Preparation and electronic properties of rhenium(V) complexes with bis(diphenylphosphino)ethane¹

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Abstract: Complexes of bis(diphenylphosphino)ethane (dppe) of the types ReOX₃(dppe) and ReO(OR)X₂(dppe) (with X= Cl or Br, and R = Me, Et, Pr, Ph, cyclohexyl (Cy), or -CH₂CH₂OH) were prepared to evaluate the influence of ligand changes on the low-energy d-d transitions in these Re(V) low-spin d^2 systems. Arylimido compounds Re(NR)Cl₃(dppe) (with R = Ph and p-ClC₆H₄) were also obtained. X-ray diffraction studies on ReO(OPr)Cl₂(dppe), $ReO(OPh)Br_3(dppe)$, and $ReO(OCy)Cl_2(dppe)$ confirmed the presence of the trans O=Re-OR unit and showed that the structural characteristics of the Re-O-R segment are not affected by the presence of a bulky cyclohexyl substituent or an aromatic phenyl group. The structure of the arylimido complex $Re(p-ClC_6H_4N)Cl_3(dppe)$ was also determined. The electronic absorption spectra of the ReOX₃(dppe) compounds include two low-energy components at ~11 500 and ~16 000 cm⁻¹, assigned to the two spin-allowed d-d transitions expected for these low-symmetry systems. Substitution of the oxo ligand by an arylimido group has little effect on the lower-energy component, but moves the two components closer together. Replacing the halogen trans to the Re=O bond by an alkoxo group shifts the whole system to higher energies. These variations were found to correlate well with the energies of the frontier orbitals determined from DFT calculations. While attempting to prepare ReOCl₃(dppe) from ReOCl₃(PPh₃)₂, the Re(III) compound fac- $ReCl_{3}(PPh_{3}){Ph_{2}PC_{2}H_{4}PPh_{2}(O)}$ was obtained, in which one end of dppe had become a phosphine oxide. Upon standing in DMSO, this compound gave the octahedral compound $\text{ReCl}_4\{\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2(\text{O})\}$, in which the formation of a chelate ring involving a phosphine and a phosphine oxide was ascertained by X-ray diffraction.

Key words: rhenium, crystal structure, DFT calculations, d-d electron transitions.

Résumé : Des complexes du bis(diphénylphosphino)éthane (dppe) de types $ReOX_3(dppe)$ et $ReO(OR)X_2(dppe)$ (où X = Cl ou Br, et R = Me, Et, Pr, Ph, cyclohexyl (Cy) ou -CH₂CH₂OH), ont été préparés afin d'évaluer l'influence de changements de ligands sur les transitions d-d de basse énergie dans ces systèmes d^2 de Re(V) à spin faible. Des composés arylimido Re(NR)Cl₃(dppe) (où R = Ph et p-ClC₆H₄) ont aussi été obtenus. Les études par diffraction des rayons X sur ReO(OPr)Cl₂(dppe), ReO(OPh)Br₂(dppe) et ReO(OCy)Cl₂(dppe) ont confirmé la présence du motif trans O=Re-OR et montré que les particularités structurales de l'ensemble Re-O-R ne sont pas affectées par la présence du substituant volumineux cyclohexyle ou du groupe aromatique phényle. La structure du complexe arylimido Re(p-ClC₆H₄N)Cl₃(dppe) a également été determinée. Les spectres d'absorption électroniques des composés ReOX₃(dppe) comportent deux composantes de basse énergie à ~11 500 et ~16 000 cm⁻¹, attribuées respectivement aux deux transitions d-d permises de spin, attendues pour ces systèmes de basse symétrie. La substitution du ligand oxo par un groupe arylimido a peu d'influence sur la composante de plus basse énergie, mais elle rapproche les deux composantes l'une de l'autre. Le remplacement de l'halogène trans au lien Re=O par un group alkoxo déplace l'ensemble du système vers des énergies supérieures. Ces variations sont en bonne corrélation avec les énergies des orbitales frontières déterminées par calculs DFT. En tentant de préparer ReOCl₃(dppe) à partir de ReOCl₃(PPh₃)₂, le composé de Re(III) fac-ReCl₃(PPh₃){Ph₇ $PC_2H_4PPh_2(O)$ a été obtenu, dans lequel l'une des extrémités du dppe est devenue un oxyde de phosphine. En laissant reposer dans le DMSO, ce composé a conduit au complexe octaédrique ReCl₄{Ph₂PC₂H₄PPh₂(O)}, où la formation de chélate impliquant une phosphine et un oxyde de phosphine a été confirmée par diffraction des rayons X.

Mots clés : rhénium, structure cristalline, calculs DFT, transitions électroniques d-d.

Introduction

Over the past decades, many research groups have been examining various rhenium(V) compounds containing the $Re=O^{3+}$, $Re=NR^{3+}$, and $Re\equiv N^{2+}$ cores for eventual applica-

tions in radiopharmacy as labeling or therapeutic agents (1-4). Our contributions to this field include compounds with amino acids (5, 6), nitrogen heterocycles (7–12), and various bidentate ligands containing a soft phosphine group and a hard oxygen donor (13–18). Multiple-bonded Re(V) com-

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pounds are of interest in many other fields of chemistry and biochemistry. For instance, their role in oxygen transfer and other catalytic processes is under active investigation at the moment (19–23). The optical properties associated with the multiple bonds have produced a large number of publications and are still extensively studied (24–28).

In the perspective of developing devices for storage of information at the molecular level, these simple diamagnetic d^2 centers would be potentially useful systems if a lowenergy paramagnetic high-spin state can be readily accessed. The oxygen or nitrogen p_x and p_y orbitals of the multiplebonded ligand form strong π bonds with the d_{xz} and d_{yz} orbitals, which become antibonding and higher in energy than the other interaxial d orbital $(d_{xy} \text{ or } d_{x^2-y^2})$, depending on point group symmetry). Occupancy of the latter orbital by the two *d* electrons results in a diamagnetic ground state. However, in a previous study (29), we showed that the HOMO-LUMO gap is relatively small in certain oxo compounds (I) containing O-P ligands. If the gap becomes comparable with the pairing energy, the molecule could possess a high-spin excited state accessible at low energy cost via a spin-crossover process. Such systems may be of interest as catalysts and materials with unusual optical or magnetic properties.



To cast some light on the factors leading to small HOMO-LUMO gaps, we first examined a series of simple compounds retaining an equatorial cis-P,P arrangement perpendicular to an (axial) Re=O or Re=NR bond. The common bis(diphenylphosphino)ethane (dppe) ligand was chosen to provide this arrangement. The strongly π -donor trans- $O=Re=O^+$ and $Re=N^{2+}$ cores were not considered at this point, since their energy gaps had been found to be substantially higher (29). ReOCl₃(dppe) was originally prepared by Chatt and Rowe (30), and X-ray work showed that it indeed corresponds to the structural type considered (31). The corresponding phenylimido compound Re(NPh)Cl₃(dppe) was obtained by Cotton et al. (32). In the present study, the chloro and bromo compounds ReOX₃(dppe) were prepared, together with trans-ReO(OR)X₂(dppe) derivatives with various R groups. A few arylimido compounds were also included. In addition to the preparation and characterization of these compounds, we are reporting preliminary electronic spectra showing how absorption is affected by ligand substitution. DFT calculations are used to rationalize these results.

Experimental section

Reactants and methods

KReO₄, dppe, and all other reactants were obtained from Aldrich and used without further purification.

 $\text{ReOCl}_3(\text{PPh}_3)_2$ was prepared by a literature method (30). Deuterated solvents were purchased from Aldrich or CDN Isotopes.

IR spectra were recorded on Perkin-Elmer 1600 (4000-400 cm⁻¹, KBr pellets) or 1430 spectrophotometers (4000– 200 cm^{-1} , CsI pellets). The NMR spectra were measured with Bruker AMX-300, ARX-400, or AV-300 spectrometers. For the ¹H spectra, the residual solvent signal (DMSO- d_6 , 2.50 ppm) was used as internal reference and the chemical shifts are expressed in ppm vs. $SiMe_4$. H_3PO_4 was used as an external reference ($\delta = 0$) for the ${}^{31}P{}^{1}H{}$ spectra. Electronic spectra were recorded in quartz cells with a UV-vis-NIR Cary 5E spectrometer. The solution spectra were taken as DMSO solutions. Spectra of crystalline samples were obtained with a tungsten-halogen lamp, the CCD detector of a Renishaw 3000 Raman imaging microscope, and a 10% neutral density filter to avoid blinding the detector. FAB⁺ mass spectra in NBA were measured at the Centre de Spectrométrie de Masse de l'Université de Montréal. Elemental analyses were run at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal.

Preparation of ReOX₃(dppe) (X = Cl, Br)

Modifications were introduced in the procedure originally described by Chatt and Rowe (30) for $\text{ReOCl}_3(\text{dppe})$ to eliminate impurities of MX salts and reduced complexes.

The K^+ ion of KReO₄ was first replaced by H^+ on a cation-exchange resin (Dowex 50W-X8, 20-50 mesh). The column (2 cm diameter) was filled with 10 g of resin, which was activated with 15 mL of 6mol/L HCl to obtain the H⁺ form and washed with boiling water (75 mL) to neutrality. KReO₄ (1.5 g, 5.2 mmol) dissolved in a minimum amount (ca. 18 mL) of boiling water was poured into the hot column and the elution was done with boiling water. The HReO₄ solution was collected as long as it remained acidic. Water was then removed with a rotating evaporator and a viscous light yellow-green liquid containing HReO4 and Re2O7 was obtained. To this oily material was added concentrated HX (5 mL) and the mixture was refluxed for 2 min. A 25 mL fraction of a chloroform solution of dppe (3.90 g, 9.80 mmol in 150 mL) was first added and the mixture darkened immediately. The rest of the dppe solution was then added in small portions over a period of 4 h. The mixture was cooled to room temperature (RT) and the precipitate (green for Br, blue for Cl) was filtered, washed with acetone (to remove water), chloroform, and diethyl ether. The compound was recrystallized from acetonitrile.

ReOCl₃(dppe)

Yield: 82%. IR (CsI, cm⁻¹): 980 (s) v(Re=O); 320 (w), 290 (w) v(Re-Cl). ¹H NMR (DMSO- d_6) (ppm) δ : 8.01 (m, 8H, H_o), 7.48 (s br, 12H, H_{m,p}), 3.79 (m, 2H, ethylene), 3.24 (m, 2H, ethylene). ³¹P NMR (DMSO- d_6) (ppm) δ : 5.7 (s). MS FAB⁺ (m/z): 706 [M]⁺; 671 [M – Cl]⁺. Anal. calcd. for C₂₆H₂₄OP₂Cl₃Re (%): C 44.17, H 3.42; found: C 44.24, H 3.34.

ReOBr₃(dppe)

Yield: 76%. IR (KBr, cm⁻¹): 971 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) & 8.03 (m, 8H, H_o), 7.48 (s br, 12H, H_{mp}), 3.90 (m, 2H, ethylene) 3.17 (m, 2H, ethylene). ³¹P

NMR (DMSO- d_6) (ppm) δ : -1.0 (s). MS FAB⁺ (m/z): 840 [M]⁺, 760 [M - Br]⁺, 680 [M - 2Br]⁺.

Preparation of $ReOX_2(OR)(dppe)$ (X = Cl, Br)

Method A (R = Me, Et, Pr)

For ReOCl₂(OEt)(dppe), a suspension of ReOCl₃(dppe) (0.31 g, 0.44 mmol) in 35 mL of ethanol was refluxed for 3 days, during which time the blue solid progressively turned violet. It was filtered hot, washed with ethanol and diethyl ether, and recrystallized in acetonitrile.

This method was used to introduce alkoxo groups corresponding to low-boiling alcohols (methanol, ethanol, *n*-propanol). Reaction time varied (2–6 days) from one system to another. The reaction was stopped ~24 h after the reaction mixture has become clear violet. When there was no color change after 3 days, adding fresh alcohol helped to accelerate the reaction.

ReOCl₂(OEt)(dppe)

Yield: 90%. IR (KBr, cm⁻¹): 950 (s) v(Re=O), 913 (s) δ (O-CH₂). ¹H NMR (DMSO- d_6) (ppm) δ : 8.14 (m, 8H, H_o), 7.48 (s br, 12H, H_{m,p}), ~3.31 (m, 2H, ethylene, near water peak), 3.14 (m, 2H, ethylene), 2.28 (q, 2H, ³J = 7.0 Hz, ethoxo CH₂), -0.07 (t, 3H, ³J = 6.9 Hz, ethoxo CH₃). ³¹P NMR (DMSO- d_6) (ppm) δ : 16.5 (s). MS FAB⁺ (m/z): 716 [M]⁺, 681 [M - Cl]⁺, 671 [M - OEt]⁺, 637 [M - Cl - OEt]⁺. Anal. calcd. for C₂₈H₂₉O₂P₂Cl₂Re (%): C 46.93, H 4.08; found: C 46.66, H 3.94.

ReOCl₂(OMe)(dppe)

Yield: 79%. IR (KBr, cm⁻¹): 944 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ : 8.11 (m, 8H, H_o), 7.49 (s br, 12H, H_{m,p}), ~3.23 (m, 2H, ethylene, near water peak), 3.15 (m, 2H, ethylene), 1.91 (s, 3H, methoxo CH₃). ³¹P NMR (DMSO- d_6) (ppm) δ : 16.6 (s).

ReOCl₂(OPr)(dppe)

Yield: 85%. IR (KBr, cm⁻¹): 938 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ: 8.16 (m, 8H, H_o), 7.48 (s br, 12H, H_{m,p}), 3.34 (m, 2H, ethylene), 3.15 (m, 2H, ethylene), 1.99 (t, 2H, ³*J* = 6.5 Hz, propoxo α-CH₂), 0.34 (m, 2H, propoxo β-CH₂), 0.11 (t, 3H, ³*J* = 7.3 Hz, propoxo CH₃). ³¹P NMR (DMSO- d_6) (ppm) δ: 15.8 (s).

*ReOBr*₂(*OEt*)(*dppe*)

Yield: 61%. IR (KBr, cm⁻¹): 951 (s) v(Re=O), 913 (s) δ (O-CH₂). ¹H NMR (DMSO-*d*₆) (ppm) δ : 8.12 (m, 8H, H_o), 7.50 (m br, 12H, H_{m,p}), 3.39 (m, 2H, ethylene), 3.07 (m, 2H, ethylene), 2.35 (q, 2H, ³*J* = 6.8 Hz, ethoxo CH₂), -0.03 (t, 3H, ³*J* = 6.9 Hz, ethoxo CH₃). ³¹P NMR (DMSO-*d*₆) (ppm) δ : 18.2 (s).

ReOBr₂(OMe)(dppe)

Yield: 75%. IR (KBr, cm⁻¹): 936 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ : 8.12 (m, 4H, H_o), 8.01 (m, 4H, H_o), 7.51 (s br, 12H, H_{m,p}), ~3.35 (m, 2H, ethylene, near water peak), 3.08 (m, 2H, ethylene), 2.02 (s, 3H, methoxo CH₃). ³¹P NMR (DMSO- d_6) (ppm) δ : 18.8 (s).

*ReOBr*₂(*OPr*)(*dppe*)

Yield: 74%. IR (KBr, cm⁻¹): 937 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ: 8.13 (m, 8H, H_o), 7.49 (s br, 12H, H_{m,p}), 3.38 (m, 2H, ethylene, near water peak), 3.08 (m, 2H, ethylene), 2.06 (t, 2H, ³J = 6.5 Hz, propoxo α-CH₂), 0.38 (m, 2H, propoxo β-CH₂), 0.11 (t, 3H, ³J = 7.4 Hz, propoxo CH₃). ³¹P NMR (DMSO- d_6) (ppm) δ: 17.4 (s). Anal. calcd. for C₂₉H₃₁O₂P₂Br₂Re (%): C 42.50, H 3.81; found: C 42.78, H 3.87.

Method B ($\mathbf{R} = cyclohexyl, -CH_2CH_2OH$)

A suspension of $\text{ReOCl}_2(\text{OEt})(\text{dppe})$ (0.20 g, 0.28 mmol) in 25 mL of an acetone–cyclohexanol (or –ethylene glycol) (4:1, v/v) mixture was refluxed for 3 days. The color of the solid did not change appreciably during the reaction. The violet precipitate was filtered, washed with ethanol and diethyl ether, and recrystallized in acetonitrile. For the soluble ethylene glycol complex, the final mixture was evaporated to dryness, diethyl ether was added, and the violet product was filtered.

ReOCl₂(OCy)(dppe)

Yield: 72%. IR (KBr, cm⁻¹): 926 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ: 8.27 (m, 4H, H_o), 8.16 (m, 4H, H_o), 7.47 (s br, 12H, H_{m,p}), ~3.45 (m, 2H, ethylene, in the tail of the water peak), ~3.18 (m, 2H, ethylene, near water peak); cyclohexyl signals assigned from a 2D spectrum: 2.33 (m, 1H, α-CyO), 1.03 (m, 3H, γ/δ-CyO), 0.56 (m, 2H, β-CyO), 0.38 (m, 3H, γ/δ-CyO), -0.11 (m, 2H, β-CyO). ³¹P NMR (DMSO- d_6) (ppm) δ: 16.9 (s).

ReOCl₂(OCH₂CH₂OH)(dppe)

Yield: 85%. IR (KBr, cm⁻¹): 948 v(Re=O), 907 (s) δ (O-CH₂). ¹H NMR (DMSO-*d*₆) (ppm) δ : 8.10 (m, 8H, H_o), 7.49 (s br, 12H, H_{m,p}), 3.43 (m, 2H, ethylene, near water peak), 3.11 (m, 2H, ethylene), 2.42 (t, 2H, ³J = 6.2 Hz, β-CH₂CH₂OH), 2.17 (t, 2H, ³J = 6.3 Hz, α-CH₂CH₂OH). ³¹P NMR (DMSO-*d*₆) (ppm) δ : 19.1 (s). MS FAB⁺ (*m*/*z*): 732 [M]⁺, 697 [M - Cl]⁺, 671 [M - OC₂H₄OH]⁺, 661 [M - 2Cl]⁺, 636 [M - Cl - C₂H₄OH]⁺.

Method C ($\mathbf{R} = \mathbf{Ph}$)

A solution of phenol (5.5 g, 59 mmol) in 70 mL of benzene was heated to the boiling point and $\text{ReOBr}_2(\text{OPr})(\text{dppe})$ (0.49 g, 0.60 mmol) was added. The violet mixture turned orange quickly. After 1 day, the solvent was evaporated, the raw product was added to 50 mL of diethyl ether, and refluxed for 30 min to dissolve the unreacted phenol. The dark-brown precipitate was filtered hot, washed with diethyl ether, and recrystallized in acetonitrile.

*ReOBr*₂(*OPh*)(*dppe*)

Yield: 83%. IR (KBr, cm⁻¹): 959 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ : 8.13 (m, 4H, H_o), 8.00 (dd, 4H, ³J = 7.6 Hz, ³J_{H-P} = 10.9 Hz, H_o), 7.53 (s br, 6H, H_{m,p}), 7.35 (t, 2H, ³J = 7.0 Hz, H_p), 7.26 (t, 4H, ³J = 7.5 Hz, H_m), 6.62 (m, 3H, phenoxo H_{m,p}), 5.67 (d, 2H, ³J = 8.0 Hz, phenoxo H_o), 3.55 (m, 2H, ethylene), 3.23 (m, 2H, ethylene). ³¹P NMR (DMSO- d_6) (ppm) δ : 17.3 (s). MS FAB⁺ (m/z): 854 [M]⁺, 773 [M - Br]⁺, 761 [M - OPh]⁺, 680 [M - Br - OPh]⁺. Anal. calcd. for $C_{32}H_{29}O_2P_2Br_2Re$ (%): C 45.03, H 3.42; found: C 45.09, H 3.39.

ReOCl₂(OPh)(dppe)

Yield: 90%. IR (KBr, cm⁻¹): 960 (s) v(Re=O). ¹H NMR (DMSO- d_6) (ppm) δ : 8.13 (m, 4H, H_o), 8.00 (dd, 4H, ³J = 7.7 Hz; ³J_{H-P} = 11.1 Hz, H_o), 7.51 (s br, 6H, H_{m,p}), 7.30 (m, 2H, H_p), 7.23 (m, 4H, H_m), 6.59 (m, 3H, phenoxo H_{m,p}), 5.63 (d, 2H, ³J = 7.9 Hz, phenoxo H_o), 3.57 (m, 2H, ethylene), 3.32 (m, 2H, ethylene, near water peak).³¹P NMR (DMSO- d_6) (ppm) δ : 16.3 (s).

Preparation of Re(NPh)Cl₃(dppe)

The compound was prepared following the literature method (32). ReOCl₃(dppe) (0.15 g, 0.21 mmol) was added to 30 mL of a refluxing aniline–benzene (1:5, v/v) mixture. The blue solution was refluxed for 36 h, during which time it turned green. The light-green precipitate was filtered, and washed with benzene and diethyl ether. It recrystallized in acetonitrile as light-green fibers.

Re(*NPh*)*Cl*₃(*dppe*)

Yield: 75%. ¹H NMR (DMSO- d_6) (ppm) & 8.16 (m, 4H, H_o), 7.96 (m, 4H, H_o), 7.52 (t, 1H, ³J = 8.2 Hz, phenylimido H_p), 7.41 (s br, 6H, H_{m,p}), 7.16 (s br, 6H, H_{m,p}), 6.79 (t, 2H, ³J = 8.5 Hz; phenylimido H_m), 6.15 (d, 2H, ³J = 8.7 Hz, phenylimido H_o), ~3.59 (m, 2H, ethylene), 3.33 (m, 2H, ethylene). ³¹P NMR (DMSO- d_6) (ppm) & 11.3 (s).

Preparation of Re(NC₆H₄Cl)Cl₃(dppe)

This variation of the previous method was used to introduce a phenylimido group derived from a solid aniline. A solution of *p*-chloroaniline (5.56 g, 43.6 mmol) in 25 mL of benzene was heated to its boiling point and $\text{ReOCl}_3(\text{dppe})$ (0.15 g, 0.21 mmol) was added. The solution was refluxed for 1 day, during which time the blue solution turned dark green. The solvent was evaporated completely, the solid obtained was placed in 50 mL of diethyl ether, and the solution was refluxed for 30 min to dissolve unreacted *p*chloroaniline. The green precipitate was filtered hot, washed with diethyl ether, and recrystallized in acetonitrile.

$Re(NC_6H_4Cl)Cl_3(dppe)$

Yield: 78%. ¹H NMR (DMSO- d_6) (ppm) δ : 8.16 (m, 4H, H_o), 7.96 (m, 4H, H_o), 7.42 (s br, 6H, H_{m,p}), 7.19 (s br, 6H, H_{m,p}), 6.88 (d, 2H, ³J = 8.8 Hz, arylimido H_m), 6.13 (d, 2H, ³J = 8.6 Hz, arylimido H_o), 3.56 (m, 2H, ethylene), 3.33 (m, 2H, ethylene, near water peak). ³¹P NMR (DMSO- d_6) (ppm) δ : 11.1 (s).

Preparation of ReCl₃(PPh₃)(dppe=O)

ReOCl₃(PPh₃)₂ (0.112 g, 0.13 mmol) was added to a solution of dppe (0.311 g, 0.79 mmol) in 25 mL CH₂Cl₂ under a dynamic inert atmosphere. The resulting lime-green solution was stirred at room temperature for 1 h. The beige precipitate formed during the reaction was filtered, washed with chloroform and diethyl ether. Yield: 51%. It corresponded to the 1.5CH₂Cl₂ solvate. IR (KBr, cm⁻¹): 1058 (s), 1125 (s). ¹H NMR (DMSO-*d*₆): see text. MS FAB⁺ (*m*/*z*): 968 [M]⁺, 933 [M - Cl]⁺, 706 [M - PPh₃]⁺, 635 [M - 2Cl - PPh₃]⁺.

Anal. calcd. for $C_{45.5}H_{42}Cl_6OP_3Re$ (%): C 49.83, H 3.86; found: C 49.68, H 3.98.

X-ray diffraction studies

Three data sets were collected with a Bruker Smart 2K CCD diffractometer controlled by the SMART software (33), using the graphite-monochromatized CuK α radiation. Sets of 30 oscillation frames of 0.3° over a range of 9° were recorded in four regions of the reciprocal space, from which the reduced cell was determined by least-squares refinement. For data collection, frames were recorded for different orientations of the crystal and detector so as to cover at least 95% of the reciprocal sphere. At the end, the first 101 frames were remeasured to check for crystal decomposition. The frames were analyzed with the SAINT software (34), which determined the intensity and the position of each spot. Accurate cell parameters were obtained by least-squares refinement over the positions of the whole data set.

For one compound, the X-ray work was done with an Enraf-Nonius CAD-4 diffractometer using graphitemonochromatized CuK α radiation under the control of the CAD-4 software (35). The reduced cell was initially determined from 20 to 25 spots located on a preliminary rotation photograph and centered in the detector aperture. Accurate cell parameters were then determined from the positions of 25 high-angle reflections centered with the SETANG and DETTH procedures. The intensities were recorded by $\omega/2\theta$ scan. Possible crystal decomposition was monitored by measuring five standard reflections every hour.

Another data set was collected with the Bruker P-4 diffractometer of the Université du Québec à Montréal, using the graphite-monochromatized MoK α radiation. The procedures to determine the cell parameters and collect the intensity data (XSCANS software) (36) were similar to those described above for the CAD-4 system. Three standard reflections were measured every 97 reflections during data collection.

The data were interpreted with the SHELXTL software (37). The XPREP procedure (38) was used to apply to the raw intensities an absorption correction based on crystal morphology and to determine the Laue symmetry, systematic absences, and space group. The structure was solved by the direct methods or the heavy-atom method with SHELXS (39). The heavy atoms were initially found and the remaining atoms were then located from structure-factor calculations and ΔF maps with SHELXL (40). The structure was refined by least squares on F^2 . The non-hydrogen atoms were generally refined anisotropically. The hydrogens were first placed at idealized positions with the standard (C,N,O)-H distances of SHELXL and allowed to ride on the supporting atom. Their isotropic temperature factors (U_{iso}) were fixed at values related to the equivalent temperature factor $(U_{\rm eq})$ of the supporting atom by $U_{\rm iso} = k \times U_{\rm eq}$ (where k =1.5 (methyl) or 1.2 (others)). The ORTEP diagrams (40% probability ellipsoids) were produced with the XP routine of SHELXTL.

The crystals of $\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{dppe})$ and the three $\text{ReOX}_2(\text{OR})(\text{dppe})$ compounds were obtained by slow crystallization of concentrated acetonitrile solutions, whereas those of $\text{ReCl}_4(\text{dppe=O})$ appeared in a DMSO solution of $\text{ReCl}_3(\text{PPh}_3)(\text{dppe=O})$ kept at room temperature for

	ReOCl ₂ (OPr)(dppe)	ReOBr ₂ (OPh)(dppe)	ReOCl ₂ (OCy)(dppe)	Re(NC ₆ H ₄ Cl)Cl ₃ (dppe)	ReCl ₄ (dppe=O)•DMSO
Formula	$C_{29}H_{31}Cl_2O_2P_2Re$	$\mathrm{C}_{32}\mathrm{H}_{29}\mathrm{Br}_{2}\mathrm{O}_{2}\mathrm{P}_{2}\mathrm{Re}$	$C_{32}H_{35}Cl_2O_2P_2Re$	$C_{32}H_{28}Cl_4NP_2Re$	$C_{28}H_{30}Cl_4O_2P_2SRe$
Formula weight	720.62	853.43	770.64	816.55	820.52
Crystal shape	Purple plates	Brown blocks	Purple blocks	Green blocks	Green blocks
<i>T</i> (K)	293(2)	293(2)	293(2)	220(2)	293(2)
Diffractometer	Smart CCD	P-4	Smart CCD	Smart CCD	CAD-4
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>Pbca</i> (No. 61)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	$P2_1/n$ (No. 14)	P1 (No. 2)
a (Å)	18.1737(2)	9.793(2)	19.4762(4)	8.3710(1)	9.609(2)
b (Å)	9.9663(1)	17.695(2)	9.9284(2)	19.7638(1)	11.472(2)
<i>c</i> (Å)	16.6086(2)	36.086(4)	17.2379(4)	19.2872(1)	16.080(3)
α (°)	06	06	06	06	91.98(3)
β (°)	99.268(1)	06	111.063(1)	90.995(1)	98.82(3)
χ (°)	06	90	06	06	114.07(3)
Volume (Å ³)	2968.96(6)	6253.2(16)	3110.54(11)	3190.45(4)	1590.0(5)
Ζ	4	∞	4	4	2
$d_{\rm calcd}~({ m g/cm^3})$	1.634	1.813	1.646	1.700	1.714
Rfls cell params	8971	54	1011	32 575	25
Crystal dimensions (mm)	$0.02 \times 0.32 \times 0.65$	$0.19 \times 0.23 \times 0.35$	$0.42 \times 0.32 \times 0.20$	$0.30 \times 0.20 \times 0.15$	$0.25 \times 0.25 \times 0.30$
Radiation, λ (Å)	CuKo, 1.54178	MoKα, 0.71073	CuKo, 1.54178	CuKα, 1.54178	CuKα, 1.54178
μ (cm ⁻¹)	108.69	65.72	104.09	116.58	123.3
Rfls measured	34 223	12 164	37 335	38 094	11 842
Rfls independent	$5807 (R_{\text{int}} = 0.076)$	6136 ($R_{\rm int} = 0.091$)	$5984 \ (R_{\rm int} = 0.048)$	$6146 \ (R_{\rm int} = 0.125)$	$6022 \ (R_{\rm int} = 0.040)$
Rfls obs $(I > 2\sigma)$	5201	3500	5705	5527	5176
Params refined/restraints	351/46	365/84	406/70	362/0	357/60
R^a $(I > 2\sigma)$	0.0387	0.0519	0.0327	0.0616	0.0518
$wR2^{b} (I > 2\sigma)$	0.1012	0.0935	0.0871	0.1573	0.1379
S^{c} $(I > 2\sigma)$	1.022	1.137	1.082	1.071	1.056
$ {}^{a}R = \Sigma F_{o} - F \Sigma F_{o} . $ $ {}^{b}wR2 = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma V_{o} $ $ {}^{c}S = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/(N_{o}) $	F_{0}^{2}] ² $^{1/2}$. V _{param})} ^{1/2} .				

Table 1. Crystal data.

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3 months. In all cases, the intensities of the standard reflections revealed no crystal decomposition during data collection. Space groups were defined unambiguously from the Laue symmetry and systematic absences, except for the triclinic compound $\text{ReCl}_4(\text{dppe=O}) \cdot \text{Me}_2\text{SO}$. Crystal data are collected in Table 1.

In most cases, disorder was observed in the alkoxo group, phosphine phenyl rings, or lattice solvent molecules. It was modeled by means of two individual orientations, whose occupancies were first refined with a constraint applied to normalize the sum of the occupancies to unity. For the final cycles, these occupancies were rounded off to the nearest 0.05 and then fixed. The non-hydrogen atoms were usually refined anisotropically, but the thermal parameters were restricted (ISOR) so as to obtain reasonable ellipsoids. In severe cases, the interatomic distances were simultaneously constrained with DFIX. Details are provided in the CIF files.³

For ReOCl₂(OPr)(dppe), the propyl unit adopted two conformations in a 80:20 ratio (Fig. S-1, supplementary material).³ The major conformer (C61-C63) was stretched, whereas the other (C81-C83) was bent. DFIX constraints based on the average data found for propoxo groups in the Cambridge Structural Database (41) (C-O (1.42 Å), C-C (1.45 Å), O•••C_β (2.39 Å), C_{α} •••C_γ (2.41) Å) were applied.

Data were also collected on crystals of the related ReOBr₂(OPr)(dppe) complex. It is not isostructural with the chloro compound, since it belongs to the triclinic space group $P\overline{1}$ and the unit cell (a = 9.848(3) Å, b = 17.602(6) Å, c = 18.082(6) Å, $\alpha = 78.83(2)^{\circ}$, $\beta = 89.98(3)^{\circ}$, $\gamma = 89.03(2)^{\circ}$) contains four molecules. The two independent molecules are almost identical and differ very little from the chloro analog. Even the packing patterns of the two compounds are very close. However, the *R* factor could not be reduced below 0.094 and large correlations between the two independent molecules led to high instability in the refinement. Subtle twinning is suspected to be present and the structure of the bromo compound is not described in detail here.

In the case of $\text{ReOBr}_2(\text{OPh})(\text{dppe})$, rotational disorder about a P—C bond of dppe led to two orientations (60:40 ratio) for one of its phenyl groups (Fig. S-2).³ With ReOCl_2 -(OCy)(dppe), the cyclohexyl group in a chair conformation was disordered over two orientations (60:40 ratio, Fig. S-2).³ In these cases, only ISOR restrictions were applied.

For $\text{Re}(\text{NC}_6\text{H}_4\text{Cl})\text{Cl}_3(\text{dppe})$, the crystal shape was difficult to describe and the absorption correction was not totally satisfactory. Nevertheless, the structure solved and refined normally.

The data for the triclinic ReCl₄(dpp=O)•(CH₃)₂SO compound were interpreted in the centric $P\overline{1}$ space group, which turned out to be the correct choice. The ReCl₄(dpp=O) molecule itself showed no disorder, but the lattice DMSO molecule was found to be disordered over two interlocked orientations (0.65:0.35, Fig. S-3).³ DFIX constraints based on the average distances found for lattice DMSO in the Cambridge Structural Database (41) (S=O (1.50 Å), C-S (1.76 Å), C•••O (2.61 Å), C•••C (2.65 Å)) were applied.

Results and discussion

Preparation of ReOX₃(dppe) and ReOX₂(OR)(dppe)

The procedure originally described to prepare ReOCl₃(dppe) (30) required a tedious series of recrystallizations to remove the MX salt and various reduction products. By starting with a HReO₄-Re₂O₇ solution and using chloroform as solvent, we obtained good yields of pure chloro and bromo compounds. The IR spectra show the strong v(Re=O) band at 970–980 cm⁻¹ expected for a monooxo system (42). Clean isotopic patterns are found in FAB⁺ spectra for the parent ion and the $[M - X]^+$ fragment. The presence of only one ³¹P{¹H} NMR singlet confirms the formation of the fac isomer, since the P donors would be inequivalent in the mer isomer. Although a "frozen" puckered chelate ring contains four inequivalent aliphatic protons, a fast flip-flop motion across the equatorial plane generates a vertical mirror plane (including the axial Re=O bond and bisecting the P-Re-P angle) on the NMR timescale. In the "average" molecule, the pair of protons on the same side of the equatorial plane become equivalent. Accordingly, two complex multiplets are found between 3 and 4 ppm, one of which is often obscured by the residual water peak in DMSO. Because of the anisotropic effect of the Re-oxo bond, the protons on the oxo side are believed to be the more deshielded (43, 44). Similarly, two distinct sets of phenyl signals are expected. However, only two complex peaks (2:3 intensity ratio) are found. The weaker one at \sim 8.0 ppm is due to the eight ortho protons, whereas the other at ~7.5 ppm includes the meta and para protons of both types of rings. This assignment is based on a comparison with ReOX₂(OPh)(dppe), where one set of phosphine aromatic signals is displaced by the anisotropic effect of the phenoxo ring.

The ReOX₂(OR)(dppe) compounds were obtained by controlled alcoholysis of ReOX₃(dppe). For R = Me, Et, and Pr, refluxing for several days in the neat alcohol gave good yields of pure products. For the higher-boiling alcohols cyclohexanol and ethylene glycol, decomposition took place upon refluxing in the pure liquid and the reaction was carried out in a 4:1 acetone–alcohol mixture. With phenol, a solid, the reaction was run in benzene.

In all cases, halide substitution occurs only at the position trans to the Re=O bond. This is supported by the presence of only one singlet in the ${}^{31}P{}^{1}H$ spectra, downfield from that of the corresponding trihalo complex. The strong v(Re=O) vibration appears at ~940 cm⁻¹. The ethoxo and 2hydroxyethoxo compounds also give a very strong band at ~910 cm⁻¹ involving an O-CH₂ deformation mode (30). The FAB⁺ spectra generate characteristic patterns for the parent ion and other fragments obtained by removing X or OR. The ¹H aromatic regions of the alkoxo compounds are similar to those of the trihalo systems, except that the ortho signals are displaced downfield slightly (8.1 - 8.2)ppm). For ReOX₂(OPh)(dppe), one of the two overlapping ortho signals is displaced upfield (~8.00 ppm) by the anisotropy of

³Supplementary data may be purchased from the Directory of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 210020–210024) contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

the phenoxo ligand and it can be safely assigned to ortho protons, since ${}^{3}J_{\text{H-P}}$ couplings of ~11 Hz are observed (45). Anisotropy also displaces the meta and para signals upfield: they become resolved at ~7.3 (para) and ~7.2 ppm (meta), whereas the meta and para multiplets for the rings on the oxo side remain unresolved at ~7.5 ppm.

The alkoxo protons are shielded considerably compared with those of the corresponding alcohol. This is consistent with the alkoxo group lying trans to the oxo ligand, since it was noticed (13) that these protons are deshielded when they occupy a position cis to the oxo. For the 2-hydroxyethoxo compound, the protons α to the coordinated oxygen are assumed to be more shielded than the β protons, whose chemical shift returns to a normal value (3.34 ppm) (46) for free ethylene glycol. The phenoxo ligand gives a doublet at ~5.65 ppm for the ortho protons and a multiplet including the meta and para protons at ~6.60 ppm. Therefore, with respect to uncoordinated phenol, whose signals occur at 6.77 (ortho and para) and 7.16 ppm (meta), coordination induces upfield shifts whose amplitude decreased with the distance from the O atom.

Preparation of Re(NR)Cl₃(dppe)

Cotton et al. (32) first prepared the phenylimido compound by reacting ReOCl₃(dppe) with aniline. A similar procedure was used to obtain the *p*-chlorophenylimido complex here. The original stereochemistry of the oxo complex is retained, as evidenced from X-ray crystallography (see below) and from NMR spectroscopy, namely the presence of only one singlet in the ³¹P{¹H} spectrum.

Isolation of reduced species

Attempts were made to obtain ReOCl₃(dppe) by displacing the phosphines of ReOCl₃(PPh₃)₂. When the reaction was run in CH₂Cl₂ at room temperature for 1 h, a beige solid precipitated. The parent peak and fragmentation pattern in the FAB⁺ spectrum were consistent with the presence of one PPh₃, one dppe, a ReCl₃ unit, and one extra oxygen. The absence of the strong IR v(Re=O) band and the presence of ¹H NMR signals extending far outside the standard 0–10 ppm range ruled out the possibility of a diamagnetic oxorhenium(V) species. Therefore, rhenium-to-phosphorus oxygen transfer had probably occurred, generating a Re(III) center and a phosphine oxide, as observed before (47, 48). This was supported by the strong IR bands appearing at 1058 and 1125 cm⁻¹, one of which could be assigned to a v(P=O) vibration (49). In the structure **II** proposed, the oxygen is part



Fig. 1. ¹H NMR signals of the aromatic protons of the phosphine groups in ReCl₃(PPh₃)(dppe=O).



of the bidentate $Ph_2PC_2H_4PPh_2(O)$ ligand (dppe=O). The phosphine oxide unit is believed to be derived from dppe instead of PPh₃, since the fragmentation products observed in the FAB⁺ spectra correspond to the loss of PPh₃, not Ph₃PO. Furthermore, upon aging, this compound gives a Re(IV) compound ReCl₄(dppe=O), whose crystal structure is described hereafter. Even though the complex is paramagnetic, its ¹H NMR spectrum could be fully analyzed.

We previously reported ¹H NMR data of arylphosphine complexes of Re(III) and Re(IV) (50, 51). In these complexes, the aromatic phosphine signals usually occur between 10 and 20 ppm for the ortho protons, and between 7 and 11 ppm for the meta and para protons. As shown in Fig. 1 and Table 2, this generalization is obeyed here. ${}^{3}J$ couplings typical of aromatic rings are observed and proton positions around the rings are readily identified from multiplicities and integrations. A 2D experiment allowed us to distribute the nine peaks between 12 and 7.5 ppm into three groups of three, corresponding to PPh₃ and to the two inequivalent phenyl rings at the PPh₂ end of the dppe=O ligand. Two extra sets of three coupled signals are also found at higher field for the aromatic protons of two phenyl rings in the phosphine oxide group. In the latter sets, the ortho protons appear at relatively high field (1.8 and -3.0 ppm)and they are somewhat broadened. Finally, broad multiplets with suitable intensities are observed for the aliphatic protons, two of which occur at extreme chemical shifts (40.5 and -8.5 ppm, respectively). These multiplets, which were already complex for diamagnetic systems, showed extra broadening because of the paramagnetism. They did not give clear cross-peaks in the 2D spectrum and could not be assigned to individual protons.

These available data and the crystallographic results on ReCl₄(dppe=O) suggest that the metal center is coordinated to six ligands: three Cl, one PPh₃, and one Ph₂PC₂H₄PPh₂(O). Of the three possible isomers for an octahedral ReX₃L(L'-L") compound, only the fac isomer (**II**) is consistent with the presence of four inequivalent phenyl

	ortho	meta	para	
PPh ₃	11.62 (d, 6H) ${}^{3}J = 7.7$	8.25 (t, 6H) ${}^{3}J = 7.7$	7.51 (t, 3H) ${}^{3}J = 7.4$	
PPh ₂ (A)	11.70 (d, 2H) ${}^{3}J = 7.4$	8.64 (t. 2H) ${}^{3}J = 7.4$	9.94 (t, 1H) ${}^{3}J = 7.4$	
PPh ₂ (B)	11.44 (d, 2H) ${}^{3}J = 7.4$	8.69 (t, 2H) ${}^{3}J = 7.5$	9.01 (t, 1H) ${}^{3}J = 7.3$	
$O=PPh_2$ (A)	1.80 (br, 2H)	7.76 (t, 2H) ${}^{3}J = 7.5$	6.74 (t, 1H) ${}^{3}J = 7.5$	
$O=PPh_2$ (B)	-2.99 (d, 2H) $^{3}J = 7.9$	3.69 (t, 2H) ${}^{3}J = 7.9$	4.99 (t, 1H) ${}^{3}J = 7.5$	
C_2H_4	-8.47 (m br, 1H), 2.45 (m br, 1H), 4.81 (m br, 1H), 40.47 (m br, 1H)			

Table 2. ¹H NMR chemical shifts (ppm) and coupling constants (Hz) for ReCl₃(PPh₃)(dppe=O) (in DMSO- d_6).

rings in the dppe=O ligand, as revealed by ¹H NMR spectroscopy.

Crystal structures of the ReOX₂(OR)(dppe) compounds

Since the Re-O-R angle in the known structures of this type spans a broad range (125°-180°, based on 33 structures in the Cambridge Structural Database) (41) and the oxygento-rhenium π interactions could be sensitive to this factor, structures with three different OR groups were studied: the n-propoxo unit was considered as a "normal" group, the cyclohexyl substituent was expected to be sterically demanding, whereas the phenoxo group was used to probe the influence of an extended π system.

The three ReOX₂(OR)(dppe) molecules (Fig. 2) consist of octahedral molecules containing the trans-oxo-alkoxo unit observed for the bis(diphenylphosphino)propane complex (52). Selected distances and angles are listed in Table 3.

In the three compounds, the O=Re-O unit shows a significant, but relatively small, deviation from linearity (171°-173°), corresponding to small displacements of the two oxygen donors to the dppe side. Despite the fact that the three R groups have different sizes and (or) electronic properties, the OR groups are all roughly end-on coordinated (Re-O-C ~ 160°). Our Re=O and Re-OR distances in the two alkoxo compounds are in good agreement with the mean values of 1.70(3) and 1.89(5) Å, respectively, obtained from the literature (41). For the phenoxo complex, our distances of 1.686(6) and 1.900(6) Å are not very different from those reported for $\text{ReOCl}_3(\text{PPh}_3)(L)$ with L = 2-diethylaminomethyl-4-methyl-phenol (1.669(3) and 1.915(3) Å, respectively), where the Re-O-C angle $(166.0(3)^{\circ})$ is similar to ours (16). In the two other structures published so far with simple phenolates, the distances tend to be greater (1.666(6) and 1.969(5) Å, 1.703(6) and 1.989(6) Å, respectively) (53, 54), which could be correlated with the pronounced bent in the Re-O-C region $(146.5(5)^{\circ} \text{ and } 137.7(6)^{\circ}, \text{ respectively}).$

In the three known structures of 1:1 Re(V)-dppe compounds (31, 55), the mean Re-P distance is 2.45(2) Å, the bite angle P-Re-P is 82.9(6)°, and the P-C-C-P torsion angle in the chelate ring is 58(4)°. Our results are in good agreement with these data and the phenyl rings also adopt very similar orientations. The Re-Cl (2.428–2.457 Å, σ = 0.001 Å) and Re-Br (2.570(1), 2.599(1) Å) distances are appreciably greater than the mean values from the literature for Re—X bonds cis to Re=O (Re—Cl = 2.38(3) Å, Re—Br = 2.51(3) Å; based on 130 and 14 structures, respectively) (41). Although these bonds could be weakened by the phosphine trans influence, this cannot be the controlling factor, since the corresponding distances are normal in the $ReOX_3(dppe)$ complexes (Re-Cl = 2.38 Å, Re-Br =2.52 Å) (31). The lengthening of the Re—X bonds may be ascribed to the good π donor character of the end-on coordinated OR group, whose donation into d_{xz} and d_{yz} makes these orbitals less electrophilic and reduces their ability to accept π -electron density from the equatorial halides. This pattern is also observed for the trans bis-PPh₃ complexes: the cis Re—Cl bonds in $\text{ReOCl}_3(\text{PPh}_3)_2$ (56) are shorter (2.397(1) Å) than in the related oxo-alkoxo complexes (2.41 Å) (31, 57, 58).

The oxo ligand tends to repel the adjacent bonds, resulting in a displacement of the Re atom from the "equatorial" P_2X_2 plane on the oxo side, as evidenced from the mean of the O=Re-L_{cis} angles being ~93° compared with ~88° for the RO-Re-L_{cis} angles. The puckered conformation of the ring creates systematic differences in the coordination geometry of the two ends of dppe. The trans-X_A-Re-P_A units (involving the $P_{\rm A}$ atom bonded to the methylene group on the oxo side of the P_2X_2 plane) are more linear (alkoxo (~177°), halo $(\sim 174^{\circ})$ (31)) than the *trans*-P_B-Re-X_B unit (alkoxo ($\sim 172^{\circ})$), halo (~164°)). Also, our Re-X_A distances are systematically ~0.025 Å longer than Re-X_B, whereas the opposite trend is noted, to a lesser extent, for the Re-P distances. This pattern of bond lengths is not shared by the ReOX₃(dppe) compounds, however (31).

The molecules are packed in the unit cell with normal van der Waals contacts (Figs. S-4 and S-5).³

Crystal structure of Re(NC₆H₄Cl)Cl₃(dppe)

The Re(NC₆H₄Cl)Cl₃(dppe) molecule adopts the structure shown in Fig. 3. The octahedral coordination of Re includes a multiple-bonded 4-chlorophenylimido group with the trans site filled by a chloro ligand, leading to the fac configuration observed for the corresponding bis(diphenylphosphino)ferrocene complex (59). Selected interatomic distances and bond angles are given in Table 4.

The Re=NR distance (1.707(5) Å) and the small departure from linearity in the Re=N-C unit (171.5(5)°) correspond well with the available data on arylimido complexes (mean values: Re=N (1.716(15) Å), Re=N-C (172(5)°); based on 42 structures) (41). A detailed comparison with the related compounds Re(NPh)Cl₃(PPh₃)₂ (trans-P,P) (60), Re(NPh)Cl₃{bis(diphenylphosphino)ferrocene} (cis-P,P) (59), and Re(NPh)Cl₃(PMe₃)₂ (cis-P,P) (61) is provided in the supplementary material (Table S-1).³ For the dppe ligand, the P-Re-P "bite" angle and the ring conformation are close to those of the above oxo-alkoxo compounds, but the Re-P



Fig. 2. ORTEP drawings of $\text{ReOCl}_2(\text{OPr})(\text{dppe})$ (A), $\text{ReOBr}_2(\text{OPh})(\text{dppe})$ (B), and $\text{ReOCl}_2(\text{OCy})(\text{dppe})$ (C). For simplicity, only the major conformations are shown and the hydrogens are omitted.

bond lengths are ~0.01 Å shorter here. The Re-Cl distances range from 2.417(2) to 2.438(2) Å, in agreement with the average value of 2.40(3) Å from the literature. As noted for oxo-alkoxo complexes, the metal is displaced from the P_2X_2 plane on the nitrogen side by ~0.20 Å. Steric interactions with the dppe phenyl rings probably explain that the departure from linearity in the trans RN=Re-Cl unit (168.0(2)°) is slightly greater than commonly found (mean for 16 structures ~174(4)°). The phenyl rings at the P_A end of dppe are oriented in the same way (Re-P_A-C_i-C_o = 28° and -71°) as in the oxo-alkoxo complexes, but those of the P_B phosphine group adopt a different orientation corresponding to the opposite pattern of torsion angles (Re-P_B-C_i-C_a = -67° and 15°, respectively). This is likely due to stacking interactions between the C41-C46 dppe group and the phenylimido ring, roughly parallel to the Re-PA bond. This orientation, also observed in the phosphinoferrocene complex, positions the rings nearly parallel to each other (dihedral angle = $24.3(4)^{\circ}$) with a relatively small mean inter-ring distance of 3.6 Å. The complexes are packed individually in the unit cell (Fig. S-6, supplementary material),³ where the aromatic rings participate in various stacking interactions.

The Re(NC₆H₄Cl)Cl₃(dppe) molecule is compared to the isoelectronic ReOCl₃(dppe) compound in Table 4. In the imido complex, the Re—Cl_{cis} bonds are ~0.05 Å longer, whereas the Re—P bonds are ~0.04 Å shorter. This is consistent with the fact that the π donation of the imido group into the metal d_{xz} and d_{yz} orbitals is greater that for the oxo ligand. This should strengthen the bonds with the π -acceptor phosphine, but weaken the Re—X bonds, since the halogens are competing with the oxo or imido ligands for π donation into the same metal orbitals. Interestingly, the orientations of the dppe rings in ReOCl₃(dppe) do not follow the pattern found for Re(NC₆H₄Cl)Cl₃(dppe) and the ReO(OR)Cl₂(dppe) compounds. This conformational change has no appreciable effect on the coordination geometry.

$ReCl_4(dppe=O) \bullet (CH_3)_2 SO$

In the $\text{ReCl}_4(\text{dppe=O})$ complex shown in Fig. 4, the Re(IV) center possesses an octahedral coordination. The

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R	Propyl	Cyclohexyl	Phenyl ^b			
Х	Cl	Cl	Br			
Bond distances (Å)						
Re=O	1.698(3)	1.700(2)	1.686(6)			
Re—OR	1.885(3)	1.877(2)	1.900(6)			
Re—P _A	2.4260(10)	2.4305(9)	2.432(2)			
Re—P _B	2.4320(10)	2.4364(8)	2.446(3)			
Re—X _A	2.4475(10)	2.4570(10)	2.5990(11)			
Re—X _{B'}	2.4280(11)	2.4296(9)	2.5700(11)			
Bond angles (°)						
P _A -Re-P _B	83.26(3)	83.19(3)	83.59(9)			
X _A -Re-X _B	87.57(4)	87.11(3)	87.41(4)			
O=Re-OR	172.57(14)	172.87(11)	171.8(3)			
P _A -Re-X _A	176.37(4)	177.03(3)	176.81(7)			
P _B -Re-X _B	170.61(4)	172.93(3)	172.65(7)			
P _A -Re-X _B	95.96(4)	95.45(3)	94.92(6)			
P _B -Re-X _A	93.13(4)	94.09(3)	93.82(7)			
O=Re-P _A	86.29(10)	86.27(9)	86.7(2)			
O=Re-P _B	92.49(11)	91.52(9)	90.1(2)			
O=Re-X _A	96.80(11)	95.02(9)	95.2(2)			
O=Re-X _B	94.17(10)	95.32(9)	97.0(2)			
RO-Re-P _A	87.89(9)	87.95(8)	87.50(19)			
RO-Re-P _B	82.24(10)	83.65(8)	83.47(19)			
RO-Re-X _A	88.38(10)	90.57(8)	90.36(19)			
RO-Re-X _B	91.36(10)	89.37(8)	89.28(18)			
Re-O-C	160.8(5) (80%) ^c	$153.6(3) (60\%)^c$	162.3(5)			
	159.5(9) (20%) ^c	$157.0(6) (40\%)^c$				
P _A -C-C-P _B	58.9(3)	57.1(3)	57.9(9)			
$C-C-P_A-C_i$	-168.3(3)	-168.7(2)	-171.7(7)			
	79.7(3)	80.2(3)	76.7(7)			
$C-C-P_B-C_i$	81.6(3)	82.3(3)	84.3(8)			
	-169.2(3)	-169.2(2)	$-166.8(9) (60\%)^c$			
			$-185.4(7) (40\%)^{c}$			
$\operatorname{Re-P_A-C_i-C_o}$	34.3(5)	26.6(4)	14.2(10)			
	-60.7(4)	-64.8(3)	-57.5(7)			
$\text{Re-P}_{\text{B}}\text{-}\text{C}_{i}\text{-}\text{C}_{o}$	-16.5(4)	-22.0(4)	-27.3(10)			
	/5.8(5)	69.0(4)	88(2) (60%) ^c			
Re•••PPXX	0.1053(6)	0.0882(4)	0.1012(10)			
${}^{a}P_{A}$ bonded to the CH ₂	^{<i>a</i>} P, bonded to the CH ₂ group on the oxo side of the P_2X_2 plane. P_2 bonded to the CH ₂ group on the OR side. X.					

Table 3. Distances (Å) and angles (°) in the ReOX₂(OR)(dppe) compounds.^a

 ${}^{a}P_{A}$ bonded to the CH₂ group on the oxo side of the P₂X₂ plane, P_B bonded to the CH₂ group on the OR side, X_A trans to P_A, X_B trans to P_B.

^bTorsion angles calculated for the (-x, -y, -z) molecule for consistency.

^cValues corresponding to the two disordered orientations, occupancies within round brackets.

bidentate ligand is actually $Ph_2PC_2H_4PPh_2(O)$, which is a dppe ligand in which one end has been oxidized to phosphine oxide. A similar arrangement was observed for ReCl₄(dppm=O). Selected interatomic distances and bond angles are given in Table 5.

The angles in the octahedron are close to ideality. The largest deviation, found for the mutually trans Re—Cl bonds, reflects a small displacement for the chlorines towards the chelate ring. The Re-ligand distances compare well with the literature results. For mutually trans Re—Cl bonds, the distances observed here are close to the mean value 2.336(14) Å determined from 21 Re(IV) structures (41). When the chloro ligand sits trans to a different donor atom, the mean value from the literature (23 structures) is similar (2.325(30) Å), but it covers a broader range, mainly because it is sensitive to the trans influence of the opposite ligand. In our structure, the Re—Cl bond trans to oxygen (2.319(2) Å) is appreciably shorter than the one trans to the phosphine group (2.335(2) Å), whose trans influence is large.

CI(64)

C(41)

C(51)

CI(1)

N(1) Son P(2

Re



CI(3) Ø

C(61)

C(11)

C(21)

CI(2)

C(31)



In the unit cell (Fig. S-7),³ the molecules form layers parallel to the a axis and oriented along the cell diagonal. Between these layers, the superposition of DMSO molecules fills channels extending along the cell a axis.

Comparisons are made in Table 5 with ReCl₄(dppm=O) (62), which differs from our compound by the size of the chelate ring. The O-Re-P angle in the six-membered ring with dppe=O (89.2(2)°) is much greater than that of the dppm=O five-membered ring (80.7°). This leaves less space for the opposite chlorines, which get closer together: the Cl-Re-Cl angle is 93.46(9)° here, compared to 97.7° for the dppm=O complex. Another difference is the Re-O=P angle, which is 140.5(3)° here, but 130.1° in ReCl₄(dppm=O). This angle is known to be very flexible: it is ~155° for monodentate O=PR₃ ligands, but it can adjust readily to ex-

Table 4. Distances (Å) and	angles (°)	in fac-Re(NC ₆	$H_4Cl)Cl_3(dppe)$
and ReOCl ₃ (dppe).			

	$NC_6H_4Cl^a$	O^b
Bond distances (Å)		
Re=NR	1.707(5)	1.680
Re-Cl _{trans}	2.420(1)	2.429
Re—P _A	2.421(1)	2.463
Re—P _B	2.414(2)	2.445
Re—Cl _A	2.438(2)	2.377
Re—Cl _B	2.417(2)	2.380
Bond angles (°)		
P _A -Re-P _B	83.37(5)	83.3
Cl _A -Re-Cl _B	85.92(6)	86.3
RN=Re-Cl _{trans}	168.0(2)	163.0
P _A -Re-Cl _A	174.96(5)	173.2
P _B -Re-Cl _B	165.56(6)	164.5
P _B -Re-Cl _A	96.56(5)	92.9
P _A -Re-Cl _B	92.92(5)	95.9
N-Re-P _A	90.5(2)	84.3
N-Re-P _B	90.6(2)	91.4
N-Re-Cl _A	94.6(2)	101.4
N-Re-Cl _B	103.4(2)	103.9
Cl _{trans} -Re-P _A	83.92(5)	82.2
Cl _{trans} -Re-P _B	78.19(5)	76.8
Cl _{trans} -Re-Cl _A	91.13(6)	91.5
Cl _{trans} -Re-Cl _B	87.56(6)	87.7
Re=N-C	171.5(5)	_
$P-Re \bullet C_i - C_o$ (imido)	3.9(6)	—
P _A -C-C-P _B	55.7(6)	59.8
$C-C-P_A-C_i$	-162.9(5)	-163.7
	89.2(5)	81.8
$C-C-P_B-C_i$	77.9(5)	76.4
	-175.1(5)	-173.7
$\text{Re-P}_{A}-\text{C}_{i}-\text{C}_{o}$	28.3(6)	54.3
	-70.8(6)	-58.0
$\text{Re-P}_{\text{B}}\text{-}\text{C}_{i}\text{-}\text{C}_{o}$	-67.0(6)	-28.9
DDDVV	15.1(8)	74.2
ке•••РРАХ	0.2018(7)	0.226

"Torsion angles for $Re(NC_6H_4Cl)Cl_3(dppe)$ calculated for the

(-x, -y, -z) molecule for consistency with Table 3.

^bReference 31.

ternal strain. The very small angle for the dppm=O complex reflects the high constraint for a five-membered chelate ring.

One of the Re-Cl distances (2.215 Å) reported for the dppm=O complex is extremely small. This bond, trans to the phosphine oxide group, seems to be ~0.1 Å shorter than the corresponding bond in our dppe=O complex. Partial substitution of the Re(IV) complex ReCl₄(dppm=O) in the crystal by Re(V) molecules *mer*-ReOCl₃(dppm=O) (63, 64) could explain this "apparent" shortening, since the oxo ligand would be trans to the phosphine oxide in the latter species. Such solid solutions of "quasi-isostructural" oxo-Re(V) and chloro-Re(IV) complexes have already been detected (65) and in the resulting average structure, the "Re—Cl(O)" bond

Table 5. Distances (Å) and angles (°) in $\text{ReCl}_4(\text{dppe=O})$ and $\text{ReCl}_4(\text{dppm=O})$.

	ReCl ₄ (dppe=O)	ReCl ₄ (dppm=O) ⁴
Bond distances (Å)		
Re—O(1)	2.039(5)	2.087(7)
Re—P(2)	2.512(2)	2.467(3)
Re—Cl(1)	2.319(2)	2.215(5)
Re—Cl(2)	2.353(2)	2.353(3)
Re—Cl(3)	2.312(2)	2.340(3)
Re—Cl(4)	2.339(2)	2.361(3)
O(1)—P(1)	1.517(6)	1.523(8)
Bond angles (°)		
Cl(3)-Re-Cl(4)	173.61(8)	173.8
P(2)-Re-Cl(1)	176.37(7)	169.1
O(1)-Re-Cl(2)	178.02(15)	173.2
O(1)-Re-P(2)	89.2(2)	80.7(2)
Cl(1)-Re-Cl(2)	93.46(9)	97.7(1)
O(1)-Re-Cl(2)	87.2(2)	88.6(2)
O(1)-Re-Cl(3)	86.3(2)	87.1(2)
O(1)-Re-Cl(4)	88.1(2)	86.7(2)
P(2)-Re-Cl(1)	90.16(7)	93.0(1)
P(2)-Re-Cl(3)	88.69(7)	86.8(1)
P(2)-Re-Cl(4)	87.98(8)	92.6(1)
Cl(3)-Re- $Cl(1)$	91.76(9)	95.3(2)
Cl(1)-Re-Cl(4)	93.70(9)	90.9(2)
Cl(3)-Re-Cl(2)	90.90(8)	90.1(1)
Cl(4)-Re- $Cl(2)$	92.08(9)	89.4(1)
Re-O(1)-P(1)	140.5(3)	130.1(4)
P(1)-C(11)-C(12)-P(2)	-78.8(6)	_
Re-O(1)-P(1)-C(11)	15.1(6)	-2.5
Re-O(1)-P(1)-C(21)	134.8(5)	-123.8
Re-O(1)-P(1)-C(31)	-106.3(6)	115.1
O(1)-Re-P(2)-C(12)	-1.2(3)	22.8
O(1)-Re-P(2)-C(41)	117.9(3)	139.2
O(1)-Re-P(2)-C(51)	-116.0(3)	-96.5
Re-P(2)-C(41)-C _{ortho}	55.0(7)	-9.0
Re-P(2)-C(51)-C _{ortho}	69.5(7)	-71.9
O(1)-P(1)-C(21)-C _{ortho}	-8.2(7)	63.3
O(1)-P(1)-C(31)-C _{ortho}	-23.8(8)	5.6

^aReference 62 esds not calculated for all entries.

seems to be shortened with respect to a normal Re—Cl bond, but to be stretched when compared to an Re=O bond.

Electronic spectra and DFT calculations

The low-energy portions $(8000-25\ 000\ \text{cm}^{-1})$ of the absorption spectra of representative compounds are shown in Fig. 5. Spectra taken with crystalline $\text{ReOX}_3(\text{dppe})$ and $\text{ReOX}_2(\text{OR})(\text{dppe})$ compounds confirmed that the species in the solid is retained in DMSO. In all cases, this spectral region shows two major components. The data are listed in Table 6.

Strictly speaking, the molecules examined here have no symmetry, but if chelate ring puckering and other minor distortions are ignored, a mirror plane containing the Re=O(NR) bond bisects the P-Re-P angle, so that the metal environment has an approximate C_s symmetry. Under this low symmetry, the antibonding d_{xz}/d_{yz} orbitals, which are de-

Fig. 5. Typical electronic spectra of the ReEX₂(Y)(dppe) complexes in DMSO.



Fig. 6. Ground and low-energy excited states for the Re(V) d^2 systems: singlet ground state (S), first triplet excited state (T*), first singlet excited state (S*), second singlet excited state (S**).



generate under D_{4h} symmetry, become inequivalent. For this point group symmetry, the interbond orbital in the *xy* plane is labeled $d_{x^2-y^2}$ (instead of d_{xy}), and for consistency with the recent study on isoelectronic oxo-molybdenum(IV) systems by Da Re and Hopkins (66), the d_{yz} will be assumed to lie at lower energy than d_{xz} . The two absorption features in Fig. 5 are assigned to the two spin-allowed singlet-singlet transitions $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1 (d_{yz})^1 [S \rightarrow S^*]$ and $(d_{x^2-y^2})^2 \rightarrow$ $(d_{x^2-y^2})^1 (d_{xz})^1 [S \rightarrow S^{**}]$, respectively (Fig. 6). Therefore, the position of these bands can be used to estimate the two HOMO–LUMO energy gaps. Singlet–triplet processes [S \rightarrow T*] could in principle take place, but there is no evidence for these much weaker spin-forbidden transitions in the spectra recorded here.

Two well-differentiated components (12 000 and 16 400 cm⁻¹) are visible for ReOCl₃(dppe). Replacing Cl by Br produces similar red shifts on both (11 300 and 15 500 cm⁻¹). Upon substitution of the oxo ligand by a phenylimido group in Re(NPh)Cl₃(dppe), the two components are not equally displaced: the low-energy component undergoes a very small red shift of ~900 cm⁻¹, whereas the shift on the other is greater ($\sim 3000 \text{ cm}^{-1}$). This could be connected with the different symmetries of these two ligands. For the cylindrical oxo ligand, the p_x and p_y orbitals are equally available for π interacting with the metal d_{xz} and d_{yz} orbitals. In contrast, for the imido group, the phenyl ring renders these orbitals inequivalent, since only one is participating in the aromatic π system. Consequently, π interactions with the metal d_{xz} and d_{yz} orbitals being no longer equal, the transitions to these orbitals are anticipated to be differently affected.

	X = Cl		X = Br	
	$[S \rightarrow S^*]$	$[S \rightarrow S^{**}]$	$[S \rightarrow S^*]$	$[S \rightarrow S^{**}]$
ReOX ₃ (dppe)	12.0(13)	16.4(25)	11.3(13)	15.5(21)
ReO(OMe)X ₂ (dppe)	17.0(11)	20.1(23)	16.8(14)	20.2(34)
ReO(OEt)X ₂ (dppe)	16.4(12)	20.0(21)	16.4(15)	20.0(33)
ReO(OPr)X ₂ (dppe)	16.5(10)	20.0(22)	16.6(16)	20.0(35)
ReO(OPh)X ₂ (dppe)	$\sim 15.1(sh)^{a}$	_	_	_
Re(NPh)X ₃ (dppe)	11.1(118)	13.4(74)	_	_
$Re(NC_6H_4Cl)X_3(dppe)$	11.5(115)	13.5(70)		

Table 6. $[S \rightarrow S^*]$ and $[S \rightarrow S^{**}]$ of the low-energy components of the electronic spectra.

^aThe position of the shoulder produced by the lower-energy component was estimated; the higher energy component was completely masked by a phenoxo strong band.

Table 7. Comparison of the experimental transition energies with the DFT-calculated values (cm⁻¹ × 10⁻³) for the E=ReX₂Y(dppe) compounds.

	Х		$[S \rightarrow S^*]$		$[S \rightarrow S^{**}]$	
E		Y	Experimental $(cm^{-1} \times 10^{-3})$	Calculated $(cm^{-1} \times 10^{-3})$	Experimental $(cm^{-1} \times 10^{-3})$	Calculated $(cm^{-1} \times 10^{-3})$
0	Cl	OEt	16.4	9.42	20.0	10.21
0	Cl	OPh	15.1	8.41	_	8.71
0	Cl	Cl	12.0	6.78	16.4	8.25
0	Cl	OC_6F_5	—	5.95	—	6.63
0	Br	Br	11.3	6.63	15.5	7.66
0	Ι	Ι	_	6.15	_	7.09
NPh	Cl	Cl	11.1	5.91	13.4	7.55
NC ₆ H ₄ Cl	Cl	Cl	11.5	5.91	13.5	6.94
NC ₆ F ₅	Cl	Cl		4.74		6.54

Substitution of the trans halogen of ReOX₃(dppe) by an -OR group has a more drastic effect. In the ReOX₂(OR)(dppe) compounds, both components undergo relatively large blue shifts to ~16 600 and 20 000 cm⁻¹, respectively, and the separation (~3000 cm⁻¹) is a little smaller than in the tris-halogen complexes (~4000 cm⁻¹). Again, these unequal variations can be ascribed to the noncylindrical symmetry of the bent alkoxo group. One of the oxygen *p* orbitals (perpendicular to the Re-O-C plane) remains suitably oriented for optimal π interacting with one of the *d* orbitals, but partial hybridization will decrease the participation of the other *p* orbital (in the Re-O-C plane) in π interactions.

To understand the behavior of these oxo- and arylimidorhenium(V) systems and orient our research strategies, theoretical calculations were performed with the PCSPARTAN PRO software (67). A simplified model was used to reduce computation time. Structure optimization on molecules containing dppe itself were time consuming, because adjusting the orientation of the four phenyl rings required many refinement cycles and convergence was not always reached. Since the comparisons to be made always involve the same diphosphine, the calculations were run using bis(dimethylphosphino)ethane (dmpe), in which the substituents are "cylindrical" methyl groups. On the other hand, since PCSPARTAN does not include rhenium parameters for DFT calculations, technetium was used in the model. The geometry and orbital energies were obtained by DFT calculations based on the generalized gradient approximation uti**Fig. 7.** Variation of the DFT-calculated energy gap as a function of the transition energy obtained experimentally from the spectra for each of the two transitions.



lizing the functionals proposed by Becke and Perdew (67). The BP86 (self-consistent model) and DN* (double numerical polarization) options were used. The calculated energies are listed in Table 7 and they are plotted against the experimental results in Fig. 7.

For each of the two transitions, there is an approximate linear relationship between the energies determined from the spectra and those predicted from the calculations. This suggests that the calculations reflect in a satisfactory manner the factors affecting the energy levels in these systems. The re-

duction of the transition energy upon substitution of the oxo ligand by an arylimido moiety and the energy increase by replacing the trans halogen with an -OR group are reproduced well by the calculations. Even the small red shift resulting from the substitution of chlorine by bromine is consistent with the DFT predictions. However, this approach was unable to explain various fine features, for instance the fact that the difference between the two transition energies does not vary smoothly. The calculations did not reveal any substantial effect of the orientation of the noncylindrical arylimido or -OR groups on the transition energies and it is not clear whether orientation is actually unimportant or masked by model simplification or other weaknesses in our approach. The fact that the calculations were actually carried out on Tc complexes could introduce some distortions when the results are applied to Re compounds, the more so that spin-orbit coupling, which cannot be taken into account in PCSPARTAN, could play a role. Another weakness of our results is that significant geometrical distortions, namely nonlinearity in the RN(O)=Re-L unit and displacement of the Re atom above the equatorial plane, were not accurately reproduced in the converged model and this could introduce small distortion in the orbital energy pattern. Nevertheless, the method is believed to reproduce the general absorption features sufficiently well to be useful in the orientation of future studies.

Concluding remarks

On the basis of the two low-energy UV-vis absorptions observed for the series of ReEX₂Y(dppe) compounds (with E = O or NR, X = Cl or Br, Y = Cl, Br, OR), it was established that the energies of the spin-allowed transitions between the nonbonding interbond orbital $(d_{x^2-y^2})$ and the π -antibonding d_{xz}/d_{yz} orbitals follow the order RN=Re-X < O=Re-X < O=Re-OR. Replacing chlorine by bromine reduces the energies slightly, whereas the lengthening of the alkyl chain in the -OR group (R = Me, Et, Pr, $-C_2H_4OH$) had no detectable effect. We expected the bulky cyclohexyl substituent would force the Re-O-R segment to be more linear, but these expectations did not materialize (see crystal structure) and the absorption spectrum of this compound does not differ from those of compounds with a smaller R group. The aromatic group in ReOX₂(OPh)(dppe) seems to reduce the first transition energy slightly, but this is difficult to evaluate, because the weak d-d transitions are masked here by a strong allowed transition involving the phenoxo group.

Although the DFT calculations cannot explain all the fine details present in the data, the general trends observed experimentally are reproduced sufficiently well to attribute some predictive capability to this approach. Transition energies calculated for a few promising systems are included in Table 7. The calculations suggest that incorporating strong electro-attracting features into either the phenylimido or the phenoxo group should shift the transitions to lower energies. On this basis, perfluorophenoxo complexes ReOX₂-(OC₆F₅)(dppe) or perfluorophenylimido compounds Re(NC₆F₅)X₃(dppe) could be interesting candidates. Replacing chlorine or bromine by iodine also seems to be a

possible strategy to reduce further transition energy. Preparative work is underway to test these predictions.

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