.330(3)	13.163(1)
α (°)		107.6020(10)			89.936(1)
β (°)	109.2910(10)	104.0000(10)	122.4100(10)	97.169(5)	81.331(1)
γ (°)		103.4130(10)			84.025(1)
V (Å ³)	8311.3(6)	4766.3(6)	4068.8(7)	7436.5(19)	1468.7(2)
Z	4	2	4	8	2
Absorption coefficient (mm ⁻¹)	3.279	2.741	9.232	8.037	4.421
Reflections collected	44 472	45 948	18 408	16 622	17 517
Independent reflections (R _{int})	7316 (0.0879)	16 700 (0.0442)	3578 (0.0471)	6376 (0.0511)	5172 (0.0802)
Final R indices [I ² > 2σ(I ²)]	R ₁ = 0.0430, wR ₂ = 0.0904	R ₁ = 0.0417, wR ₂ = 0.0982	R ₁ = 0.0289, wR ₂ = 0.0725	R ₁ = 0.0486, wR ₂ = 0.1040	R ₁ = 0.0335, wR ₂ = 0.0570
R indices (all data)	R ₁ = 0.0629, wR ₂ = 0.0976	R ₁ = 0.0514, wR ₂ = 0.1030	R ₁ = 0.0298, wR ₂ = 0.0731	R ₁ = 0.0585, wR ₂ = 0.1080	R ₁ = 0.0390, wR ₂ = 0.0583

(more intense signal) [s, Ph₂P=O]. MS (*m/e*): 1826, [K{Re₂(CO)₆[Ph₂P(O)NP(O)Ph₂]₃}]⁺; 1787, [Re₂(CO)₆[Ph₂P(O)NP(O)Ph₂]₃]⁺; 1619, [Re₂{Ph₂P(O)NP(O)Ph₂]₃]⁺; 602, [Re{Ph₂P(O)NP(O)Ph₂}]⁺; 456, [K{Ph₂P(O)NP(O)Ph₂}]⁺.

When the reaction was effected with a 1:1 molar ratio the yield was 70%; while a molar ratio of 3:2 (K[N(OPPh₂)₂], ReBr(CO)₅; resp.) afforded **2** in 81% yield. Suitable crystals for an X-ray analysis were obtained from a 2:1 mixture of chloroform–hexane, respectively, at 4 °C for several days.

4.1.4. IR monitoring experiment of formation of **1**

ReBr(CO)₅ (0.06 g, 0.16 mmol) was added to a solution of Li[Ph₂P(O)NP(O)Ph₂] (0.2 g, 0.47 mmol) in 100 mL of dry degassed toluene. The reaction mixture was heated to 85 °C and maintained at 85–90 °C for 16 h. Samples were taken at 1, 4, 8, 12 and 16 h of reaction and their IR spectra in the ν(CO) region were obtained.

4.1.5. Synthesis of Re₂(CO)₆(μ-Br)[μ-Ph₂P(Se)NP(Se)Ph₂-κ²Se,Se'], (μ-bromido)(hexacarbonyl)(μ-tetraphenylimidodiselenophosphinato-κ²Se,Se')dirhenium (**3**)

K[N(SePPh₂)₂] (0.5 g, 0.86 mmol) and 0.69 g, 1.7 mmol of ReBr(CO)₅ were dissolved in 100 mL of dry degassed toluene. The reaction mixture was set at toluene reflux temperature for 1.5 h. The reaction color turned yellow-brown. Filtration of the hot reaction mixture was achieved over diatomaceous earth. A light brown powder was obtained. Compound **3** was extracted from the powder with hot dichloromethane (3 × 10 mL) with a yield of 85%, 0.85 g. When the reaction was carried out with a 1:1 molar ratio the yield was 70%; while a molar ratio of 3:2 (ReBr(CO)₅, K[N(SePPh₂)₂]; resp.) afforded **3** with 78% yield.

4.1.6. Alternative preparation of **3**

Re(CO)₄[Ph₂P(Se)NP(Se)Ph₂-κ²Se,Se'], **5**, [8C] (0.22 g, 0.26 mmol) and 0.106 g, 0.23 mmol of ReBr(CO)₅ were dissolved in 100 mL of dry degassed toluene. The reaction mixture was heated at toluene reflux temperature for 1 h. The reaction color turned yellow-brown. Filtration of the hot reaction mixture was achieved over diatomaceous earth. A light brown powder was obtained. Compound **3** was extracted from the powder with hot dichloromethane (5 × 10 mL) in an 80% (0.24 g) yield. Suitable crystals for an X-ray analysis in the solid state were obtained from a 2:1 mixture of chloro-

form–hexane, respectively, at 4 °C for several days. (*Anal. Calc.* for C₃₀H₂₀BrNO₆P₂Re₂Se₂: C, 30.99; H, 1.74. Found: C, 31.2; H, 1.81%). ν_{max}(KBr) cm⁻¹: 2024 s, 1922 vs. (CO); 1255 m, (P₂N), 529 m (P–Se). ν_{max}(CH₂Cl₂) cm⁻¹ 2024 s, 1930 s (CO). ¹H NMR (CDCl₃, 300 MHz): δ/ppm: 8.0 [ddd, H_o, ³J_{Ho-P} = 14 Hz, ³J_{Ho-m} = 8 Hz, ⁴J_{Ho-p} = 2 Hz], 7.5 [m, H_m and H_p]. ¹³C NMR{¹H} (CDCl₃, 75.6 MHz): δ/ppm: 188.5 [s, Re–CO], 134.0 [d, C_i, J_{Ci-P} = 98 Hz], 132.7 [s, C_p], 130.0 [d, C_m, ³J_{Cm-P} = 8 Hz], 128.8 [d, C_o, ²J_{Co-P} = 15 Hz]. ³¹P NMR{¹H} (CDCl₃, 121.7 MHz): δ/ppm: 28.0 [s, Ph₂P=Se].

4.1.7. Synthesis of Re₂(CO)₆(μ-Br)[μ-Ph₂P(S)NP(S)Ph₂-κ²S,S'], (μ-bromido)(hexacarbonyl)(μ-tetraphenylimidodithiophosphinato-κ²S,S')dirhenium (**4**)

0.5 g, 1.02 mmol of K[N(SPPH₂)₂] and 0.83 g, 2.04 mmol of ReBr(CO)₅ were added to 100 mL of dry degassed toluene. The reaction mixture was refluxed for 1 h 40 min after which it was passed through a bed of diatomaceous earth. The solvent was retired under vacuum. Complex **6** was extracted from the resulting off-white solid with hot dichloromethane (3 × 10 mL). Yield 84%, 0.92 g. When the reaction was achieved with a 1:1 molar ratio the yield was 68%.

4.1.8. Alternative preparation of **4**

0.1 g, 0.13 mmol of **6**, Re(CO)₄[Ph₂P(S)NP(S)Ph₂-κ²S,S'], and 0.054 g, 0.13 mmol of ReBr(CO)₅ were added to 100 mL of dry degassed toluene. The reaction mixture was refluxed for 90 min after which it was cooled to room temperature and the solvent was eliminated under vacuum. Complex **4** was extracted from the resulting off-white solid with hot dichloromethane (5 × 10 mL). Yield 91%, 0.13 g. Suitable crystals for an X-ray analysis in the solid state were obtained from a mixture 2:1 dichloromethane–hexane at 4 °C for several days. mp 125–126 °C (from CH₂Cl₂). (*Anal. Calc.* for C₃₀H₂₀BrNO₆P₂Re₂S₂: C, 33.71; H, 1.89. Found: C, 33.39; H, 2.15%) ν_{max}(KBr) cm⁻¹ 2028 s, 1929 vs (CO); 1248 m (P₂N). ν_{max}(CH₂Cl₂) cm⁻¹ 2028 s, 1935 s (CO). ¹H NMR (CDCl₃, 300 MHz): δ/ppm: 8.1 [ddd, H_o(PNP), ³J_{Ho-P} = 14 Hz, ³J_{Ho-m} = 8 Hz, ⁴J_{Ho-p} = 1 Hz], 7.4 [m, H_m and H_p]. ¹³C NMR{¹H} (CDCl₃, 75.6 MHz): δ/ppm: 189.7 [s, Re–CO], 133.7 [d, C_i, J_{Ci-P} = 112 Hz], 132.7 [s, C_p], 130.2 [d, C_m, ³J_{Cm-P} = 15 Hz], 129.1 [d, C_o, ²J_{Co-P} = 15 Hz]. ³¹P NMR{¹H} (CDCl₃, 121.7 MHz): δ/ppm: 41.0 [s, Ph₂P=S]. MS (*m/e*): 1068, [Re₂(CO)₆Br{Ph₂P(S)NP(S)Ph₂}]⁺; 988,

$[\text{Re}_2(\text{CO})_6(\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2)]^+;$ 691, $[\{\text{Re}(\text{CO})_2[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]\} + 1]^+;$ 635, $[\{\text{Re}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]\} + 1]^+.$

4.1.9. Synthesis of $\text{Re}(\text{CO})_4[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2-\kappa^2\text{S},\text{S}']$, (tetra carbonyl)-(tetraphenyl-imidodithiophosphinato- $\kappa^2\text{S},\text{S}'$)rhenium, 6

0.25 g (0.62 mmol) of the rhenium precursor $\text{ReBr}(\text{CO})_5$ were dissolved in 200 mL of dry degassed toluene in a previously nitrogen purged device. $\text{K}[\text{N}(\text{SPPH}_2)_2]$ (0.3 g; 0.62 mmol) was added and the solution was heated to 80 °C and maintained for 0.5 h after which the solution was filtered through diatomaceous earth to remove KBr. Toluene was eliminated under reduced pressure remaining an off-white solid from which the product was extracted with dichloromethane (0.45 g, 98% yield). Adequate crystals for X-ray analysis were grown from dichloromethane at 4 °C for several days; mp 150 °C (dec) (from CH_2Cl_2). (Anal. Calc. for $\text{C}_{28}\text{H}_{20}\text{NO}_4\text{P}_2\text{Re}_2\text{S}_2$: C, 45.04; H, 2.7. Found: C, 44.76; H, 2.91%). $\nu_{\text{max}}(\text{KBr}) \text{ cm}^{-1}$ 2100 s, 2006 vs, 1983 sh, 1935 vs (CO); 1215 s (P_2N). $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2) \text{ cm}^{-1}$ 2105 vs, 2010 vs, 1987 vs, 1940 vs (CO). ^1H NMR (CDCl_3 , 300 MHz): δ/ppm : 7.9 [ddd, $\text{H}_o(\text{PNP})$, $^3J_{\text{H}_o-\text{P}} = 14 \text{ Hz}$, $^3J_{\text{H}_o-\text{m}} = 8 \text{ Hz}$, $^4J_{\text{H}_o-\text{P}} = 1 \text{ Hz}$], 7.4 [m, H_m and H_p]. ^{13}C NMR{ ^1H } (CDCl_3 , 75.6 MHz): δ/ppm : 184.3 [s, Re–CO], 183.3 [s, Re–CO], 137.0 [d, C_i , $J_{\text{C}_i-\text{P}} = 106 \text{ Hz}$], 131.3 [s, C_p], 130.8 [d, C_m , $^3J_{\text{C}_m-\text{P}} = 12 \text{ Hz}$], 128.3 [d, C_o , $^2J_{\text{C}_o-\text{P}} = 14 \text{ Hz}$]. ^{31}P NMR{ ^1H } (CDCl_3 , 121.7 MHz): δ/ppm : 37.0 [s(broad), $\text{Ph}_2\text{P}=\text{S}$]. MS (m/e): 747, [M+1], $[\text{Re}(\text{CO})_4\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\}]^+;$ 718, $[\text{Re}(\text{CO})_3\{\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2\}]^+;$ 691, $[\{\text{Re}(\text{CO})_2[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]\} + 1]^+;$ 662, $[\text{Re}(\text{CO})[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]]^+;$ 635, $[\{\text{Re}[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]\} + 1]^+.$

4.1.10. Preparation of (hexacarbonyl) (μ -tetraphenylimidodiselenophosphinato- $\kappa^2\text{Se},\text{Se}'$) (μ -tetraphenylimidodithiophosphinato- $\kappa^2\text{S},\text{S}'$)dirhenium 7

0.15 g (0.14 mmol) of $\text{Re}_2(\text{CO})_6(\mu\text{-Br})[\mu\text{-Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2-\kappa^2\text{S},\text{S}']$ **4** and 0.16 g (0.27 mmol) of $\text{K}[\text{Ph}_2\text{P}(\text{Se})\text{NP}(\text{Se})\text{Ph}_2]$ were dissolved in 100 mL of dry degassed toluene in a nitrogen purged 200 mL two-neck flask. The solution was refluxed for 24 h after which an off-white precipitate was formed. After cooling to ambient temperature the solid was filtered off and washed with hot toluene ($3 \times 10 \text{ mL}$) affording the product. Complex **7** was obtained in 75.0% yield (0.16 g, 0.11 mmol), mp 280–285 °C (from toluene). $\nu_{\text{max}}(\text{KBr}) \text{ cm}^{-1}$ 2015 s, 1931 vs, 1899 vs (CO); 1210 s, (P_2N). $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2) \text{ cm}^{-1}$ 2013 s, 1932 vs, 1897 vs (CO). ^{31}P NMR{ ^1H } (CDCl_3 , 121.7 MHz): δ/ppm : 37.99 [s, $\text{Ph}_2\text{P}=\text{S}$], 28.53 [s, $\text{Ph}_2\text{P}=\text{Se}$].

4.2. Crystal data

See Table 1.

4.3. Crystal structure determinations

Data for complexes were collected on a Bruker Smart Apex CCD diffractometer and used in the full matrix least squares refinement. The structures were solved by direct methods from final difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Suitable crystals of **1** and **3** were obtained from concentrated solutions of chloroform and **2** from hexane all of them after several days at –4 °C, while crystals for **4** and **6** were obtained by slow vapor phase diffusion of their methylene chloride solutions and hexane at 5 °C.

5. Supplementary data

CCDC 780509, 780510, 780511, 780512 and 780513 contain the supplementary crystallographic data for **1**, **2**, **6**, **3**, and **4**. These data

can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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