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Formation of "A-frame" dirhenium(I) hexacarbonyl complexes by *trans*-1,2-bis(diphenylphosphino)ethylene and bis(bidentate) ligands

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Abstract

A series of A-frame dirhenium(I) hexacarbonyl complexes bridged by *trans*-1,2-bis(diphenylphosphino)ethylene (dppene) and bis(bidentate) ligands (L) were synthesized: $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-L})]$ (L = 1,2-dithioooxalate, **1**; tetrathiooxalate, **2**; dithiooxamidate, **3** and oxamidate, **4**). X-ray crystallographic analysis of **1** – **3** confirmed that the dppene ligand adopts a *syn* bridging conformation with nearly eclipsed P-Re bonds in these complexes. The angle between the phosphorus lone pairs of the diphosphine is adjusted to suit different Re···Re distances (5.6 – 6.4 Å) mainly by twisting the ethylene C=C bond and enlarging the P-C=C angles of the phosphine backbone. Complex **2** forms dimers in the solid state via intermolecular S···S interactions (3.39 Å). Proton and ^{31}P NMR data indicate that these dimers persist in chloroform solution but not in DMSO. Natural bond orbital analysis revealed the S···S interactions to be between the orbital occupied by the lone pair electrons in each sulfur atom as a donor, and virtual orbitals consisting of S-C σ*, S-Re σ*, and S-C π* states on the acceptor sulfur atom. The binding energy of the dimer was explicitly computed to be 8.14 kcal/mol.

Keywords:

Rhenium(I) carbonyl; 1,2-dithiooxalate; tetrathiooxalate; dithiooxamidate; *trans*-1,2-bis(diphenylphosphino)ethylene; chalcogen-chalcogen interaction

1. Introduction

Dirhenium(I) hexacarbonyl units with bridging bis(bidentate) ligands like 2,2′-bipyrimidine,[1] bis(benzimidazolate) [2] and chloranilate [3] are useful building blocks for molecular rectangles. The bis(bidentate) ligands generally form the shorter edges of the rectangle, while rigid *exo*-bidentate ligands, such as 4,4′-bipyridine and *trans*-1,2-bis(pyridyl)ethylene,[1] are used to form the longer edges. Linear oligomers/polymers or catenanes can, in principle, also be formed in the reaction of *exo*-bidentate ligands with $\{Re_2(CO)_6L\}$ units [L = bis(bidentate) ligand]. We have studied the reaction of $[Re_2(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]_n$ with *trans*-1,2-bis(diphenylphosphino)ethylene (dppene). Surprisingly, the major product (79% yield) of the reaction was $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$, which has an “A-frame” structure with a *syn*-bridging dppene (Figure 1).[4] This structure, with almost perfectly eclipsed Re-P bonds (Re–P···P–Re torsional angle of 0.7°) and a rather short Re···Re distance (5.613 Å), was unexpected in view of the rigid backbone and *trans*-oriented phosphino groups of dppene. Indeed, amongst the μ_2-dppene complexes found in the Cambridge Structural Database (Version 5.33, May 2012), [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)] has the smallest M–P···P–M torsional angle and shortest M···M distance, there being only six other crystal structures of dppene complexes with nearly eclipsed M-P bonds (M–P···P–M torsional angle 7.0 – 13.8°). The latter structures (Refcodes WIJSAK, WIJRUD, WINWUM, QAGSEW, QAGSIA, QUBGEZ) have much larger M···M distances (6.71 – 6.80 Å), however, and they all contain a 10-membered {M_2(μ_2-dppene)$_2$} ring without additional bridging ligands.

The facile formation of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)] and its stability raised the possibility of preparing analogous complexes, wherein the oxalate ligand is replaced by 1,2-dithioooxalate (dto), tetrathiooxalate (tto), dithiooxamidate (dtox) or oxamidate (oxa) (Scheme 1). To our knowledge, no rhenium(I) carbonyl complexes, except $Cs_4[Re_2(CO)_6(dto)_3]$,[5] have been reported for the latter ligands. In this paper, we report the synthesis and spectroscopic characterisation of the complexes [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-L)] (L = dto, **1**; tto, **2**; dtox, **3**; oxa, **4**). The crystal structures of **1** – **3** are also analysed and compared with that of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)]. Interestingly, complex **2** forms dimers in the crystal lattice via S···S interactions. Theoretical investigations on the nature of chemical bonding in these interactions were carried out. Variable-temperature and two-dimensional ^{31}P NMR evidence for the persistence of these dimers in chloroform will be discussed.

2. Results and discussion

2.1 Syntheses

2.1.1 $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]$, **1**

Complex **1** was prepared in a similar way as its oxalate analogue, $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$.[4] The precursor, $[\{Re(CO)_5\}_2(\mu_2\text{-}C_2S_2O_2\text{-}\kappa^2 S,S)]$, **A**, was first prepared via the reaction of $[Re(CO)_5(CF_3SO_3)]$ with potassium 1,2-dithiooxalate, $[K_2C_2S_2O_2]$, in water. Compound **A** shows a similar pattern of $\nu(C{\equiv}O)$ absorption bands as its manganese analogue $[\{Mn(CO)_5\}_2(\mu_2\text{-}C_2S_2O_2\text{-}\kappa^2 S,S)]$.[6] It also shows a sharp IR band at 1645 cm^{-1}, which is assigned to the non-coordinated C=O groups.

On refluxing in THF, compound **A** is slowly converted (18 h, monitored by IR spectroscopy) to the polymeric complex $[Re_2(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]_n$ (Scheme 2). The latter is analogous to $[Re_2(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]_n$, which is formed by the thermal decarbonylation (1 h in refluxing THF) of $[\{Re(CO)_5\}_2(\mu_2\text{-}C_2O_4\text{-}\kappa^2 O,O)]$.[4] The longer reaction time required for the decarbonylation of **A** compared to the oxalate analogue is consistent with the fact that dithiooxalate is a stronger Lewis base than oxalate. Being a stronger base, the dithiooxalate ligand would increase the electron density on rhenium and hence strengthen the Re-CO backbonding. The IR spectrum of $[Re_2(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]_n$ shows two broad bands at 2025 and 1909 cm^{-1}, indicating that the decarbonylated compound contains the tricarbonyl rhenium moiety. The $\nu(C{=}O)$ absorption band at 1645 cm^{-1} is also diminished, indicating that the oxygen atoms are coordinated to the Re atoms.

Reaction of $[Re_2(CO)_6(\mu,\eta^2:\eta^2-C_2S_2O_2)]_n$ with one molar equivalent (based on dithiooxalate) of dppene yields $[Re_2(\mu\text{-dppene})(CO)_6(\textit{cis}-\mu,\eta^2:\eta^2-C_2S_2O_2)]$, **1** (Scheme 2). Complex **1** shows two peaks in its ^{31}P NMR spectrum, indicating the non-equivalence of the two Re centres. The peak at lower field (42.4 ppm) is assigned to the phosphorus bonded to the *O,O*-chelated rhenium, which would be more electron-deficient than that bonded to the *S,S*-chelated rhenium centre (δ_P 25.0 ppm). The *cis* configuration of the dithiooxalate ligand is confirmed by X-ray crystallography (*vide infra*).

2.1.2 $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{- }C_2S_4)]$, **2**

Reaction of $[Re(CO)_5(CF_3SO_3)]$ with $[Et_4N]_2[C_2S_4]$ in water gives a dark blue precipitate which shows $\nu(C\equiv O)$ bands at 2102, 2011, 1944 and 1909 cm^{-1}, respectively. The frequency of the highest-energy $\nu(C\equiv O)$ absorption ($\tilde{\upsilon}_{max}$) suggests that the precipitate contains $\{Re(CO)_4\}$ instead of $\{Re(CO)_5\}$ units, *i.e.*, $[\{Re(CO)_4\}_2(\mu,\eta^2:\eta^2-C_2S_4)]$ was formed instead of $[\{Re(CO)_5\}_2(\mu_2-C_2S_4-\kappa^2 S,S)]$. The displacement of an additional CO group on each rhenium atom by tetrathiooxalate is probably favoured due to the greater stability of Re-S bonds.

As the above precipitate was resistant to further decarbonylation (no apparent reaction after refluxing in THF for 20 h), a different strategy was adopted to synthesize complex **2**. Reaction of $[NEt_4]_2[ReBr_3(CO)_3]$ in THF with $AgBF_4$, followed by $[Et_4N]_2[C_2S_4]$, affords a deep blue intermediate (possibly $[Re_2(THF)_2(CO)_6(\mu,\eta^2:\eta^2-C_2S_4)]$) that reacts with dppene to form complex **2** (Scheme 3).

2.1.3 $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2-C_2S_2N_2H_2)]$, **3** and $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2-$

$C_2O_2N_2H_2$)], **4**

The dithiooxamidate and oxamidate complexes [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2S_2N_2H_2$)], **3** and [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2O_2N_2H_2$)], **4** were prepared by reacting [$Re(CO)_5(CF_3SO_3)$] with dithiooxamide and oxamide, respectively, in refluxing THF, followed by reaction with dppene (Scheme 4). Complex **3** exists as two isomers, [Re_2(μ-dppene)$(CO)_6$(*cis*-μ,η^2:η^2-$C_2S_2N_2H_2$)] (*cis*-**3**) and [Re_2(μ-dppene)$(CO)_6$(*trans*-μ,η^2:η^2-$C_2S_2N_2H_2$)] (*trans*-**3**). Although the isomers could not be resolved by thin layer chromatography (TLC), they could be separated based on a difference in their solubility. While *cis*-**3** is sparingly soluble in cold (5 ºC) chloroform, *trans*-**3** is readily soluble. Complex *cis*-**3** shows two ^{31}P NMR peaks (δ_P 37.3 and 20.9 ppm), which are assigned to the phosphorus atoms bonded to the *N,N*-chelated and *S,S*-chelated Re centres, respectively. Only one ^{31}P signal (31.0 ppm) is displayed by *trans*-**3**, reflecting the equivalence of the phosphorus atoms.

Complex **4**, [Re_2(μ-dppene)$(CO)_6$(*cis*-μ,η^2:η^2-$C_2O_2N_2H_2$)] was obtained in low yield together with the bis-dppene-bridged compound [Re_2(μ-dppene)$_2(CF_3SO_3)_2(CO)_6$] **5** (Scheme 4). The low yield of **4** and the formation of a significant amount of the oxamide-free compound, **5**, are probably due to the low solubility of oxamide in THF (solvent for the reaction). Many complexes with the {M_2(μ-dppene)$_2$} motif have been reported.[7-12] Complex **4** shows two singlet ^{31}P peaks, at 33.6 and 30.4 ppm respectively. The chemical shift difference between these peaks in $CDCl_3$ ($\Delta\delta_P$ 3.2 ppm) is smaller than those for **1** ($\Delta\delta_P$ 17.4 ppm) and *cis*-**3** ($\Delta\delta_P$ 14.3 ppm) since the difference in electronegativity between N and O is smaller than that between N and S.

Only one peak (δ_P 5.3 ppm) is observed in the ^{31}P-NMR spectrum of complex **5**, indicating that all phosphorus atoms are equivalent. The presence of [$Re(CO)_3$]

groups in **5** is indicated by the positions of the ν(C≡O) peaks (2048, 1975, and 1909 cm^{-1}) in its IR spectrum. Medium ν(C–F) absorptions (1233 and 1200 cm^{-1}) indicate the presence of the triflate groups.

2.2 Infrared spectra of complexes **1 – 4**

The C≡O stretching patterns of complexes **1 – 4** are very similar to that of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$.[4] As expected, the $\tilde{\upsilon}_{max}$ of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$ (2033 cm^{-1}) is much higher than that of its tetrathiooxalate analogue, **2** (2018 cm^{-1}). Oxygen, being more electronegative than sulfur, would contribute less electron density to rhenium than sulfur. Hence, there would be a smaller extent of back-donation of electron density to the π* orbitals of the CO ligands in $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$. Interestingly, the $\tilde{\upsilon}_{max}$ of **1** (2027 cm^{-1}) is closer to that of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$ than to that of **2**. This high $\tilde{\upsilon}_{max}$ value is attributed to the presence of an *O,O*-chelated $\{Re(CO)_3\}$ group in **1**. The low $\tilde{\upsilon}_{max}$ of complex **3** (2016 cm^{-1}) is somewhat surprising, considering that an *N,N*-chelated $\{Re(CO)_3\}$ group is present in *cis*-**3**. A plausible explanation for this is that the nitrogen donor atoms of dithiooxamidate are strong π-donors in addition to being strong σ-donors.

2.3 X-ray crystallography

Compounds **1, 2** and **3** are iso-structural to $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$, each comprising two $\{Re(CO)_3\}$ fragments linked by a bis(bidentate) ligand (L) and a bridging dppene ligand, giving an “A-frame” structure (Figures 2 – 4). The $\{Re_2L\}$ core adopts a boat conformation, with the two Re atoms forming the ends of the boat.

Generally, replacing oxygen or nitrogen by sulfur roughly doubles the dihedral angle between the Re-X-X plane (X = *cis*-donor atoms of L) and the mean plane of L (see Table 1). This correlates with the widening of the Re-P···P angle and increasing Re···Re distance (Table 1). Interestingly, the Re-P···P-Re torsional angle of **2** (0.3°) is even smaller than that of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)], while those of **1** and **3** (2.7 and 21.2°, respectively) are much larger. It thus appears that the torsional angle increases when the bis(bidentate) ligand is of lower symmetry.

It is noteworthy that the P···P distance (4.46 – 4.55 Å) is fairly constant for complexes **1** – **3** and [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)], despite the large variation in Re···Re distance (5.61 – 6.38 Å). This suggests that the angle between the phosphorus lone pairs is adjusted to the Re···Re distance mainly by distortion of the dppene backbone. Indeed, the P-C···C-P torsional angles of **1** – **3** and [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)] show large deviations from 180° (see Table 1), indicating that the C=C bond of dppene can be twisted very significantly (by up to 18°). It is also noteworthy that the P-C=C angles (122.4 – 128.9°) (Figures 2 – 4 and Reference [4]) differ significantly from 120°.

The coordination environments of the Re atoms in complexes **1** – **3** are severely distorted from the ideal octahedral geometry, as seen from the Re centered bond angles (Figures 2 – 4). In addition, the average Re-P bond lengths of **1**, **2** and **3** **(**2.519, 2.525 and 2.485 Å, respectively) are longer than usual (cf. 2.467 Å for the chelated diphosphine complex, [(η^2-dppe)$(OC)_3$Re-OC(O)O-Re$(CO)_3$(η^2-dppe)]).[13] The Re-P bonds of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-C_2O_4)] (average 2.502 Å) are similarly elongated.[4]

Centrosymmetric dimers linked by short intermolecular S···S contacts (3.39 – 3.41 Å, cf. van der Waals separation of 3.70 Å [14]) occur in the crystal of complex **2**

(Figure 5). Although non-bonded S···S interactions are well known,[15, 16] those involving sulfur atoms of tetrathiooxalate have not, to our knowledge, been reported before. We therefore carried out theoretical investigations on the nature of chemical bonding of S···S contacts in complex **2** (see below).

2.4 Theoretical investigations on the chemical bonding of S···S contacts in dimers of complex **2**

The most stable structure of the dimer of complex **2** (Figure S1) (optimized using density functional theory with hybrid functional M06-2X and hybrid basis sets) agrees well with the structure determined crystallographically (RMSD 0.77 Å). Agreement is especially good in the $\{Re_2C_2S_4\}$ cores of the interacting monomers, and the main deviations occur in the phenyl rings (Figure S2). The intermolecular S···S distances in the optimized structure (3.33 – 3.45 Å) are also very close to those observed in the crystal structure (3.39 – 3.41 Å). Since the bonding analysis would be focused on the interface between the two monomers, further analysis was based on the simulated structure which resembles most of the core part of the dimer complex.

Natural bond orbital (NBO) analysis revealed that the sulfur-sulfur interactions within the dimer are donor-acceptor like. The sulfur related NBO second-order interaction terms between the two molecular units are given in Figure 6. In all cases, these terms arise from p-σ*- and p-π*-type NBO interactions. Electrons are donated from the lone pair in the p-orbital of one sulfur atom, to the empty σ* or π* orbital on the neighboring sulfur atom. The empty σ* and π* orbitals are mainly in the form of S-C σ*, S-Re σ* and S-C π* orbitals. It should be noted that only half of the donor-acceptor interactions are shown in Figure 6 (with the donor on the left) – equivalent reciprocal donor-acceptor interactions (right to left “back-donation”) also occur. The binding energy of the dimer was explicitly computed to be 8.14 kcal/mol.

Considering the existence of three S···S pairs, the average binding energy for a single S···S interaction would be 2.71 kcal/mol, which is within the range of 2-3 kcal/mol calculated by Bleiholder *et al.* [17, 18] for one pair of interacting sulfur atoms in organosulfur compounds. It is also noteworthy that the computed binding energy of the dimer is about ten times the thermal energy (*kT*) at 298 K (0.6 kcal/mol), hence it is possible for dimers to exist at room temperature in solution (see below).

2.5 NMR spectroscopic studies of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_4)]$ **2**

The ^{31}P NMR spectrum of **2** in $(CD_3)_2SO$ shows only one singlet peak (at 36.3 ppm), which is consistent with the symmetrical structure of the complex. Two peaks (at 36.3 and 38.8 ppm) are observed, however, when the solvent is changed to $CDCl_3$. Samples recovered from $CDCl_3$, when re-dissolved in $(CD_3)_2SO$, show only the peak at 36.3 ppm, and addition of one volume of $CHCl_3$ to a solution of **2** in $(CD_3)_2SO$ did not produce the 38.8 ppm peak. Hence, the presence of two peaks in $CDCl_3$ is not due to chemical reaction of **2** with $CDCl_3$.

The above observations are attributed to the existence of only unassociated molecules of **2** (“monomers”) in $(CD_3)_2SO$, and a mixture of dimers (as found in the crystal structure) and monomers in $CDCl_3$. The ^{31}P peak at 36.3 ppm is assigned to monomers, while that at 38.8 ppm is assigned to dimers. Presumably, $(CD_3)_2SO$, being more strongly solvating than $CDCl_3$, is able to disrupt the intermolecular S···S interactions, thereby preventing the formation of dimers.

The 2D ^{31}P-^{31}P TOCSY spectrum of complex **2** in $CDCl_3$ shows no coupling between the peaks at 36.3 and 38.8 ppm (Figure 7), indicating that these peaks are not due to phosphorus atoms from the same molecule of **2**. This is consistent with the existence of separate populations of dimers and monomers of **2** in $CDCl_3$.

Correspondingly, the 2D ^{1}H-^{31}P HSQC spectrum showed that the 36.3 ppm ^{31}P signal is coupled only to the ethylene proton signal at 8.00 ppm (assigned to monomers), while the 38.8 ppm ^{31}P signal is coupled only to the ethylene proton signal at 5.00 ppm (assigned to dimers).

Variable temperature ^{31}P NMR spectra of complex **2** in $CDCl_3$ were also recorded (Figure 8). Between 213 and 323 K, both the 36.3 and 38.8 ppm peaks shift downfield as temperature decreases, with the 38.8 ppm peak (assigned to dimers) shifting much more. While the 36.3 ppm peak (assigned to monomers) broadens as temperature decreases, the opposite is true for the 38.8 ppm peak. At all temperatures studied, the 38.8 ppm peak (FWHM 12 – 30 Hz) is much broader than the 36.3 ppm peak (FWHM 2 – 6 Hz). The strong temperature dependence of the linewidth and chemical shift of the 38.8 ppm peak suggests that dynamic processes, including some form of oscillation about an equilibrium configuration, are occurring within the dimer. There is negligible change in the relative areas of the 36.3 and 38.8 ppm peaks between 213 and 323 K, indicating that the relative amounts of monomers and dimers remain largely constant in this temperature range.

3. Conclusion

A series of A-frame dirhenium(I) hexacarbonyl complexes bridged by *trans*-1,2-bis(diphenylphosphino)ethylene and bis(bidentate) ligands (1,2-dithioooxalate, tetrathiooxalate, dithiooxamidate and oxamidate) were synthesized. The facile formation of these complexes confirms that *trans*-1,2-bis(diphenylphosphino)ethylene (dppene) is able to bridge metal centres less than 6.4 Å apart by adopting a *syn* conformation with nearly eclipsed phosphorus-metal bonds. The angle between the phosphorus lone pairs of the diphosphine is adjusted to suit different Re···Re distances mainly by twisting of the ethylene C=C bond and enlarging the P–C=C angles of the phosphine backbone. The complex $[Re_2(\mu\text{-dppene})(CO)_6(\mu,(\mu,\eta^2:\eta^2\text{-}C_2S_4)]$ forms dimers in the solid state via S···S interactions. These dimers persist in chloroform solution but not in DMSO. The S···S interactions are donor-acceptor like, with the lone pair of one sulfur atom acting as the donor, and the antibonding orbital on the neighboring sulfur atom (S-C σ^*, S-Re σ^* or S-C π^*) as the acceptor.

4 Experimental

4.1 General techniques

All the reactions were performed under nitrogen or argon using standard Schlenk techniques [19]. Chemical reagents, unless otherwise stated, were obtained commercially and were used as received without any pre-treatment. Solvents were dried by standard methods [20] and distilled under nitrogen prior to use. The compounds $[Re(CO)_5(CF_3SO_3)]$,[21] $[NEt_4]_2[ReBr_3(CO)_3]$,[22] $[K_2C_2S_2O_2]$ [23] and $[NEt_4]_2[C_2S_4]$ [24] were prepared by published procedures. Preparative TLC was carried out on pre-coated silica plates of layer thickness 0.25 mm. Proton and proton-decoupled phosphorus NMR spectra were recorded at 298 K on a Bruker DRX400 spectrometer at 400 and 162 MHz respectively. Proton chemical shifts were quoted in ppm downfield of internal tetramethylsilane (TMS), and the phosphorus chemical shifts were quoted downfield of external 85% H_3PO_4. Infrared spectra (4000-450 cm^{-1}) were recorded on a Perkin-Elmer Spectrum One B FTIR spectrometer. Elemental analyses were conducted using a EURO Vector EA 3011 Elemental Analyser.

4.2 Synthesis of $[\{Re(CO)_5\}_2(\mu_2\text{-}C_2S_2O_2\text{-}\kappa^2 S,S)]$, **A**

This synthesis is analogous to that of $[\{Re(CO)_5\}_2(\mu_2\text{-}C_2O_4\text{-}\kappa^2 O,O)]$.[25] An aqueous solution (12 mL) of $[Re(CO)_5(CF_3SO_3)]$ (0.48 g, 1.0 mmol) was added to an aqueous solution (5 mL) of potassium dithiooxalate (0.10 g, 0.50 mmol), and the resultant mixture was stirred for 4 h under Ar. The yellow precipitate formed was allowed to settle, and the supernatant was removed carefully with a Pasteur pipette under argon cover. The remaining precipitate was washed several times with deionized water, each time removing the washing with a Pasteur pipette. The washed product was dried under vacuum and re-dissolved in acetone. Layering with hexane at 10°C afforded yellow crystals of compound **A**. Yield 0.35 g (91 %). IR (KBr)/cm^{-1}: 2147 (w), 2095 (m), 2058 (s), 2006 (vs), 1963 (vs) $\nu(C\equiv O)$; 1645(m) $\nu(C=O)$. *Anal.* Calcd for $C_{12}O_{12}Re_2S_2$: C, 18.6%. Found: C, 18.8%.

4.3 Thermal decarbonylation of compound **A**

Compound **A** (0.050 g, 0.065 mmol) and distilled THF (20 mL) were placed in a 120 mL Schlenk flask with a magnetic stirrer. The suspension was vacuum-degassed and refilled with Ar, then stirred under reflux for 20 h to give a dark red solution. The solvent was removed under reduced pressure, and the residue was dissolved in a minimum amount of CH_2Cl_2. Layering with hexane gave a dark red precipitate, which was washed with hexane and dried under high vacuum to give $[Re_2(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]_n$. IR (KBr)/$cm^{-1}$: 2026 (s), 1909 (vs) $\nu(C\equiv O)$. *Anal.* Calcd for $C_8O_8Re_2S_2$: C, 14.5%. Found: C, 15.0%.

4.4 Synthesis of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]$, **1**

A suspension of compound **A** (0.020 g, 0.026 mmol) in THF (20 mL) was stirred under reflux for 18 h. The resultant dark red solution was cooled to r.t., and dppene (0.0138 g, 0.035 mmol) was added. The mixture was degassed and heated to 60 °C for 4 h, after which the solvent was evaporated under reduced pressure. The residue was dissolved in a minimum volume of CH_2Cl_2 and applied to silica TLC plates. An ethyl acetate-hexane (3:7) mixture eluted an orange band ($R_f = 0.65$), from which $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_2O_2)]$, **1** was recovered by acetone extraction. Red crystals of compound **1** were grown by layering a solution of the compound in CH_2Cl_2 with hexane at r.t. Yield 0.013 g (47%). IR (KBr)/cm^{-1}: 2027 (s), 1948 (s), 1914 (s) ν (C≡O); ($CHCl_3$)/ cm^{-1}: 2042 (m), 2031 (s), 1951 (s), 1919 (s) ν (C≡O). ^1H NMR ($CDCl_3$): 7.80-7.20 (m, 20 H, Ph), δ 5.45 (q, 1H, -CH=C), δ 5.20 (q, 1H, -CH=C), $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 42.4 (s), 25.0 (s). *Anal.* Calcd for $C_{34}H_{22}O_8P_2Re_2S_2\cdot0.25C_6H_{14}$: C, 39.5; H, 2.4%. Found: C, 39.3; H, 2.7%.

4.5 Synthesis of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_4)]$, **2**

A suspension of $[NEt_4]_2[ReBr_3(CO)_3]$ (0.0385 g, 0.050 mmol) and $AgBF_4$ (0.034g, 0.17 mmol) in THF (10 mL) was shielded from light and stirred for 2 h at r.t. The precipitated AgBr and unreacted $AgBF_4$ were filtered off by suction, and $[NEt_4]_2[C_2S_4]$ (0.011 g, 0.027 mmol) was added to the filtrate. The dark blue mixture formed was stirred at r.t. for 26 h before being filtered again. An amount of dppene (0.0085 g, 0.021 mmol) was added to the filtrate, and the resultant mixture was stirred for 8 h. The solvent was evaporated under reduced pressure, and the residue was re-dissolved in a minimum volume of acetone and applied to TLC plates. Elution with ethyl acetate-hexane (3:7) mixture gave an intense blue band ($R_f = 0.74$), from which $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2S_4)]$, **2**, was recovered by acetone extraction. Blue crystals of compound **2** were grown by layering a solution of the compound in CH_2Cl_2 with hexane at r.t. Yield 0.011 g (45%). IR (KBr)/cm^{-1} : 2018 (s), 1956 (m), 1925 (s) ν (C≡O); ($CHCl_3$)/cm^{-1}: 2040 (w, sh), 2024 (s), 1953 (sh), 1922 (s) ν (C≡O). ^{1}H NMR [$(CD_3)_2SO$]: δ 7.98 (t, 2H, -CH=CH-), 7.76-7.26 (m, 20 H, Ph) ^{31}P{^{1}H}-NMR [$(CD_3)_2SO$]: δ 36.3 (s); ^{1}H NMR [$CDCl_3$]: δ 8.00 (t, 2H, -CH=CH-), 7.80-7.25 (m, 40 H, Ph), 5.00 (t, 2H, -CH=CH-), ^{31}P{^{1}H}-NMR ($CDCl_3$): 38.8 (br), 36.3 (s). *Anal.* Calcd for $C_{34}H_{22}O_6P_2Re_2S_4{\cdot}0.55C_6H_{14}$: C, 39.4; H, 2.6%. Found: C, 39.0; H, 3.1%.

4.6 Synthesis of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2S_2N_2H_2$)], **3**

To a solution of [$Re(CO)_5(CF_3SO_3)$] (0.040 g, 0.084 mmol) in THF (12 mL) was added H_2dtox (0.0051 g, 0.043 mmol). The mixture was refluxed for 18 h to give an orange-red solution. The solution was cooled to r.t. and dppene (0.017 g, 0.043 mmol) was added. The mixture was heated at 60°C for another 6 h before the volume of solvent was reduced to *ca.* 1 mL under reduced pressure. Application to silica TLC plates and elution with ethyl acetate-hexane (3:7) mixture afforded an orange band (R_f = 0.70), from which [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2S_2N_2H_2$)] **3** was recovered by acetone extraction. Orange crystals of **3** were grown by layering a solution of the compound in CH_2Cl_2 with hexane at r.t. Yield 0.018 g (41%). IR of (KBr)/cm^{-1}: 2016 (s), 1943 (sh), 1929 (s), 1899 (s) ν(C≡O). ^{1}H NMR ($CDCl_3$): δ9.06 (s, 2 H, NH), 9.00 (s, 2 H, NH), 7.78-7.20 (m, 40 H, Ph), 5.71 (q, 1 H, -CH=C), 5.48 (t, 2 H, -CH=CH-), 5.18 (q, 1 H, -CH=C). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 37.3 (s), 31.7 (s), 20.9 (s). *Anal.* Calcd for $C_{34}H_{24}N_2O_6P_2Re_2S_2{\cdot}0.55C_6H_{14}$: C, 40.5; H, 2.8; N, 2.5%. Found: C, 40.1; H, 4.0; N, 2.3%. Storing a $CDCl_3$ solution of **3** overnight at *ca.* 5°C resulted in the precipitation of the isomer, *cis*-**3**, which was separated by filtration and washed with cold $CHCl_3$. $^{31}P\{^1H\}$-NMR [$(CD_3)_2CO$]: δ 33.0 (s), 18.7(s). The filtrate contained mainly *trans*-**3**, $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 31.7 (s).

4.7 Synthesis of [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2O_2N_2H_2$)], **4**

The experiment was similar to that described in Section 4.6 except that H_2dtox was replaced by H_2oxa and the reaction mixture was heated for 8 h instead of 6 h after the addition of dppene. Two colourless bands were isolated by TLC [ethyl acetate:hexane = 3:7]: the first band (R_f = 0.64) was identified to be complex **4**, [Re_2(μ-dppene)$(CO)_6$(μ,η^2:η^2-$C_2H_2N_2O_2$)] (0.008 g, 20% yield) and the second (R_f = 0.28) was [Re_2(μ-dppene)$_2$$(CF_3SO_3)_2$$(CO)_6$], complex **5** (0.011 g, 16 % yield based on Re).

IR of compound **4**, (KBr)/cm^{-1}: 2029 (s), 2015 (s), 1889 (s), 1882 (vs) ν(C≡O); 1635 (m) , 1603 (s) ν(C=O). ^{1}H NMR ($CDCl_3$): δ 7.70-7.30 (m, 20 H, Ph), 5.68 (q, 1 H, CH=C), 5.50 (q, 1 H, CH=C). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 33.6 (s), 30.4 (s). *Anal.* Calcd for $C_{34}H_{24}N_2O_8P_2Re_2$: C, 39.9; H, 2.4; N, 2.7%. Found: C, 40.2; H, 3.2; N, 2.2%.

IR of compound **5**, (KBr)/cm^{-1}: 2048 (vs), 1975 (s), 1909 (s) ν(C≡O); 1233 (m), 1200 (m) ν(CF). ^{1}H NMR ($CDCl_3$): δ 7.61-7.28 (m, 40 H, Ph), 6.61 (t, 4 H, -CH=CH-). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 5.3 (s). *Anal.* Calcd for $C_{60}H_{44}F_6O_{12}P_4Re_2S_2 \cdot 0.5C_6H_{14}$: C, 45.2; H, 3.1%. Found: C, 44.7; H, 3.7%.

4.8 X-ray crystallography

Crystals of compounds **1**, **2** and **3** were mounted on glass fibres, and data were collected at 298±2 K using the θ-2θ mode, on a Siemens P4 diffractometer with Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were performed using psi-scan data (for **1** and **2**) or by integration (for **3**). Crystal structures of **1** and **3** were solved by the heavy-atom method, while that of **2** was solved by direct methods. The structures were refined using the full matrix least-squares method on F^2.

The crystal of compound **1** contains one CH_2Cl_2 solvate position (not disordered) per molecule of **1**. The atoms of the CH_2Cl_2 molecule were however best modeled as having half occupancy; this is attributed to partial desolvation. The following distance restraints were applied to the CH_2Cl_2 molecule: C-Cl 1.7600(1) and Cl···Cl 2.8800(1) Å.

The *cis* and *trans* isomers of **3** co-crystallize, giving rise to disorder in the dtox ligand in the crystal structure. There are two alternative positions for the N(2) and S(2) atoms of the ($C_2S_2N_2H_2$) ligand (Figure 4). The N(2) and S(2) positions each has 60% occupancy, and the N(2A) and S(2A) positions each has 40% occupancy. The following distance restraints were applied to the {Re_2(dtox)} unit: Re(1)-N(2A) and Re(2)-N(2) 2.170(1), Re(1)-S(2) and Re(2)-S(2A) 2.490(1), C(8)-N(2) and C(8)-N(2A) 1.300(1), C(8)-S(2) and C(8)-S(2A) 1.700(1) Å.

All non-hydrogen atoms, except N(2A) and S(2A) of compound **3**, were refined anisotropically. In addition, the following atoms of compound **3** were restrained to approximate isotropic behaviour to prevent their thermal motion from becoming negative: N(1), N(2), C(1), C(2), C(8), C(10), C(12), C(13), C(43), C(21) and C(35). Hydrogen atoms were introduced in calculated positions and allowed to ride on their carrier atoms with idealized bond lengths and angles.

Crystal and refinement data for compounds **1 – 3** are given in Table 2.

4.9 Computational methods

With the crystal structure as input, the geometry of the dimer of complex **2** was fully optimized by density functional theory using the hybrid functional of Truhlar and Zhao [26] as built into the Gaussian 09 package [27]. We used Pople's 6-311G basis set [28] for the lighter atoms (H, C), the triple Dunning's correlation consistent basis sets cc-PVTZ [29] for sulfur, oxygen and phosphorus, and the Los Alamos effective-core potential (ECP) Lanl2DZ [30-32] basis set with relativistic effect for rhenium atoms, where the [Xe]4f inner electrons of Re are treated as core electrons and the outermost valence electrons are explicitly described using a double-zeta basis set. The convergence thresholds were 10^{-3} a.u. on the gradient, 10^{-3} a.u. on the displacement, and 10^{-6} a.u. on the energy. To this end, NBO analyses [33, 34] were performed on the dimer's optimized geometries using the HF/cc-PVTZ-ECP density. The principal interacting groups, such as sulfur-sulfur contacts were identified by means of NBO analysis [33, 34].

5. Supplementary Material

Crystallographic data for complexes **1**, **2** and **3** may be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: _/44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on quoting the depository numbers CCDC 1040114, 1040115 and 1040116, respectively. Details of the computational data are given in the Supplementary Information online.

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Table 1. Comparison of selected structural parameters of $[\mathrm{Re}_2(\mu\text{-dppene})(\mathrm{CO})_6(\mathrm{L})]$ complexes [L = bis(bidentate) ligand].

L	Angles between mean plane of L and ReXX planes[b] (°)	Re-P···P angles (°)	Re···Re (Å)	P···P (Å)	Torsional angles (°)	
					Re-P···P-Re	P-C-C-P
oxalate[a]	7.7 8.7	102.4 104.0	5.61	4.47	0.7	162.8
cis-dithiooxamidate	10.4 (X = N) 24.9 (X = S)	109.3 106.4	6.05	4.46	21.2	161.8
trans-dithiooxamidate	16.0 18.7					
dithiooxalate	8.2 (X = O) 16.2 (X = S)	106.7 108.7	6.06	4.53	2.7	168.3
tetrathiooxalate	17.3 16.8	112.3 110.3	6.38	4.55	0.3	173.6

[a] Data taken from CCDC 239510.

[b] XX = *cis* donor atoms of L

Table 2. Crystallographic data for compounds **1, 2** and **3**

Empirical formula	$C_{34.50}H_{23}ClO_8P_2Re_2S_2$, **1**	$C_{34}H_{22}O_6P_2Re_2S_4$, **2**	$C_{34}H_{24}N_2O_6P_2Re_2S_2$, **3**
Formula weight	1099.44	1089.1	1055.01
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	Pbca	P-1
Unit cell dimensions	a = 10.812(3) Å, α =83.87(1)°	a = 17.226(4) Å, α = 90 °	a = 11.413(6) Å, α = 68.32(3)°
	b = 12.899(2) Å, β = 89.97(1)°	b = 19.37(1) Å, β = 90 °	b = 11.934(8) Å, β = 88.55(3)°
	c = 13.980(2) Å, γ = 81.37(2)°	c = 21.911(5)Å, γ = 90 °	c = 14.144(6) Å, γ = 78.51(4)°
Volume (Å^3), Z	1916.4(7), 2	7312(6), 8	1752 (2), 2
Density (calculated) (Mg/m^3)	1.905	1.979	2.000
Absorption coefficient (mm^{-1})	6.620	6.975	7.161
F(000)	1046	4144	1004
Crystal size (mm^3)	0.3 x 0.3 x 0.2	0.3 x 0.3 x 0.2	0.3 x 0.1 x 0.1
Theta range for data collection (º)	1.91 to 25.00	1.83 to 25.01	1.82 to 25.00
Reflections collected	7902	7685	7043
Independent reflections	6730 [R(int) = 0.0258]	6404 [R(int) = 0.0416]	6043 [R(int) = 0.0776]
Max. and min. transmission	0.4928 and 0.3118	1.0000 and 0.5456	0.5362 and 0.4010
Data / restraints / parameters	6730 / 3 / 460	5878 / 0 / 367	5241 / 74 / 441
Final R indices [$I>2\delta(I)$]	R_1 = 0.0406, wR_2 = 0.0905	R_1 = 0.0406, wR_2 = 0.0905	R_1 = 0.0822, wR_2 = 0.1780
R indices (all data)	R_1 = 0.0588, wR_2 = 0.1077	R_1 = 0.0697, wR_2 = 0.1077	R_1 = 0.1606, wR_2 = 0.2057
Largest diff. peak and hole (e.Å^{-3})	2.034 and -3.676	0.739 and -1.217	2.431 and -2.951

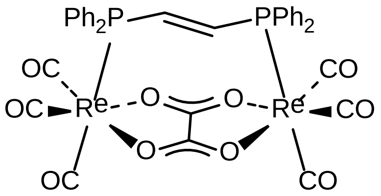


Figure 1. Structure of $[Re_2(\mu\text{-dppene})(CO)_6(\mu,\eta^2:\eta^2\text{-}C_2O_4)]$.

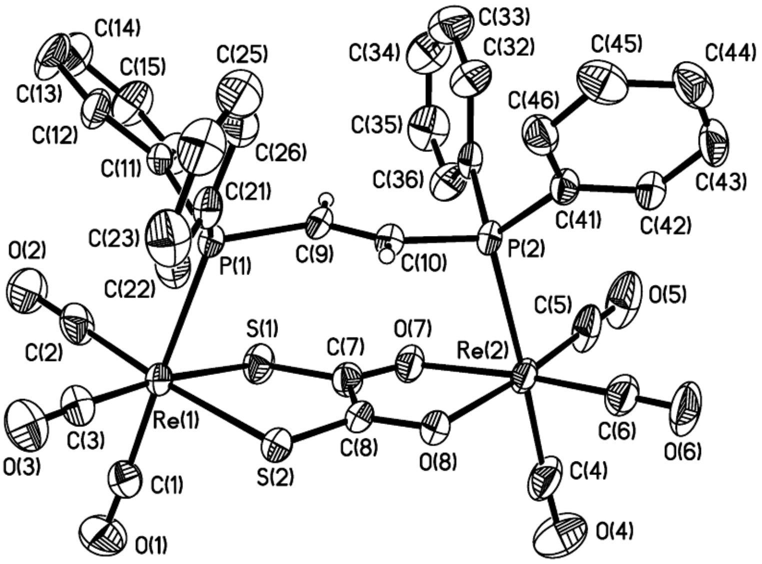


Figure 2. Crystal structure of complex **1** (40% probability ellipsoids). Hydrogen atoms of the phenyl rings are omitted for clarity. Selected bond lengths (Å): **Re(1)-P(1)** 2.520(2), **Re(2)-P(2)** 2.518(2), **C(9)-C(10)** 1.34(1). Selected bond angles (°): **Re(1)-P(1)-C(9)** 113.0(3), **P(1)-C(9)-C(10)** 126.8(6), **Re(2)-P(2)-C(10)** 110.2(3), **P(2)-C(10)-C(9)** 122.4(6), **P(1)-Re(1)-S(1)** 86.91(8), **P(1)-Re(1)-S(2)** 86.00(7), **P(2)-Re(2)-O(7)** 83.8(2), **P(2)-Re(2)-O(8)** 86.2(2), **S(1)-Re(1)-S(2)** 84.40(7), **O(7)-Re(2)-O(8)** 73.7(2).

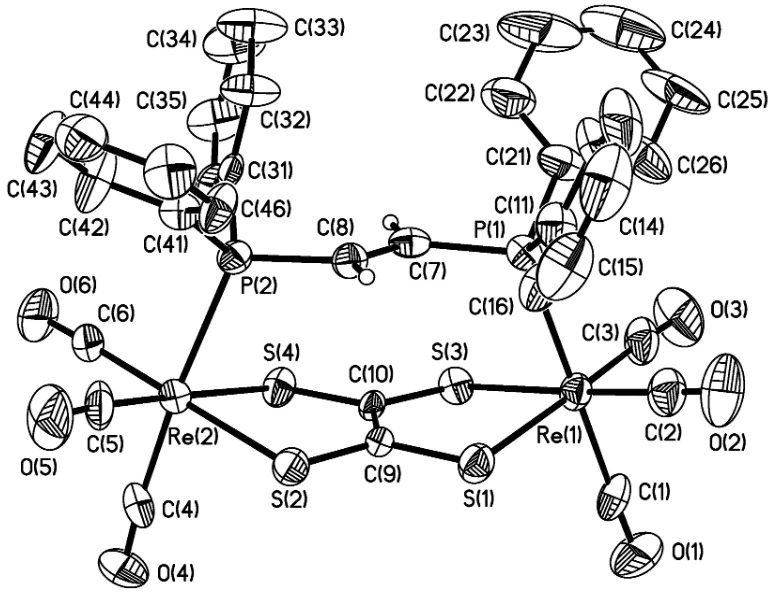


Figure 3. Crystal structure of complex **2** (40% probability ellipsoids). Hydrogen atoms of the phenyl rings are omitted for clarity. Selected bond lengths (Å): **Re(1)-P(1)** 2.535(2), **Re(2)-P(2)** 2.514(2), **C(7)-C(8)** 1.31(1). Selected bond angles (º): **P(1)-Re(1)-S(1)** 87.86(8), **P(1)-Re(1)-S(3)** 86.34(7), **S(1)-Re(1)-S(3)** 82.63(7), **P(2)-Re(2)-S(2)** 87.50(7), **P(2)-Re(2)-S(4)** 85.44(7), **S(2)-Re(2)-S(4)** 82.62(7), **Re(1)-P(1)-C(7)** 112.5(2), **P(1)-C(7)-C(8)** 128.9(6), **Re(2)-P(2)-C(8)** 113.9(3), **P(2)-C(8)-C(7)** 123.9(6).

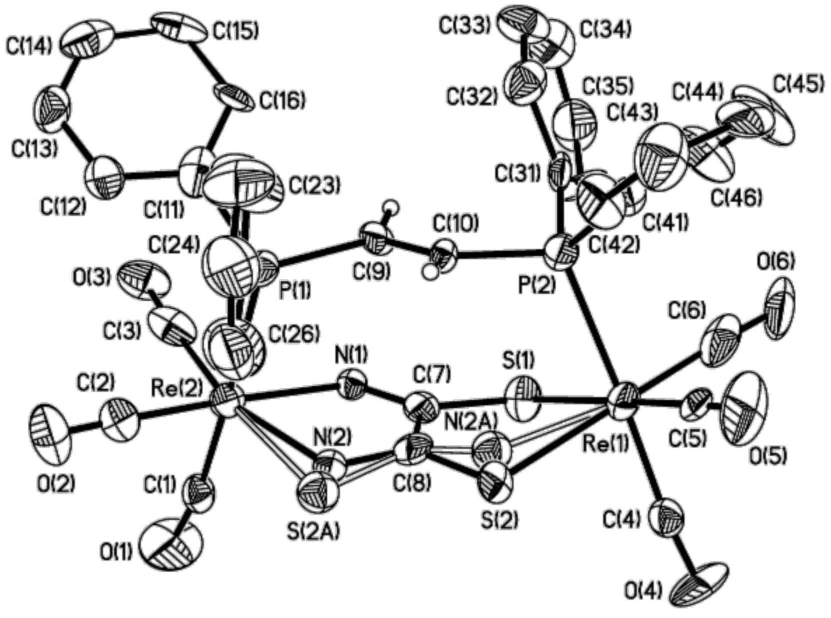


Figure 4. Crystal structure of complex **3** (40% probability ellipsoids). The N(2) and S(2) positions each has 60% occupancy, and the N(2A) and S(2A) positions each has 40% occupancy. Hydrogen atoms of the phenyl rings and nitrogen atoms are omitted for clarity. Selected bond lengths (Å): **Re(1)-P(2)** 2.489(5), **Re(2)-P(1)** 2.480(5), **C(9)-C(10)** 1.31(2). Selected bond angles (º): **P(2)-Re(1)-S(1)** 87.3(2), **P(2)-Re(1)-S(2)** 92.1(3), **S(1)-Re(1)-S(2)** 83.0(2), **P(2)-Re(1)-N(2A)** 85(1), **S(1)-Re(1)-N(2A)** 69.4(5), **P(1)-Re(2)-N(1)** 88.9(4), **P(1)-Re(2)-N(2)** 84.6(7), **N(1)-Re(2)-N(2)** 70.2(5), **P(1)-Re(2)-S(2A)** 87.6(4), **N(1)-Re(2)-S(2A)** 82.0(5), **Re(1)-P(2)-C(10)** 113.2(6), **P(2)-C(10)-C(9)** 124(2), **Re(2)-P(1)-C(9)** 110.8(7), **P(1)-C(9)-C(10)** 127(2).

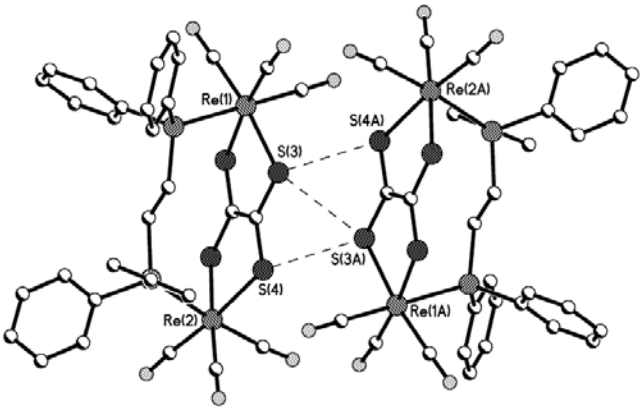


Figure 5. Dimerisation of compound **2** via S···S intermolecular interactions; S(3)···S(4A) 3.39 Å, S(3)···S(3A) 3.41 Å, S(4)···S(3A) 3.39 Å.

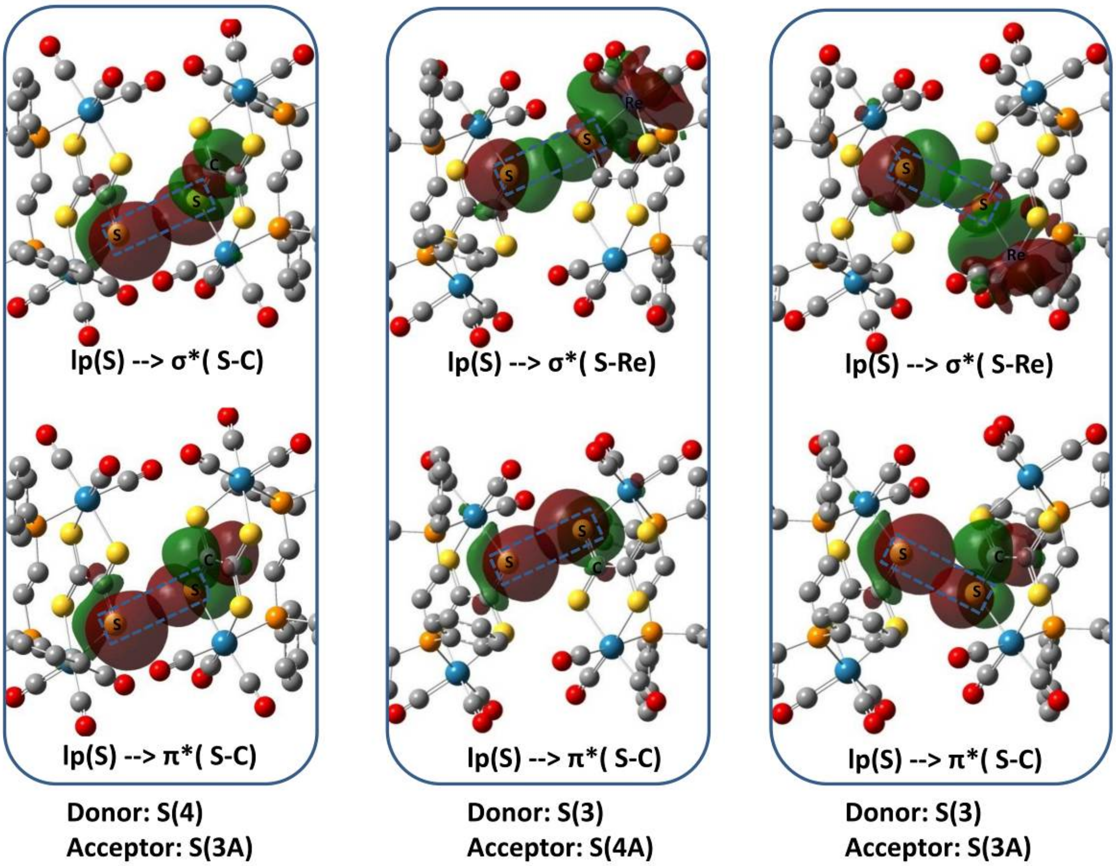


Figure 6. The sulfur related NBO second-order interaction terms between two molecules of complex **2**. Only half of the donor-acceptor interactions are shown (with the donor on the left); equivalent reciprocal donor-acceptor interactions (right to left) also occur. For clarity, the hydrogen atoms and the phenyl rings which are sticking out are not shown, and the donor-acceptor pair is outlined by a dashed box.

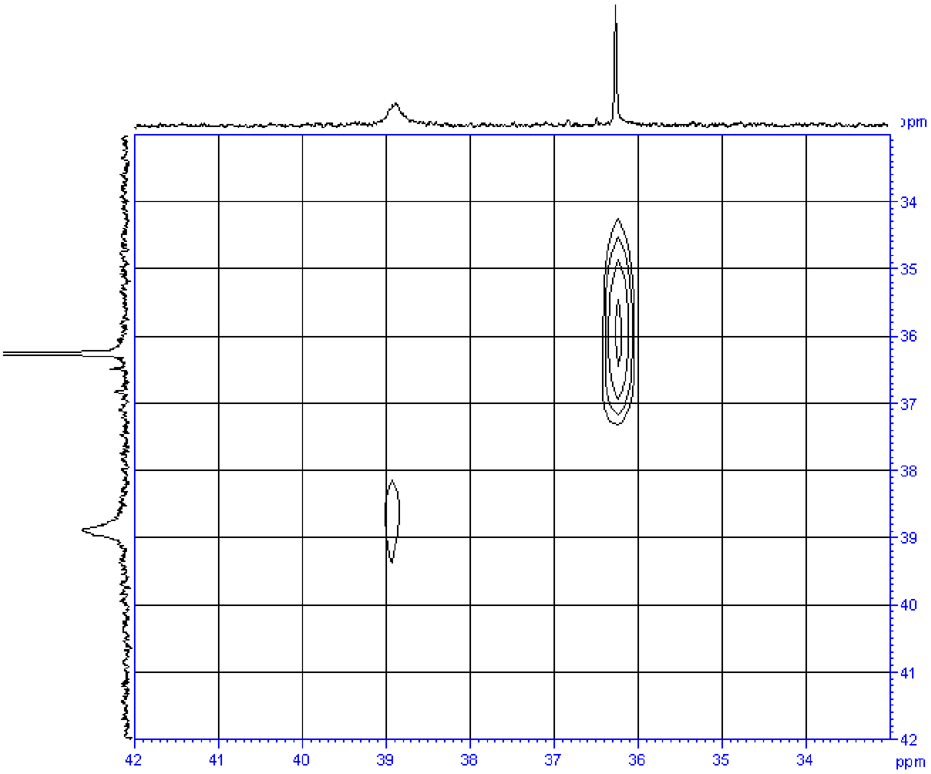


Figure 7. Proton-decoupled 2D ^{31}P-^{31}P TOCSY spectrum of compound **2** at 298 K in $CDCl_3$, mixing time = 30 μs

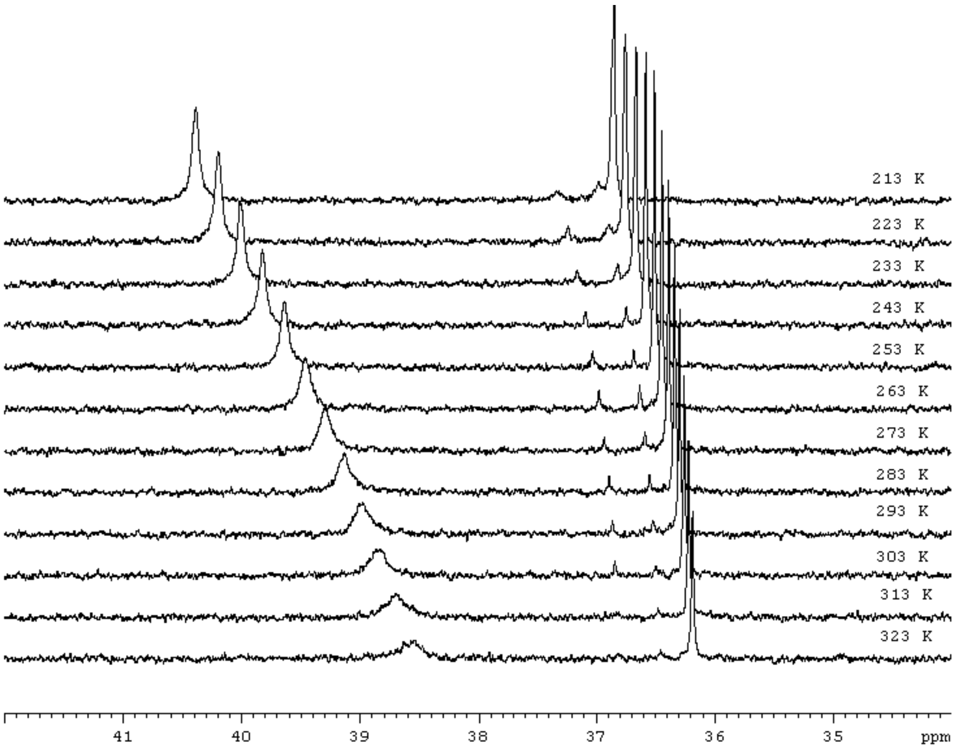
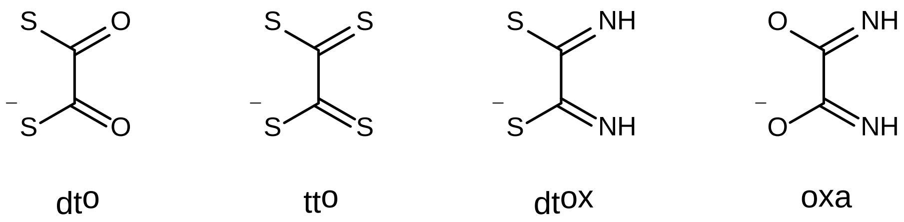
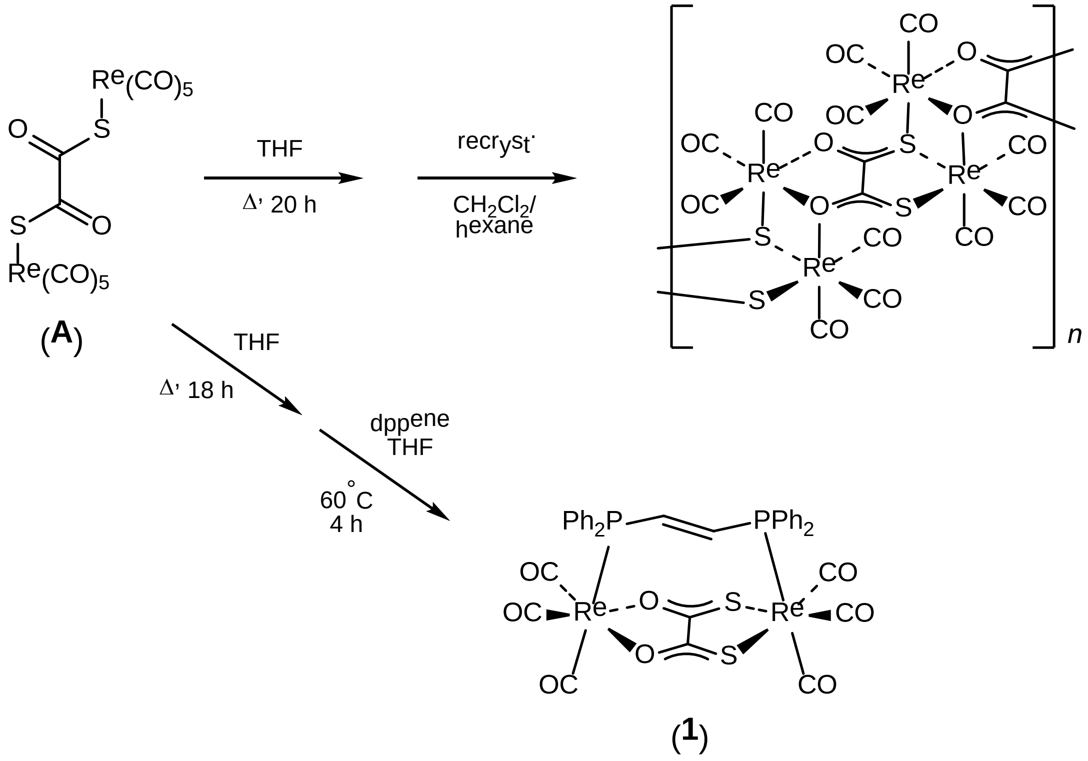


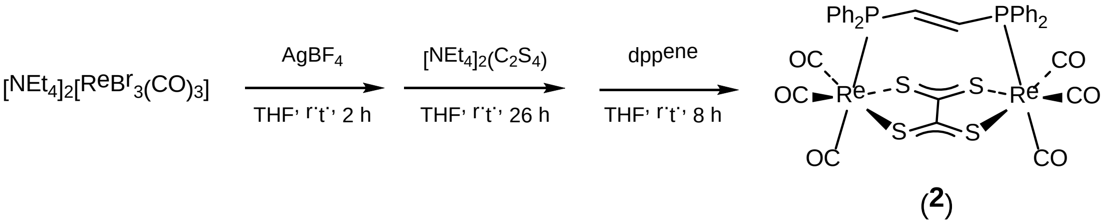
Figure 8. Variable temperature ^{31}P NMR spectra of compound **2** in $CDCl_3$ (162 MHz, 213-323 K)



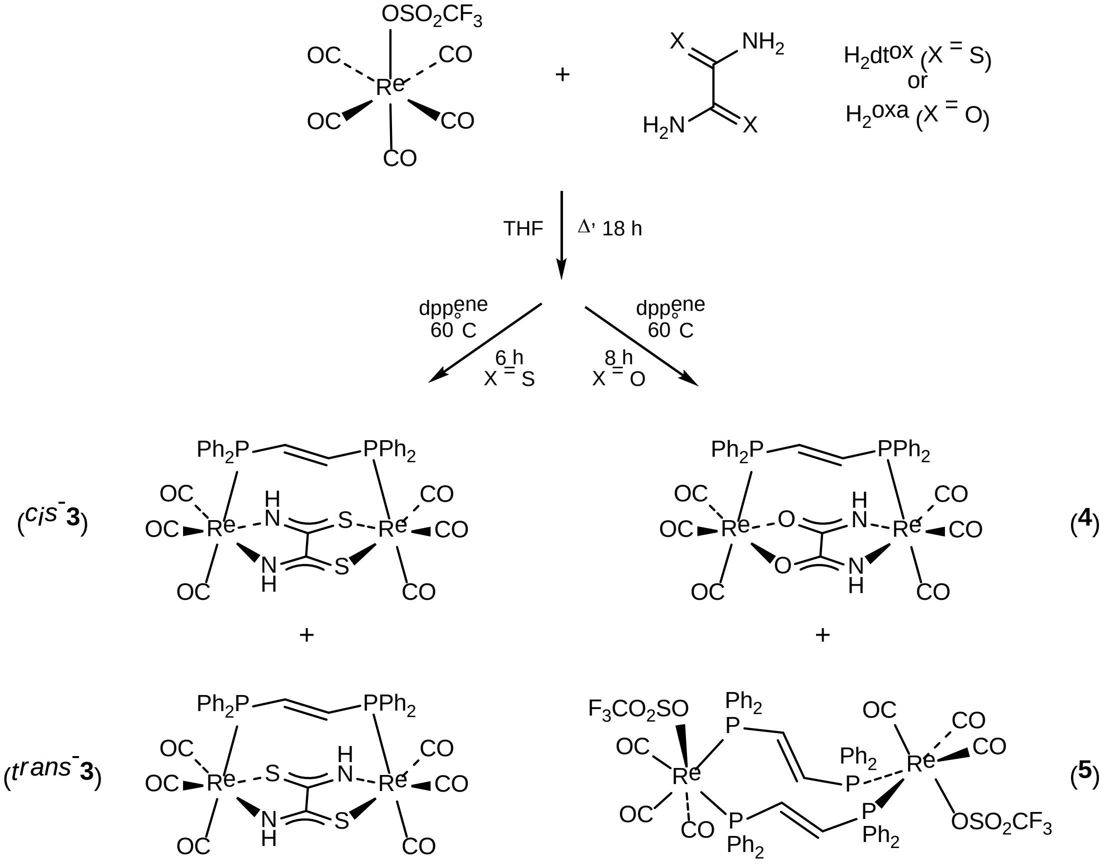
Scheme 1



Scheme 2



Scheme 3



Scheme 4