Octa(μ_3-selenido)hexarhenium(III) Complexes Containing Axial Monodentate Diphosphine or Diphosphine–Monoxide Ligands

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Abstract: A series of the octahedral hexarhenium(III) complexes containing a variable number of diphosphine (diphos) or diphosphine–monoxide (diphosO) ligands have been prepared by the substitution of the diphosphine $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ to 5) for the iodide ions in the parent octahedral hexarhenium cluster compound $[Re_6Se_8I_6]^{3-}$. The diphosphine $Ph_2P(CH_2)_nPPh_2$ ligands adopt an η^1-bonding mode with the $Re_6(\mu_3\text{-}Se)_8$ core, and the P donor atom in the pendant arm is noncoordinated and oxygenated in most cases. The series of new hexarhenium(III) complexes have been well-defined by ^1H, ^{13}C, and ^{31}P NMR spectroscopic and FAB-MS data. Four compounds among the series were characterized by X-ray structural determination. Geometrical isomers were identified by NMR spectroscopy as well as by the structural determinations. The apical ligand substitution induces significant change in the redox potentials and the photophysical properties of the $Re_6(\mu_3\text{-}Se)_8$ core. The $E_{1/2}$ value of the reversible process $Re^{III}_6/Re^{III}_5Re^{IV}$ becomes more positive with the increasing number of the coordinated P donors. The phosphine-substituted hexarhenium(III) derivatives are highly luminescent, with microsecond scale emissive lifetime at ambient temperature, and the fully substituted derivatives with the formula $[Re_6Se_8(\eta^1\text{-diphosO})_6]^{2+}$ display the strongest luminescence with the longest emission lifetimes.

Keywords: cluster compounds · luminescence · P ligand · redox chemistry · rhenium

Introduction

In recent years, much attention has been paid to octahedral hexametal cluster complexes $[M_6(\mu_3\text{-}E)_8L_6]^{q-}$ (M = transition metal, E = chalcogenide or halide, L = axial ligand) with respect to ligand substitution and redox reactions, photophysical properties, and $M_6(\mu_3\text{-}E)_8$ core-based supramolecular design.[1] These hexametal cluster cores can be regarded as giant octahedral centers, and various organic ligands may be introduced into the apical sites to produce different $M_6(\mu_3\text{-}E)_8$ core-based derivatives.[2–15] Axial ligand substitution offers an excellent means to control the chemical and physical properties by introducing organic ligands.[11d, 13, 14] It also provides the ways to use the hexametal cores as potential building blocks for aggregated cluster complexes with higher nuclearity or for molecular materials with specific function.[4b, 5b, 11a–c, 12d, 15] Diverse neutral and anionic ligands with various donors, the former including phosphine,[3, 7, 11] pyridine,[8, 13] and solvent molecules,[4a, 11b] and the latter embracing cyanide,[4b, 9, 12] alkyl oxide,[6] and carboxylate,[5] have been introduced into the apices of hexametal octahedrons.

The hexarhenium cluster complexes $[Re_6(\mu_3\text{-}E)_8X_6]^{q-}$ (E = S, Se; L = Cl, Br, I; $q = 3$, 4)[10] have been developed very recently, the substitution character of the axial ligands allows designed synthesis based on the hexarhenium core and the chemistry of these clusters is more versatile than the other hexametal complexes. To the best of our knowledge, the substitution chemistry of bi- or multidentate ligands for the axial ligand L in $[Re_6(\mu_3\text{-}E)_8L_6]^{q-}$ (E = S, Se) octahedral hexametal complexes has not been studied previously.[13b, 14] Herein we report on the stepwise substitution reactions of the bidentate diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1-5$) for the iodide ions in the parent compound $[Re_6(\mu_3\text{-}Se)_8I_6]^{3-}$ (**1**), as well as on the preparation of a series of octahedral hexarhenium derivatives $[Re_6(\mu_3\text{-}E)_8I_{(6-m)}L_m]^{(3-m)-}$ ($m = 3-6$), in which L is a monodentate diphosphine or a diphosphine–monoxide ligand. We have also prepared the compound containing $Ph_2P(CH_2)_6PPh_2$ with the "bridge-chelate" coordination mode around the octahedral hexarhenium cluster core.[14] The substitution reaction can not only be controlled in a stepwise manner, but also the substitution mode (whether monodentate or bridge-chelate) is adjustable by altering the number of the methylene spacer groups in the diphosphine $Ph_2P(CH_2)_nPPh_2$. We report herein the detailed

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preparation of the hexarhenium(III) derivatives containing the diphosphine $Ph_2P(CH_2)_nPPh_2$ or diphosphine–monoxide $Ph_2P(CH_2)_nP(O)Ph_2$ ($n = 1-5$) in a η^1-binding mode, and their structural and spectroscopic characterization as well as their redox and photophysical properties.

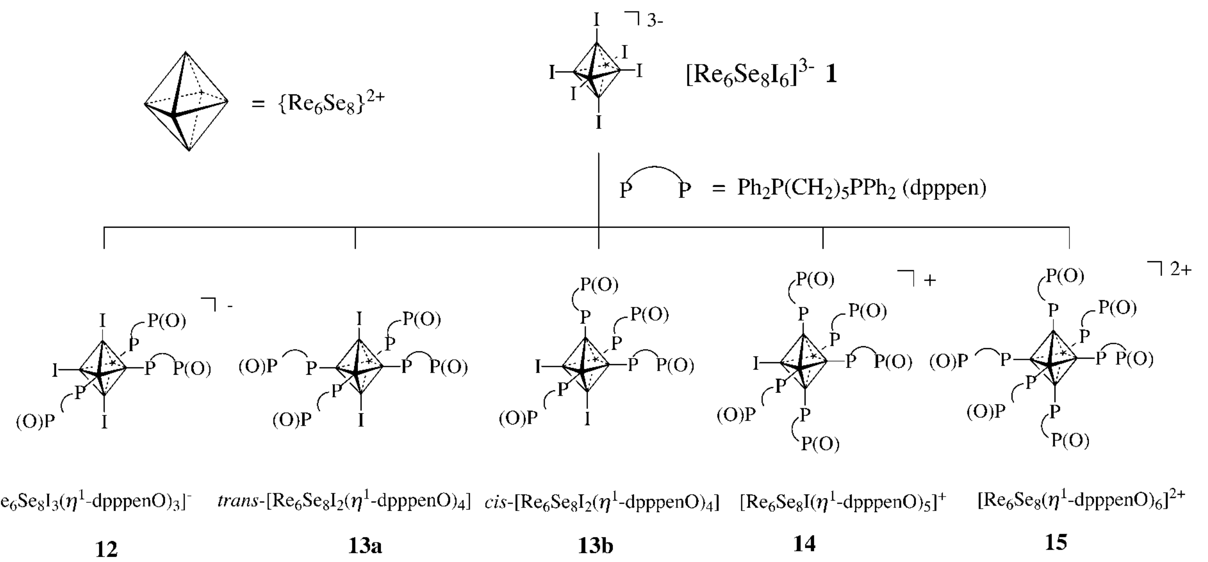
Results and Discussion

Preparation of the complexes: In general, $(Bu_4N)_3$-**1** served as the starting material, but the hexa(acetonitrile) compound $[Re_6Se_8(MeCN)_6](SbF_6)_2$ (**1b**-$(SbF_6)_2$) was used for the preparation of the hexa(diphosphine–monooxide) complexes $[Re_6Se_8(\eta^1\text{-diphosO})_6]^{2-}$. The precursor cluster compound **1** was isolated in the one-electron oxidized $Re^{III}{}_5Re^{IV}$ state due to its more negative $Re^{III}{}_6/Re^{III}{}_5Re^{IV}$ redox potential. Under controlled reaction conditions, the iodide ions in **1** were replaced by the diphosphine (diphos) $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb, $n = 5$, dpppen, $n = 6$, dpph) in a stepwise manner with concomitant reduction of the central $Re^{III}{}_5Re^{IV}$ core to $Re^{III}{}_6$. The derivatives with the general formula $[Re_6Se_8I_{6-m}(\eta^1\text{-diphos or diphosO})_m]^{m-4}$ ($m = 3-6$; diphosO is diphosphine–monoxide $Ph_2P(CH_2)_nPOPh_2$) when $n = 1-5$, or $[Re_6Se_8I_{6-2m}(\mu\text{-dpph})_m]^{2m-4}$ ($m = 1-3$) when $n = 6$ have been obtained.[14] The diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ adopt two different coordination modes depending on the number of the methylene groups. The monodentate coordination mode is utilized for $n = 1-5$, where the other P atom in the pendant arm is generally oxygenated except for the ligand with $n = 1$, while the two P donors in the diphosphine ligand $Ph_2P(CH_2)_6PPh_2$ are separated sufficiently to chelate two adjacent rhenium apices so as to achieve a bridge-chelate mode around the giant octahedral hexarhenium(III) cluster core. In the latter case, four complexes with stable ten-membered metallacycles, $[Re_6Se_8I_4(\mu\text{-dpph})]^{2-}$ (**2**), *trans*-$[Re_6Se_8I_2(\mu\text{-dpph})_2]$ (**3a**), *cis*-$[Re_6Se_8I_2(\mu\text{-diphos})_2]$ (**3b**) (X-ray structural determination was reported), $[Re_6Se_8(\mu\text{-dpph})_3](SbF_6)_2$ (**4**-$(SbF_6)_2$) were isolated. These complexes have been reported previously[14] and will not be mentioned further in detail in this paper.

As mentioned above, when the diphosphine $Ph_2P(CH_2)_nPPh_2$ adopts a η^1-bonding mode, the free P donor is oxygenated during the preparation procedures except in the case of $n = 1$. Attempts to avoid the oxygenation of the P atom in the dangling arm were unsuccessful under the reaction conditions with refluxed DMF even after the careful removal of dioxygen. For the ligand with $n = 1$, however, the pure dppm-substituted hexarhenium(III) derivatives *trans*-$[Re_6Se_8I_2(\eta^1\text{-dppm})_4]$ (**5a**) and *cis*-$[Re_6Se_8I_2(\eta^1\text{-dppm})_4]$ (**5b**) were isolated. The oxygenation of the dangling arm in the diphosphine was confirmed clearly by ^{31}P NMR spectroscopy; the chemical shift of the oxygenated P atom occurs at a much lower field. A strong vibration attributed to the P=O bond was observed in the IR spectra in the region 1150–1180 cm^{-1}. Moreover, the oxygen atom attached to the P atom of the dangling arm in the diphosphine–monoxide was confirmed in the crystal structure determinations (see below).

Five hexarhenium(III) derivatives ($m = 3-6$) (**12**, **13a**, **13b**, **14**, **15**) were isolated for the ligand $Ph_2P(CH_2)_5POPh_2$ (Scheme 1). For other diphosphine–monooxide ligands $Ph_2P(CH_2)_nPOPh_2$ ($n = 2-4$), complexes with $m = 4$ and 6 ($[Re_6Se_8I_{6-m}(\text{diphosO})_m]^{m-4}$) were isolated. Both *cis* and *trans* geometrical isomers for $m = 4$ were obtained for all these ligands including $Ph_2PCH_2PPh_2$. It is noteworthy that in each case the major product was the *cis* isomer. This is also true for $[Re_6Se_8I_2(\mu\text{-}Ph_2P(CH_2)_6PPh_2)_2]$ with bridge-chelate ligands.[14] For $[Re_6Se_8I_3(\text{dpppenO})_3]^-$, only the *mer* isomer was obtained, although the *fac* isomer might be formed as a minor product. Silica gel chromatography has been useful for the separation of the complexes owing to the variable charge or difference in polarity of geometric isomers.

Structural characterization: Compounds **5a**, **6a**, **6b**, and **10a** were characterized by X-ray crystallography. Selected interatomic distances and bond angles are listed in Table 1. The



Scheme 1. Octahedral hexarhenium complexes **12**–**15**, which contain different numbers of dpppenO ligands, showing the bonding mode and geometry of the dpppenO ligands around the cluster core.

Table 1. Selected bond lengths [Å] and angles [°] for **5a** · $6H_2O$, **6a** · $2CH_2Cl_2 \cdot 6H_2O$, **6b** · $CH_3OH \cdot 6H_2O$, and **10a** · $12H_2O$.

	5a	**6a**	**6b**	**10a**
Re–Re	2.632(1)-2.648(1)	2.6397(4) – 2.6461(4)	2.621(1) – 2.658(1)	2.6346(7) – 2.6453(5)
av	2.642	2.6425	2.642	2.6424
Re–Se	2.516(2) – 2.536(2)	2.5017(8) – 2.5230(8)	2.494(3) – 2.539(2)	2.507(2) – 2.524(2)
av	2.524	2.5153	2.514	2.512
Re–I	2.765(2)	2.7799(6)	2.763(2), 2.767(2)	2.773(1)
av			2.765	
Re–P	2.486(6), 2.492(5)	2.479(2), 2.484(2)	2.472(5) – 2.487(5)	2.497(4)
av	2.489	2.482	2.477	
Re-Re-Re	89.81(3) – 90.19(3)	89.96(1) – 90.04(1)	89.49(3) – 90.44(4)	89.74(2) – 90.46(3)
av	90.00	90.00	90.00	90.06
Re-Re-Re	59.63(3) – 60.23(3)	59.93(1) – 60.10(1)	59.44(3) – 60.56(3)	59.75(2) – 60.15(1)
av	60.00	60.00	60.00	60.04
Re-Se-Re	62.64(5) – 63.37(5)	63.13(2) – 63.51(2)	63.54(5) – 63.69(6)	63.06(5) – 63.63(4)
av	63.14	63.38	63.39	63.42
Se-Re-Se	175.77(7) – 176.46(7)	175.42(3) – 176.29(3)	174.88(7) – 176.38(7)	175.45(6) – 176.16(8)
av	176.12	175.84	175.73	175.86
Se-Re-Se	89.38(7) – 90.47(7)	89.16(3) – 90.55(3)	88.49(8) – 91.38(7)	89.06(6) – 90.81(6)
av	89.94	89.92	89.92	89.93
Se-Re-P	88.1(1) – 95.6(1)	90.10(5) – 94.04(5)	86.8(2) – 96.9(2)	92.2
av	91.9	92.19	92.2	92.1(1)-92.3(1)
Se-Re-I	90.16(6) – 93.52(5)	90.84(2) – 92.91(2)	90.28(6) – 93.79(6)	91.92(4) – 91.93(4)
av	91.98	91.87	91.97	91.93

skeletal interatomic distances Re–Re, Re–Se, and Re–I are very similar in each of the four compounds. These distances are also comparable to the corresponding distances of **1** and of other hexarhenium(III) complexes with other ligands.[10a, 11, 13] The Re–P distances are also similar to those of other hexarhenium(III) phosphine complexes.[11]

Complex **5a** is a tetra(dppm)-substituted product resulting from the displacement of four of the six iodide ions in the precursor complex **1** by the dppm ligands (Figure 1). The dppm ligand behaves as an η^1-ligand, in which only one of the P donors is bound to the apex of the hexarhenium(III) octahedron. The four monodentate dppm ligands are located at four of the six apices of the hexarhenium(III) octahedron; two oppositely oriented iodide ions remain unsubstituted thus giving the *trans* geometrical configuration. The η^1-binding mode of dppm makes **5a** a potential building block for the design of supramolecular structures, since the noncoordinated P donor is available for coordination with other metal ions or metal-containing blocks.

The structures of a pair of *trans* and *cis* isomers (**6a** and **6b**) containing four dppeO ligands ($n = 2$) are depicted in Figure 2 and 3, respectively. The dppeO ligand adopts an η^1-bonding mode, where the O atom is attached distinctly to the P atom of the dangling arm. The P–O bond length lies in the range of 1.44 – 1.49 Å. Comparison of the bond lengths (Re–P and Re–I) in the two isomers indicates that the differences are negligible, demonstrating that the distances are practically unaffected by the donor atom at the opposite side of the

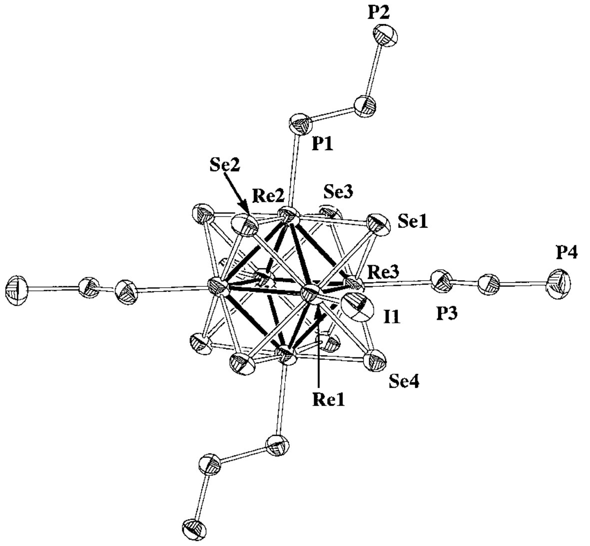


Figure 1. Molecular structure of **5a** (ORTEP drawing; ellipsoids drawn at 50% probability level). Phenyl rings on the phosphorus atoms are omitted for clarity.

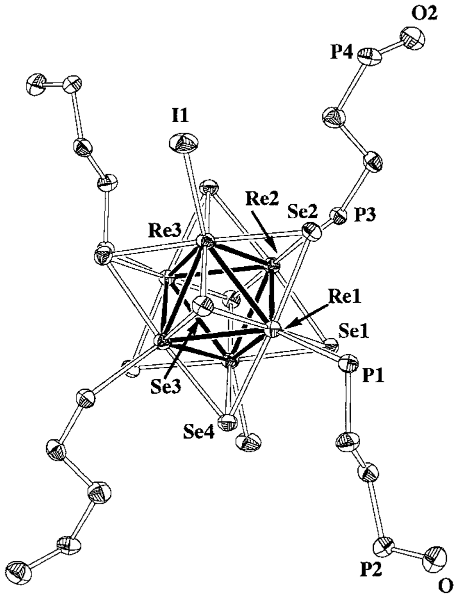


Figure 2. Molecular structure of **6a** (ORTEP drawing; ellipsoids drawn at 50% probability level). Phenyl rings on the phosphorus atoms are omitted for clarity.

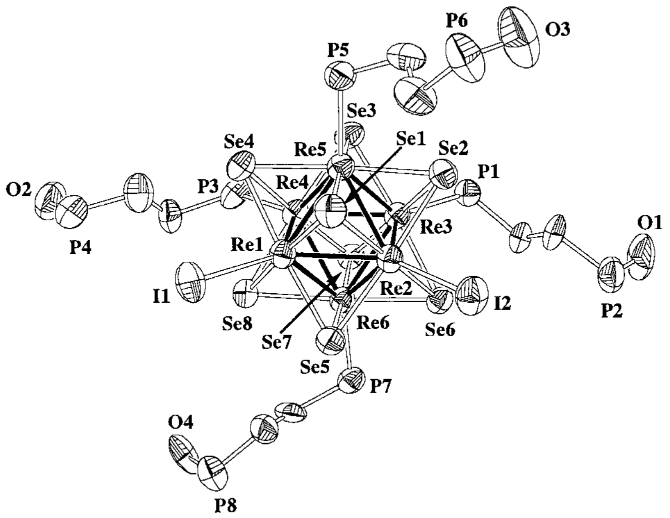


Figure 3. Molecular structure of **6b** (ORTEP drawing; ellipsoids drawn at 50% probability level). Phenyl rings on the phosphorus atoms are omitted for clarity.

$Re_6(\mu_3\text{-}Se)_8$ core. Thus, no appreciable structural "*trans*" or "*cis*" influence exists for the $Re_6(\mu_3\text{-}Se)_8$ core.

The molecular structure of **10a** which has relatively long dangling arms is given in Figure 4. Here again the *trans* geometrical structure is clearly confirmed. The orientations of the dangling arms of the dppbO ligands ($n = 4$) are interesting. The dangling arms of the neighboring dppbO ligands are oriented oppositely, and those of the opposite dppbO ligands arranged in the same direction so that the extending directions of the dangling arms for the four dppbO ligands may be described as an *up-down-up-down* orientation. This arrangement (*up-down-up-down*) is different from that observed in **6a**, where the orientation may be described as *up-up-down-down*. Thus, the number of methylene groups affects the orientations of the dangling arms in the diphosphine–monoxide-containing hexarhenium(III) derivatives in the solid state.

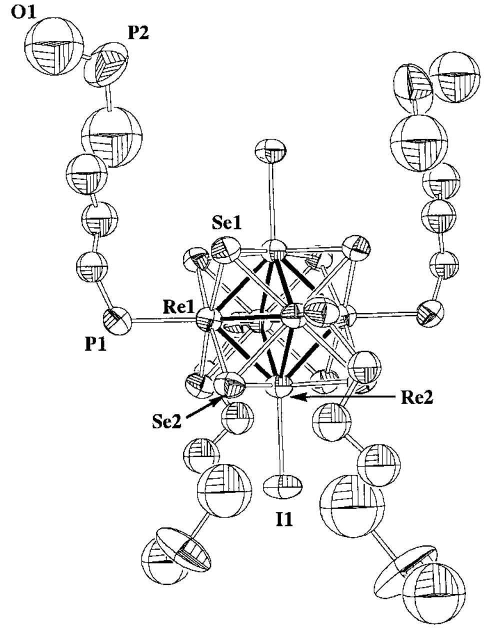


Figure 4. Molecular structure of **10a** (ORTEP drawing; ellipsoids drawn at 50% probability level). Phenyl rings on the phosphorus atoms are omitted for clarity.

NMR spectra: ^1H NMR signals of the methylene groups of the hexarhenium(III) complexes containing the diphosphine or diphosphine–monoxide ligands with shorter alkyl chains ($n \geq 3$) were assigned unambiguously. The geometrical isomers were cleraly distinguishable in the ^1H NMR spectra. For the tetra(dppm) complexes **5a** and **5b**, the methylene proton signal was observed as a single doublet in the *trans* isomer **5a**, while signals appeared as a pair of doublets in its *cis* counterpart **5b** (in both cases $J(P,H)$ is 7.3–7.8 Hz). Thus, as expected from the structures, the four dppm ligands are equivalent in **5a** whereas two nonequivalent groups are present in 1:1 ratio in **5b**. For the derivatives containing the diphosphine–monoxide ligands with $n = 2$ or 3, each group of signals for the methylene moieties in the *trans* isomer is split into two groups of signals in its corresponding *cis* counterpart. However, more complicated multiplets were observed than with the dppm complexes because of the existence of both H–H and P–H couplings. For the complexes with longer alkyl chains ($n \geq 4$), the signals were quite complicated.

^{31}P NMR spectra were even more informative with regard to the identification of the structures and the geometrical isomers of the hexarhenium(III) derivatives containing different numbers of diphosphine or diphosphine–monoxide ligands. The chemical shift of the coordinated phosphorus atoms in the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ moved to slightly higher field than the free ligands. The P signals of the free arms appeared at considerably lower field after oxygenation. Appreciable P–P coupling was observed when $n = 1$ or 2, but disappeared when $n \geq 3$. ^{31}P NMR spectra of the hexarhenium(III) derivatives containing tetra(dppm) or tetra(dppmO) are illustrated in Figure 5. The chemical shift $\delta(^{31}P)$ of the coordinated phosphorus atom (ca. $\delta = -30$) is about 6 ppm more negative than that of the noncoordinated phosphorus atom (ca. $\delta = -25.5$) in the tetra(dppm) hexarhenium(III) derivatives **5a** and **5b**. However, if the solutions of

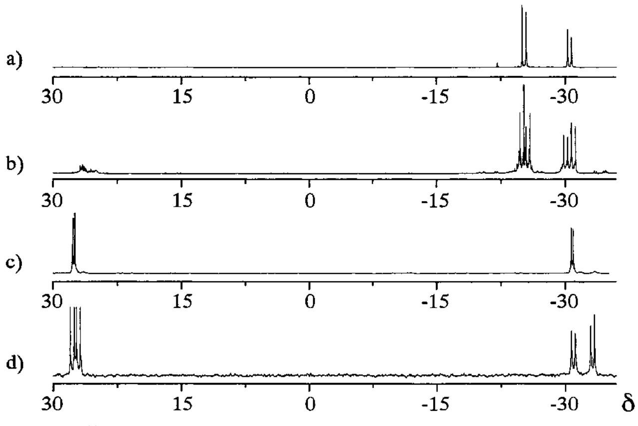


Figure 5. ^{31}P NMR spectra (109.25 MHz, $CDCl_3$) of tetra(dppm)-containing hexarhenium derivatives before (**5a** and **5b**) and after (**5a′** and **5b′**) the oxygenation of dppm: a) **5a**; b) **5b**; c) **5a′**; d) **5b′**.

5a and **5b** in chloroform in the NMR tubes were kept in air for over one month they changed dramatically, and were converted to *trans*-[$Re_6Se_8I_2(\eta^1$-dppmO$)_4$] (**5a′**) and *cis*-[$Re_6Se_8I_2(\eta^1$-dppmO$)_4$] (**5b′**) derivatives, respectively. As a result of the oxygenation the $\delta(^{31}P)$ values of the noncoordinated phosphorus atoms are shifted to remarkably more positive values ($\delta = 27$). The doublet for each phosphorus atom in the *trans* isomers **5a** or **5a′** indicates the evident P–P coupling (ca. 50 Hz) for the dppm or dppmO ligands. Moreover, each doublet signal ascribed to the coordinated and free P atoms in the *trans* isomers **5a** or **5a′** is split into two sets of signals for the doublets in the *cis* isomers **5b** or **5b′**. Thus the geometrical isomers can clearly be distinguished by ^{31}P NMR regardless of the oxygenation of the free arms.

Figure 6 shows the ^{31}P NMR spectra of the hexarhenium(III) derivatives [$Re_6Se_8I_{6-m}(\eta^1$-dpppenO$)_m]^{m-4}$ ($m = 3$–6). The respective chemical shifts of coordinated (ca. $\delta = -30$) and oxygenated free phosphorus (ca. $\delta = 30$) atoms are essentially insensitive to the value of m. As expected from the suggested structures, the respective signals of the *trans*-tetra(dpppenO) isomer **13a** and the hexa(dpppenO) complex **15**, are observed as one set, while those in the *mer*-tris(dpppenO) complex **12**, the *cis*-tetra(dpppenO) isomer **13b**, and the penta(dpppenO) complex **14** are found as two sets.

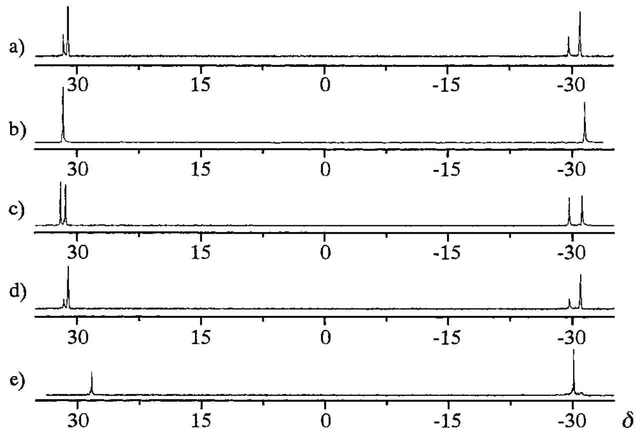


Figure 6. ^{31}P NMR spectra (109.25 MHz, $CDCl_3$) of the hexarhenium complexes **12**–**15**: a) **12;** b) **13a**; c) **13b**; d) **14**-I; e) **15**-$(SbF_6)_2$.

Although ^{13}C NMR spectra of the hexarhenium(III) derivatives containing diphosphine or diphosphine–monoxide ligands were quite complicated in the region for the phenyl groups, the signals due to the methylene groups were assigned unambiguously. A doublet was usually observed for each methylene carbon atom of the diphosphine $Ph_2P(CH_2)_nPPh_2$ or diphosphine–monoxide $Ph_2P(CH_2)_nP(O)Ph_2$ in the *trans*-tetra(diphos) or *trans*-tetra(diphosO) hexarhenium(III) complexes, where a well-resolved P–C coupling is expected between the phosphorus and the methylene carbon atoms. Whereas a single doublet for each methylene carbon atom was observed in the *trans* isomer, a pair of doublets was observed for the *cis*-tetra(diphos) or *cis*-tetra(diphosO) complexes as expected from the different geometrical locations of the axial ligands. Thus, the methylene carbon signals are also useful for the identification of the geometrical isomers.

Redox chemistry: All the hexarhenium complexes containing the diphosphine or diphosphine–monoxide ligands showed a reversible one-electron wave for the $Re^{III}_6/Re^{III}_5Re^{IV}$ process in their cyclic voltammograms. The redox potentials are listed in Table 2. Relative to the $E_{1/2}$ value for **1** (−0.02 V), that for the diphosphine- or diphosphine–monoxide-substituted derivatives is much more positive, indicating that the axial ligand substitution makes the hexarhenium(III) core less amenable to oxidation. For the hexarhenium(III) derivatives [$Re_6Se_8I_{6-m}(\eta^1$-dpppenO$)_m]^{m-4}$, the magnitude of the shift in $E_{1/2}$ to the positive side is in the order **12** ($m = 3$) < **13a**, **13b** ($m = 4$) < **14** ($m = 5$) < **15** ($m = 6$). Thus the potential evidently depends on the number of dpppenO ligands. The geometric isomerism in the hexarhenium(III) derivatives **13a** and **13b**, however, does not exert an appreciable influence on the $E_{1/2}$ value.[13]

Table 2. Electrochemical and photophysical data of complexes **1**–**15**.

Compound	$E_{1/2}$ [V][a]	λ_{em} [nm][b]	ϕ_{em}	τ_{em} [μs]
$(Bu_4N)_3$-**1**[c]	−0.02			
$(Bu_4N)_2$-**2**[14]	+0.35	787	0.007	2.4
3a[14]	+0.76	777	0.008	2.1
3b[14]	+0.79	790	0.012	3.2
4-$(SbF_6)_2$[14]	+1.06	779	0.031	6.5
5a	+0.72	774	0.010	2.7
5b	+0.74	771	0.0085	3.1
6a	+0.88	777	0.011	4.3
6b	+0.87	777	0.015	3.6
7-$(SbF_6)_2$	+1.10	761	0.061	15.4
8a	+0.86	775	0.008	2.3
8b	+0.86	784	0.011	2.8
9-$(SbF_6)_2$	+1.08	758	0.053	14.6
10a	+0.80	771	0.0094	2.8
10b	+0.81	778	0.014	3.5
11-$(SbF_6)_2$	+1.12	764	0.054	14.7
(Bu_4N)-**12**	+0.70	788	0.013	2.6
13a	+0.77	802	0.008	3.8
13b	+0.75	801	0.013	2.5
14-I	+0.85	778	0.024	5.3
15-$(SbF_6)_2$	+1.17	761	0.048	10.6

[a] A reversible process. Cyclic voltammograms were recorded at 20 °C for 0.1 mol dm^{-3} $(Bu_4N)PF_6/CH_2Cl_2$ solutions at a scan rate of 100 mV s^{-1}. [b] Excitation wavelength was 355 nm. The corrected emission spectra were measured in deoxygenated $CHCl_3$ at 298 K. [c] Compound **1** is nonemissive with the $Re^{III}_5Re^{IV}$ oxidation state.

Luminescent properties: All the complexes prepared in this study showed strong luminescence both in the solid state and in solution. The photophysical parameters are listed in Table 2. The emission lifetimes for all the hexarhenium(III) derivatives are in the microsecond order (2–16 μs) at ambient temperature. All the P_6-substituted species display much longer lifetimes (τ_{em}) and larger quantum yields (ϕ_{em}) than other derivatives with both iodide ions and P ligands (Table 2). Among the P_6-substituted derivatives, [$Re_6Se_8(\eta^1$-diphosO$)_6]^{2+}$ ($\phi_{em} = 0.048$–0.061, $\tau_{em} = 10.6$–15.4 μs) with the η^1-binding ligands possess a larger ϕ_{em} and longer τ_{em} than those ($\phi_{em} = 0.031$, $\tau_{em} = 6.5$ μs) of [$Re_6Se_8(\mu$-dpph$)_3]^{2+}$ (**4**) which has bridge-chelate ligands.[14] There is no significant change in the photophysical parameters of the hexarhenium(III) derivatives **12**–**14** ($m = 3-5$). Also, no apparent differences are seen in the photophysical properties between the pairs of geometrical isomers (**5a** and **5b**; **6a** and **6b**; **8a** and **8b**; **10a** and **10b**; and **13a** and **13b**).

It has been suggested recently that the photoemissive excited state, derived from the LMCT transition, is largely localized on the $Re_6(\mu_3\text{-}Se)_8$ core.[16]

Conclusion

A series of hexarhenium(III) complexes containing different numbers of η^1-dppm ($Ph_2PCH_2PPh_2$) or η^1-diphosphine–monoxide ($Ph_2P(CH_2)_nPOPh_2$; $n = 1-5$) ligands (L), $[Re_6(\mu_3\text{-}Se_8)I_{(6-m)}L_m]^{(4-m)-}$ ($m = 3-6$) have been prepared. The structures (as well as the geometrical isomerism) of the hexarhenium(III) complexes have been well-defined by ^1H, ^{13}C and ^{31}P NMR spectroscopy, and X-ray crystallography. The difference in the number and type of axial ligands influence the redox potentials and photophysical properties of the hexarhenium(III) clusters. The substitution reactions of the diphosphine $Ph_2P(CH_2)_nPPh_2$ for the iodide ions in the parent octahedral hexarhenium cluster $[Re_6Se_8I_6]^{3-}$ **1** described herein not only offer an excellent route to prepare new hexarhenium(III) derivatives with variable structural topologies, but also provide an efficient means to modulate the redox and photophysical properties.

Experimental Section

General: All operations were carried out under an argon atmosphere by means of standard Schlenk technique unless otherwise stated. Bis(diphenylphosphanyl)methane (dppm), 1,2-bis(diphenylphosphanyl)ethane (dppe), 1,3-bis(diphenylphosphanyl)propane (dppp), 1,4-bis(diphenylphosphanyl)butane (dppb), 1,5-bis(diphenylphosphanyl)pentane (dpppen), and 1,6-bis(diphenylphosphanyl)hexane (dpph) were available from Aldrich and used without purification. The parent haxarherium clusters $(Bu_4N)_3$-$[Re_6Se_8I_6]$ ($(Bu_4N)_3$-**1**) and $[Re_6Se_8(MeCN)_6](SbF_6)_2$ (**1b**-$(SbF_6)_2$) were prepared according to the literature methods.[10a, 11b]

***trans*-[Re$_6$Se$_8$I$_2$(η^1-dppm)$_4$] (5a) and *cis*-[Re$_6$Se$_8$I$_2$(η^1-dppm)$_4$] (5b)**: A solution of $(Bu_4N)_3$-**1** (200 mg, 0.062 mmol) and dppm (143 mg, 0.372 mmol) in DMF (20 mL) was refluxed under an argon atmosphere for 3 h. The solution was concentrated in vacuo to 2 mL and water (30 mL) was added to precipitate the product. The orange solid was filtered and dissolved in dichloromethane (3 mL). The solution was chromatographed on a silica gel column. Complex **5a** was eluted with dichloromethane and isolated as an orange-red solid. Yield, 45 mg (21 %). Complex **5b** was eluted with dichloromethane–acetonitrile (50:1). Yield, 80 mg (37 %). **5a**: Elemental analysis calcd (%) for $C_{100}H_{88}I_2P_8Se_8Re_6$: C 33.93, H 2.51, I 7.17; found: C 33.98, H 2.64, I 7.49; FAB-MS: *m/z*: 3542 [*M*]$^+$; ^1H NMR (270.05 MHz, CD_2Cl_2, 21 °C, TMS): $\delta = 7.35-6.85$ (m, 80H; Ph), 3.32 (d, $J(P,H) = 7.6$ Hz, 8H; CH$_2$); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 21 °C, TMS): $\delta =$ 137.8 and 137.6 (d, *i*-Ph), 135.5 and 134.8 (d, *i*-Ph), 134.0 (d, *o*-Ph), 133.0 (d, *o*-Ph), 128.7 (t, *m*-Ph), 127.8 (d, *p*-Ph), 38.0 (d of d, $J(P,C) = 36$ Hz, *C*H$_2$); ^{31}P NMR (109.25 MHz, $CDCl_3$, 21 °C): $\delta = -25.5$ (d, $J(P,P) = 49$ Hz, noncoordinated P), -30.5 (d, $J(P,P) = 46$ Hz, coordinated P).

5b: Elemental analysis calcd (%) for $C_{100}H_{88}I_2P_8Se_8Re_6$: C 33.93, H 2.51, I 7.17; found: C 33.67, H 2.54, I 7.58; FAB-MS: *m/z*: 3542 [*M*]$^+$; ^1H NMR (270.05 MHz, CD_2Cl_2, 21 °C, TMS): $\delta = 7.34-6.92$ (m, 80H; Ph), 3.45 (d, $J(P,H) = 7.8$ Hz, 4H; CH$_2$), 3.28 (d, $J(P,H) = 7.3$ Hz, 4H; CH$_2$); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 21 °C, TMS): $\delta = 137.8$ and 137.6 (q, *i*-Ph), 135.9 and 135.2 (t, *i*-Ph), 133.9 (q, *o*-Ph), 132.8 (q, *o*-Ph), 128.7 (m, *m*-Ph), 127 (q, *p*-Ph), 38.2 (m, *C*H$_2$); ^{31}P NMR (109.25 MHz, $CDCl_3$, 21 °C): $\delta = -25.0$ (d, $J(P,P) = 51$ Hz, noncoordinated P), -25.7 (d, $J(P,P) = 52$ Hz, noncoordinated P), -30.0 (d, $J(P,P) = 52$ Hz, coordinated P), -30.5 (d, $J(P,P) =$ 52 Hz, coordinated P).

***trans*-[Re$_6$Se$_8$I$_2$(η^1-dppeO)$_4$] (6a) and *cis*-[Re$_6$Se$_8$I$_2$(η^1-dppeO)$_4$] (6b)**: A solution of $(Bu_4N)_3$-**1** (200 mg, 0.062 mmol) and dppe (147 mg, 0.372 mmol) in DMF (20 mL) was stirred and refluxed in air for 3 h. The solution was concentrated to 3 mL in vacuo and water (50 mL) was added. An orange precipitate was filtered, and was dissolved in dichloromethane (3 mL). The solution was chromatographed on a silica gel column. Complex **6a** was eluted with dichloromethane as the first band. Yield 26 mg (12 %). Complex **6b** was eluted with dichloromethane as the second band. Yield 72 mg (32 %).

6a: Elemental analysis calcd (%) for $C_{104}H_{96}I_2O_4P_8Se_8Re_6$: C 34.13, H 2.64, I 6.93; found: C 34.49, H 2.82, I 7.30; FAB-MS: *m/z*: 3662 [*M*]$^+$; IR (KBr): $\tilde{\nu} = 1179$ cm^{-1} (P=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 325 (16500), 380 nm (6600 mol^{-1}dm^{3}cm^{-1}); ^1H NMR (270.05 MHz, CD_2Cl_2, 21 °C, TMS): $\delta =$ 7.74–7.16 (m, 80H; Ph), 2.86 (m, 8H; PCH$_2$*CH*$_2$P(O)), 2.18 (m, 8H; P*CH*$_2$CH$_2$P(O)); ^{13}C NMR (67.8 MHz, $CDCl_3$, 23 °C, TMS): $\delta = 137.1$ (s, *i*-Ph), 136.8 (s, *i*-Ph), 136.2 (s, *i*-Ph), 135.3 (s, *i*-Ph), 133.1 (d, *o*-Ph), 132.9 (d, *o*-Ph), 128.5 (q, *m*-Ph), 127.9 (d, *p*-Ph), 34.3 (q, $J(P,C) = 29$ Hz, PCH$_2$*C*H$_2$P(O)), 22.8 (q, $J(P,C) = 21$ Hz, PCH$_2$*C*H$_2$P(O)); ^{31}P NMR (109.25 MHz, $CDCl_3$, 24°C): $\delta = 30.9$ (d, $J(P,P) = 49$ Hz, PCH$_2$CH$_2$*P*(O)), -30.0 (d, $J(P,P) = 49$ Hz, *P*CH$_2$CH$_2$P(O)).

6b: Elemental analysis calcd (%) for $C_{104}H_{96}I_2O_4P_8Se_8Re_6$: C 34.13, H 2.64, I 6.93; found: C 34.56, H 3.01, I 7.41; FAB-MS: *m/z*: 3662 [*M*]$^+$; IR (KBr): $\tilde{\nu} = 1176$ cm^{-1} (P=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 325 (13800), 370 nm (8400 mol^{-1}dm^{3}cm^{-1}); ^1H NMR (270.05 MHz, CD_2Cl_2, 21 °C, TMS): $\delta =$ 7.94–6.71 (m, 80H; Ph), 2.94 (m, 4H; PCH$_2$*CH*$_2$P(O)), 2.58 (m, 4H; PCH$_2$*CH*$_2$P(O)), 2.12 (m, 4H; P*CH*$_2$CH$_2$P(O)), 1.82 (m, 4H; P*CH*$_2$CH$_2$P(O)); ^{13}C NMR (67.8 MHz, $CDCl_3$, 21 °C, TMS): $\delta = 137.1$ (s, *i*-Ph), 136.3 (s, *i*-Ph), 136.2 (s, *i*-Ph), 135.5 (s, *i*-Ph), 132.8 (m, *o*-Ph), 131.1 (m, *o*-Ph), 130.2 (q, *m*-Ph), 128.6 (d, *p*-Ph), 128.4 (d, *p*-Ph), 127.9 (q, *m*-Ph), 30.2 (m, PCH$_2$*C*H$_2$P(O)), 25.8 (m, P*C*H$_2$CH$_2$P(O)); ^{31}P NMR (109.25 MHz, $CDCl_3$, 23.7 °C): $\delta = 31.6$ (d, $J(P,P) = 46$ Hz, PCH$_2$CH$_2$*P*(O)), 30.8 (d, $J(P,P) = 49$ Hz, PCH$_2$CH$_2$*P*(O)), -27.0 (d, $J(P,P) = 49$ Hz, *P*CH$_2$CH$_2$P(O)), -29.2 (d, $J(P,P) = 49$ Hz, *P*CH$_2$CH$_2$P(O)).

[Re$_6$Se$_8$(η^1-dppeO)$_6$](SbF$_6$)$_2$ (7-(SbF$_6$)$_2$): A solution of **1b**-$(SbF_6)_2$ (100 mg, 0.04 mmol) and dppe (96 mg, 0.24 mmol) in DMF–chlorobenzene (1:2) (30 mL) was refluxed with stirring in air for 36 h. The solvent was then removed in vacuo. The residue was dissolved in dichloromethane (2 mL), and then transferred to a silica gel column. The product was obtained by eluting with dichloromethane–ethanol (30:1). Yield 85 mg (45 %). Elemental analysis calcd (%) for $C_{156}H_{144}F_{12}O_6P_{12}Sb_2Se_8Re_6$: C 39.70, H 3.08; found: C 39.56, H 3.25; FAB-MS: *m/z* 4708 [M]$^+$; IR (KBr): $\tilde{\nu} = 1179$ cm^{-1} (P=O); ^1H NMR (270.05 MHz, CD_2Cl_2, 23 °C, TMS): $\delta = 7.51-7.01$ (m, 120H; Ph), 2.48 (m, 12H; PCH$_2$*CH*$_2$P(O)), 1.79 (m, 12H; P*CH*$_2$CH$_2$P(O)); ^{31}P NMR (109.25 MHz, CD_2Cl_2, 21.5 °C): $\delta = 27.3$ (d, $J(P,P) = 34$ Hz, PCH$_2$CH$_2$*P*(O)), -27.8 (d, $J(P,P) = 37$ Hz, *P*CH$_2$CH$_2$P(O)).

***trans*-[Re$_6$Se$_8$I$_2$(η^1-dpppO)$_4$] (8a) and *cis*-[Re$_6$Se$_8$I$_2$(η^1-dpppO)]$_4$] (8b)**: A solution of $(Bu_4N)_3$-**1** (200 mg, 0.062 mmol) and dppp (153 mg, 0.372 mmol) in DMF (20 mL) was refluxed in air for 3 h with stirring. The solution was concentrated in vacuo to 3 mL and water (50 mL) was added to precipitate the products. The orange residue was collected by filtration and then dissolved in dichloromethane (3 mL). The solution was chromatographed on a silica gel column. Complex **8a** was eluted with dichloromethane. Yield 23 mg (10 %). Complex **8b** was eluted with dichlorometahne–acetonitrile (50:1). Yield 53 mg (23 %).

8a: Elemental analysis calcd (%) for $C_{108}H_{104}I_2O_4P_8Se_8Re_6$: C 34.77, H, 2.81, I 6.81; found: C 35.03, H 2.89, I 6.64; FAB-MS: *m/z*: 3718 [*M*]$^+$; IR (KBr): $\tilde{\nu} = 1175$ cm^{-1} (P=O); ^1H NMR (270.05 MHz, $CDCl_3$, 21 °C, TMS): $\delta =$ 7.70–7.00 (m, 80H; Ph), 2.58 (m, 8H; PCH$_2$CH$_2$*CH*$_2$P(O)), 2.13 (m, 8H; P*CH*$_2$CH$_2$CH$_2$P(O)), 1.42 (m, 8H; PCH$_2$*CH*$_2$CH$_2$P(O)); ^{13}C NMR (67.8 MHz, $CDCl_3$, 21 °C, TMS): $\delta = 134.9$ (s, *i*-Ph), 134.2 (s, *i*-Ph), 133.3 (d, *o*-Ph), 132.6–131.6 (m, *o*-Ph), 130.4 (m, *m*-Ph), 128.8 (s, *p*-Ph), 128.5 (s, *p*-Ph), 127.9 (t, *m*-Ph), 38.7 (d, J(P,C) = 35 Hz, PCH$_2$CH$_2$*C*H$_2$P(O)), 30.2 (d, J(P,C) = 15 Hz, P*C*H$_2$CH$_2$CH$_2$(O)), 17.8 (d, J(P,C) = 3 Hz, PCH$_2$*C*H$_2$CH$_2$P(O)); ^{31}P NMR (109.25 MHz, $CDCl_3$, 21.5 °C): $\delta = 31.7$ (s, P(CH$_2$)$_3$*P*(O)), -31.5 (s, *P*(CH$_2$)$_3$P(O)).

8b: Elemental analysis calcd (%) for $\mathrm{C_{108}H_{104}I_2O_4P_8Se_8Re_6}$: C 34.77, H, 2.81, I 6.81; found: C 34.89, H 2.80, I 7.18; FAB-MS: *m/z*: 3718 $[M]^+$; IR (KBr): $\tilde{\nu} = 1173\ \mathrm{cm^{-1}}$ (P=O); ^{1}H NMR (270.05 MHz, $\mathrm{CDCl_3}$, 21 °C, TMS): $\delta = 7.59-7.11$ (m, 80H; Ph), 2.76 (m, 4H; $\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{P(O)}$), 2.40 (m, 4H; $\mathrm{PCH_2CH_2}\mathit{CH}_2\mathrm{P(O)}$), 2.07 (m, 4H; $\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2P(O)}$), 1.78 (m, 4H; $\mathrm{P}\mathit{CH}_2\mathrm{CH_2CH_2P(O)}$), 1.53–1.32 (m, 8H; $\mathrm{PCH_2}\mathit{CH}_2\mathrm{CH_2P(O)}$); ^{13}C NMR (67.8 MHz, $\mathrm{CDCl_3}$, 21 °C, TMS): $\delta = 135.6$ (s, *i*-Ph), 135.0 (d, *i*-Ph), 134.3 (s, *i*-Ph), 133.2 (q, *o*-Ph), 131.8 (m, *o*-Ph), 130.4 (m, *m*-Ph), 129.6 (d, *p*-Ph), 128.7 (d, *p*-Ph), 127.9 (t, *m*-Ph), 38.3 (q, $\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2P(O)}$), 30.7 (q, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_2P(O)}$), 17.7(d, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2CH_2P(O)}$); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 23 °C): $\delta = 32.1$ (s, $\mathrm{P(CH_2)_3}\mathit{P}\mathrm{(O)}$), 31.5 (s, $\mathrm{P(CH_2)_3}\mathit{P}\mathrm{(O)}$), −29.9 (s, $\mathit{P}\mathrm{(CH_2)_3P(O)}$), −31.0 (s, $\mathit{P}\mathrm{(CH_2)_3P(O)}$).

$[\mathbf{Re_6Se_8(\eta^1\text{-dpppO})_6}](\mathbf{SbF_6})_2$ (9-($\mathbf{SbF_6}$)$_2$): The synthetic procedure is the same as that for **7**-$(\mathrm{SbF_6})_2$ except that dppp was used instead of dppe. Yield 72%. Elemental analysis calcd (%) for $\mathrm{C_{162}H_{156}F_{12}O_6P_{12}Sb_2Se_8Re_6 \cdot 4\,CH_2Cl_2}$: C 38.79, H, 3.22; found: C 38.36, H 3.18; FAB-MS: *m/z*: 4792 $[M]^+$; IR (KBr): $\tilde{\nu} = 1179\ \mathrm{cm^{-1}}$ (P=O); ^{31}P NMR (109.25 MHz, $\mathrm{CD_2Cl_2}$, 24 °C): $\delta = 28.1$ (s, $\mathrm{P(CH_2)_3}\mathit{P}\mathrm{(O)}$), −30.8 (s, $\mathit{P}\mathrm{(CH_2)_3P(O)}$).

***trans*-$[\mathbf{Re_6Se_8I_2(\eta^1\text{-dppbO})_4}]$ (10a) and *cis*-$[\mathbf{Re_6Se_8I_2(\eta^1\text{-dppbO})_4}]$ (10b)**: The same synthetic procedure as that for **8a** and **8b** was performed except that dppb was used instead of dppp.

10a: Yield: 12%. Elemental analysis calcd (%) for $\mathrm{C_{112}H_{112}I_2O_4P_8Se_8Re_6 \cdot 12\,H_2O}$: C 33.60, H 3.42, I 6.35; found: C 34.21, H 3.00, I 6.82; FAB-MS: *m/z*: 3774 $[M]^+$; IR (KBr): $\tilde{\nu} = 1185\ \mathrm{cm^{-1}}$ (P=O); ^{13}C NMR (67.8 MHz, $\mathrm{CDCl_3}$, 22 °C, TMS): $\delta = 135.5$ (s, *i*-Ph), 134.8 (s, *i*-Ph), 133.1 (t, *o*-Ph), 131.5 (t, *o*-Ph), 130.4 (d, *m*-Ph), 128.6 (s, *p*-Ph), 128.4 (s, *p*-Ph), 127.8 (d, *m*-Ph), 37.0 (d, ^1J(P,C) = 32 Hz, $\mathrm{PCH_2CH_2CH_2}\mathit{C}\mathrm{H_2P(O)}$), 29.4(d, $^{1'}J$(P,C) = 71 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_2CH_2P(O)}$), 26.0 (d, ^2J(P,C) = 18 Hz, $\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2CH_2P(O)}$), 22.6 (d, $^{2'}J$(P,C) = 18 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2CH_2CH_2P(O)}$); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 21.5 °C): $\delta = 31.4$ (s, $\mathrm{P(CH_2)_4}\mathit{P}\mathrm{(O)}$), −31.7 (s, $\mathit{P}\mathrm{(CH_2)_4P(O)}$).

10b: Yield: 28%. Elemental analysis calcd (%) for $\mathrm{C_{112}H_{112}I_2O_4P_8Se_8Re_6 \cdot 12\,H_2O}$: C 33.60, H 3.42, I 6.35; found: C 34.27, H, 2.91, I 7.13; FAB-MS: *m/z*: 3774 $[M]^+$; IR (KBr): $\tilde{\nu} = 1183\ \mathrm{cm^{-1}}$ (P=O); ^{13}C NMR (67.8 MHz, $\mathrm{CDCl_3}$, 22 °C, TMS): $\delta = 136.5$ (s, *i*-Ph), 135.8 (s, *i*-Ph), 135.1 (s, *i*-Ph), 134.4 (s, *i*-Ph), 133.2 (m, *o*-Ph), 131.7 (m, *o*-Ph), 130.5 (q, *m*-Ph), 128.7 (d, *p*-Ph), 128.5 (d, *p*-Ph), 127.8 (t, *m*-Ph), 37.4 (d of d, ^1J(P,C) = 34 Hz, $\mathrm{PCH_2CH_2CH_2}\mathit{C}\mathrm{H_2P(O)}$), 30.1 (d of d, $^{1'}J$(P,C) = 70 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_2CH_2P(O)}$), 26.0 (d of d, ^2J(P,C) = 18 Hz, $\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2CH_2P(O)}$), 22.8 (d, $^{2'}J$(P,C) = 18 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2CH_2CH_2P(O)}$); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 21.5 °C): $\delta = 31.9$ (s, $\mathrm{P(CH_2)_4}\mathit{P}\mathrm{(O)}$), 31.3 (s, $\mathrm{P(CH_2)_4}\mathit{P}\mathrm{(O)}$), −29.6 (s, $\mathit{P}\mathrm{(CH_2)_4P(O)}$), −31.2 (s, $\mathit{P}\mathrm{(CH_2)_4P(O)}$).

$[\mathbf{Re_6Se_8(\eta^1\text{-dppbO})_6}](\mathbf{SbF_6})_2$ (11-($\mathbf{SbF_6}$)$_2$): The synthetic procedure was the same as that for **7**-$(\mathrm{SbF_6})_2$ except that dppb was used instead of dppe. Yield: 86%. Elemental analysis calcd (%) for $\mathrm{C_{168}H_{168}F_{12}O_6P_{12}Sb_2Se_8Re_6}$: C 41.28, H 3.47; found: C 41.21, H 3.50; FAB-MS: *m/z*: 4876 $[M]^+$; IR (KBr): $\tilde{\nu} = 1185\ \mathrm{cm^{-1}}$ (P=O); ^{13}C NMR (270.05 MHz, $\mathrm{CD_2Cl_2}$, 21 °C, TMS): $\delta = 138.7$ (s, *i*-Ph), 134.3 (d, *i*-Ph), 133.1 (q, *o*-Ph), 131.6 (q, *o*-Ph), 130.8 (s, *p*-Ph), 130.6 (s, *p*-Ph), 128.8 (m, *m*-Ph), 37.9 ($\mathrm{PCH_2CH_2CH_2}\mathit{C}\mathrm{H_2P(O)}$), 30.0 ($\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_2CH_2P(O)}$), 26.6 ($\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2CH_2P(O)}$), 23.6 ($\mathrm{PCH_2}\mathit{C}\mathrm{H_2CH_2CH_2P(O)}$); ^{31}P NMR (109.25 MHz, $\mathrm{CD_2Cl_2}$, 21.5 °C): $\delta = 27.5$ (s, $\mathrm{PCH_2CH_2}\mathit{P}\mathrm{(O)}$), −30.0 (s, $\mathit{P}\mathrm{CH_2CH_2P(O)}$).

$(\mathbf{Bu_4N})[\mathbf{Re_6Se_8I_3(\eta^1\text{-dpppenO})_3}]$ (($\mathbf{Bu_4N}$)-12): A solution of $(\mathrm{Bu_4N})_3$-**1** (100 mg, 0.031 mmol) and dpppen (55 mg, 0.124 mmol) in DMF (20 mL) was heated at 100 °C with stirring for 1 h. The solution was concentrated to 3 mL in vacuo and water (30 mL) was added to precipitate the product. The red-orange precipitate was collected by filtration, and was dissolved in dichloromethane (3 mL). The solution was passed through a silica gel column to obtain $(\mathrm{Bu_4N})$-**12**. Yield 68 mg (58%). Elemental analysis calcd (%) for $\mathrm{C_{168}H_{168}F_{12}O_6P_{12}Sb_2Se_8Re_6}$: C 41.21, H 3.50, N 0.37, I 10.15; found: C 41.56, H 3.62, N 0.45, I 10.02; FAB-MS: *m/z*: 3743 $[M]^+$; IR (KBr): $\tilde{\nu} = 1178\ \mathrm{cm^{-1}}$ (P=O); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 23 °C): $\delta = 32.0$ (s, $\mathrm{P(CH_2)_4}\mathit{P}\mathrm{(O)}$), 31.2 (s, $\mathrm{P(CH_2)_4}\mathit{P}\mathrm{(O)}$), −29.4 (s, $\mathit{P}\mathrm{(CH_2)_4P(O)}$), −31.1 (s, $\mathit{P}\mathrm{(CH_2)_4P(O)}$).

***trans*-$[\mathbf{Re_6Se_8I_2(\eta^1\text{-dpppenO})_4}]$ (13a), *cis*-$[\mathbf{Re_6Se_8I_2(\eta^1\text{-dpppenO})_4}]$ (13b) and $[\mathbf{Re_6Se_8I(\eta^1\text{-dpppenO})_5}]\mathbf{I}$ (14-I)**: A solution of $(\mathrm{Bu_4N})_3$-**1** (200 mg, 0.062 mmol) and dpppen (169 mg, 0.372 mmol) in DMF (20 mL) was refluxed in air for 6 h with stirring. The solution was concentrated to 3 mL in vacuo and water (50 mL) was added to precipitate the products. The red-orange solid was collected by filtration and dissolved in dichloromethane (3 mL). Chromatography on a silica gel column gave three bands. Complex **13a** was eluted with dichloromethane as the first band. Yield 27 mg (11%). Complex **13b** was eluted with dichloromethane–acetonitrile (100:1) as the second band. Yield 58 mg (24%). Complex **14-**I was eluted with dichloromethane–acetontrile (4:1) as the third band. Yield 36 mg (14%).

13a: Elemental analysis calcd (%) for $\mathrm{C_{116}H_{120}I_2O_4P_8Se_8Re_6}$: C 36.25, H, 3.15, I 6.61; found:C 36.92, H, 3.37, I 6.86; FAB-MS: *m/z*: 3830 $[M]^+$; IR (KBr): $\tilde{\nu} = 1188\ \mathrm{cm^{-1}}$ (P=O); ^{13}C NMR (67.8 MHz, $\mathrm{CDCl_3}$, 23 °C, TMS): $\delta = 136.6$ (s, *i*-Ph), 135.5 (s, *i*-Ph), 133.1 (q, *o*-Ph), 131.5 (d, *o*-Ph), 130.5 (d, *m*-Ph), 128.6 (s, *p*-Ph), 128.4 (s, *p*-Ph), 127.8 (d, *m*-Ph), 36.9 (d, ^1J(P,C) = 30 Hz, $\mathrm{PCH_2CH_2CH_2CH_2}\mathit{C}\mathrm{H_2P(O)}$), 31.5 (d, $^{1'}J$(P,C) = 30 Hz, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2CH_2\ CH_2CH_2P(O)}$), 28.6 (d, ^2J(P,C) = 7 Hz, $\mathrm{PCH_2CH_2CH_2}\mathit{C}\mathrm{H_2CH_2P(O)}$), 23.8 (d, $^{2'}J$(P,C) = 7 Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2CH_2CH_2CH_2P(O)}$), 20.8 (s, $\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2CH_2CH_2P(O)}$); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 21.5 °C): $\delta = 32.1$ (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), −30.7 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$).

13b: Elemental analysis calcd (%) for $\mathrm{C_{116}H_{120}I_2O_4P_8Se_8Re_6}$: C 36.25, H, 3.15, I 6.61; found: C 36.42, H, 3.17, I 6.43; FAB-MS: *m/z*: 3830 $[M]^+$; IR (KBr): $\tilde{\nu} = 1188\ \mathrm{cm^{-1}}$ (P=O); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 21.5 °C): $\delta = 32.6$ (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), 32.0 (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), −29.9 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$), −31.0 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$).

14-I: Elemental analysis calcd (%) for $\mathrm{C_{145}H_{150}I_2O_5P_{10}Se_8Re_6}$: C 40.51, H 3.52, I 5.91; found: C 40.42, H, 3.37, I 6.23; FAB-MS: *m/z*: 4286 $[M]^+$; IR (KBr): $\tilde{\nu} = 1182\ \mathrm{cm^{-1}}$ (P=O); ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 21.5 °C): $\delta = 31.8$ (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), 31.1 (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), −29.7 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$), −30.8 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$).

$[\mathbf{Re_6Se_8(\eta^1\text{-dpppenO})_6}](\mathbf{SbF_6})_2$ (15-($\mathbf{SbF_6}$)$_2$): The same procedure as that for **7**-$(\mathrm{SbF_6})_2$ was applied except that dpppen was used instead of dppe. Yield: 83%. Elemental analysis calcd (%) for $\mathrm{C_{174}H_{180}F_{12}O_6P_{12}Sb_2Se_8Re_6}$: C 42.03, H 3.65; found: C 42.52, H 3.87; FAB-MS: *m/z*: 4960 $[M]^+$; ^{31}P NMR (109.25 MHz, $\mathrm{CDCl_3}$, 23.0°C): $\delta = 28.2$ (s, $\mathrm{P(CH_2)_5}\mathit{P}\mathrm{(O)}$), −30.1 (s, $\mathit{P}\mathrm{(CH_2)_5P(O)}$).

Physical measurements: Infrared spectra were recorded on a Hitachi 270–50 infrared spectrophotometer. UV/Vis absorption spectra were obtained on a Hitachi U-3410 spectrophotometer. Cyclic voltammograms were recorded by using a BAS-50W potentiostat at 20 °C for 0.1 mol dm^{-3} $(\mathrm{Bu_4N})\mathrm{PF_6/CH_2Cl_2}$ solutions at a scan rate of 100 mV s^{-1}, with a glassy carbon working electrode, a platinum coil counter electrode, and a Ag/AgCl reference electrode. The sample concentration was 1×10^{-3} mol dm^{-3}. NMR spectra were obtained on a JEOL JNM-EX 270 spectrometer. ^{1}H NMR spectra (270.05 MHz) and ^{13}C NMR spectra (67.8 MHz) were referenced to the methyl signals of TMS. ^{31}P NMR spectra (109.25 MHz) were measured relative to external $\mathrm{P(OMe)_3}$, which was set at $\delta = +141$ at the temperature quoted. Emission spectra were obtained by using a red-sensitive photodetector (Hamamatsu PMA-11, model C5966–23) and a Nd:YAG laser (Continuum Surelite) at 355 nm excitation. The instrumental responses of the system were corrected by using a software package for the detector. Lifetime measurements were conducted by using a steak camera (Hamamatsu C4334) as a detector. The corrected emission spectra were measured in deoxygenated $\mathrm{CHCl_3}$ solutions at 298 K. Integrated emission quantum yields ϕ_{em} were estimated relative to $(\mathrm{Bu_4N})_2[\mathrm{Mo_6Cl_{14}}]$ ($\phi_{\mathrm{em}} = 0.19$) as a reference.[17]

X-ray structural determinations: Well-shaped crystals of **5a**$\cdot 6\,\mathrm{H_2O}$ and **6a**$\cdot 2\,\mathrm{CH_2Cl_2} \cdot 6\,\mathrm{H_2O}$ were obtained by diffusing diethyl ether into a solution of the respective compound in dichloromethane, and those of **6b**$\cdot \mathrm{CH_3OH} \cdot 6\,\mathrm{H_2O}$ and **10a**$\cdot 12\,\mathrm{H_2O}$ were grown by the diffusion of methanol and acetonitrile, respectively, into solutions of the compounds in chloroform. Data collections were performed on a Rigaku RAXIS RAPID diffractometer (equipped with IP detector) with graphite-monochromated $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda = 0.71069$ Å) at −100 °C for **5a**$\cdot 6\,\mathrm{H_2O}$ and **6a**$\cdot 2\,\mathrm{CH_2Cl_2} \cdot 6\,\mathrm{H_2O}$ and at room temperature for **6b**$\cdot \mathrm{CH_3OH} \cdot 6\,\mathrm{H_2O}$ and **10a**$\cdot 12\,\mathrm{H_2O}$ (see Table 3). The data were corrected for Lorentz and polarization effects, and an absorption correction (ψ scans) was applied to the data set. The atomic coordinates of the metal atoms were determined by heavy-atom Patterson method and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structures were refined by full-matrix least-squares technique with anisotropic thermal parameters for all the non-hydrogen atoms in **6a**$\cdot 2\,\mathrm{CH_2Cl_2} \cdot 6\,\mathrm{H_2O}$ and **6b**$\cdot \mathrm{CH_3OH} \cdot 6\,\mathrm{H_2O}$ and the carbon atoms in **5a**$\cdot 6\,\mathrm{H_2O}$ and **10a**$\cdot 12\,\mathrm{H_2O}$ only with isotropic thermal parameters. Hydrogen atoms were included but not refined. All calculations were performed by using the TEXSAN program

Table 3. Summary of the crystallographic data for **5a**$\cdot 6H_2O$, **6a**$\cdot 2CH_2Cl_2\cdot 6H_2O$, **6b**$\cdot CH_3OH\cdot 6H_2O$, and **10a**$\cdot 12H_2O$.

	5a$\cdot 6H_2O$	**6a**$\cdot 2CH_2Cl_2\cdot 6H_2O$	**6b**$\cdot CH_3OH\cdot 6H_2O$	**10a**$\cdot 12H_2O$
formula	$C_{100}H_{88}I_2P_8Se_8Re_6\cdot 6H_2O$	$C_{104}H_{96}I_2O_4P_8Se_8Re_6\cdot 2CH_2Cl_2\cdot 6H_2O$	$C_{104}H_{96}I_2O_4P_8Se_8Re_6\cdot CH_3OH\cdot 6H_2O$	$C_{112}H_{112}I_2O_4P_8Se_8Re_6\cdot 12H_2O$
M_r	3648.41	3938.38	3782.54	3988.82
T [K]	173.2	173.2	293.2	293.2
crystal size [mm]	0.60 × 0.30 × 0.10	0.60 × 0.20 × 0.20	0.50 × 0.30 × 0.20	0.40 × 0.30 × 0.30
crystal system	triclinic	monoclinic	monoclinic	tetragonal
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$I4_1/a$ (no. 88)
a [Å]	14.861(2)	13.3101(4)	34.236(2)	19.9345(5)
b [Å]	15.984(3)	23.0970(7)	23.048(1)	19.9345(5)
c [Å]	13.072(2)	19.5858(6)	31.183(1)	35.850(1)
α [°]	100.944(7)			
β [°]	103.979(5)	92.532(1)	103.130(2)	
γ [°]	93.677(8)			
V [Å^3]	2938.5(8)	6015.2(3)	23962(1)	14246.4(6)
Z	1	2	8	4
ρ_{calcd} [g cm^{-3}]	2.062	2.174	2.097	1.86
$\mu_{MoK\alpha}$ [mm^{-1}]	9.315	9.198	9.145	7.70
λ [Å]	0.71069	0.71069	0.71069	0.71069
2θ range [°]	$4.0 < 2\theta < 55.0$	$2.8 < 2\theta < 55.0$	$3.2 < 2\theta < 55.0$	$2.9 < 2\theta < 55.0$
unique reflections	12321	13700	24737	8310
observed reflections [$I > 3\sigma(I)$]	9004	10353	11122	2871
R	0.088	0.037	0.049	0.045
R_w	0.078	0.048	0.055	0.065

package.[18] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159915 (**5a**$\cdot 6H_2O$), CCDC-159916 (**6a**$\cdot 2CH_2Cl_2\cdot 6H_2O$), CCDC-159917 (**6b**$\cdot CH_3OH\cdot 6H_2O$), and CCDC-159918 (**10a**$\cdot 12H_2O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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