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THE ISOLATION AND CHARACTERIZATION OF THE FIRST EXAMPLES OF PAIRS OF α- AND β-ISOMERS OF DIRHENIUM(II) OF TYPE $Re_2X_4(LL)_2$ (X = Cl OR Br, LL = BIDENTATE PHOSPHINE LIGAND)

LORI BETH ANDERSON, MOHAMMED BAKIR and RICHARD A. WALTON*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, U.S.A.

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Abstract—The complexes $Re_2Br_4(depe)_2$ and $Re_2X_4(dppee)_2$ (X = Cl or Br, depe = $Et_2PCH_2CH_2PEt_2$, dppee = *cis*-$Ph_2PCH{=}CHPPh_2$) have been prepared in their α- (eclipsed rotational geometry, chelating phosphine ligands) and β- (staggered rotational geometry, bridging phosphine ligands) isomeric forms. The chloro complex β-$Re_2Cl_4(depe)_2$ has also been isolated. In the case of α- and β- $Re_2Br_4(depe)_2$, the preparations involve the reactions of $Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ with depe in toluene–ethanol. While α-$Re_2X_4(dppee)_2$ are prepared from the reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ with dppee in various solvents, the β-isomers are obtained upon reacting $Re_2X_4(PR_3)_4$ (R = Et or *n*-Pr) with dppee in benzene. These are the first examples of triply bonded dirhenium(II) complexes that have been isolated in both their α- and β-forms. β-$Re_2X_4(dppee)_2$ (X = Cl or Br) constitute the first examples of complexes of this structural type which contain both C═C and M≡M units within the same fused decalin-like ring system. The isomers β-$Re_2Cl_4(depe)_2$ and β-$Re_2X_4(dppee)_2$ (X = Cl or Br) are oxidized by $NOPF_6$ in acetonitrile to give paramagnetic β-$[Re_2Cl_4(depe)_2]PF_6$ and β-$[Re_2X_4(dppee)_2]PF_6$. These oxidized complexes in turn react with CH_3CN in the presence of $TlPF_6$ to afford β-$[Re_2Cl_3(depe)_2(NCMe)](PF_6)_2$ and β-$[Re_2X_3(dppee)_2(NCMe)](PF_6)_2$, respectively. The cleavage of the Re≡Re bonds of α- and β-$Re_2Cl_4(dppee)_2$ occurs upon their reaction with CCl_4–CH_2Cl_2 to give *cis*-$ReCl_4(dppee)$. The related bromo complex *cis*-$ReBr_4(dppee)$ is formed when β-$Re_2Br_4(dppee)_2$ is reacted with CH_2Cl_2–Br_2.

The existence of the complexes β-$M_2X_4[R_2P(CH_2)_2PR_2]_2$ (M = Mo, W, or Re; X = Cl, Br or I; R = Me, Et or Ph) which contain intramolecular bridging phosphine ligands has sparked considerable interest.[1–4] This bonding mode leads to the formation of two stable six-membered rings that are fused about a common metal–metal quadruple (M = Mo or W) or triple (M = Re) bond. These compounds have proved to be of significance in metal–metal multiple bond chemistry from the point of view of the ring conformations that are present, the rotational geometry (eclipsed or staggered) about the metal–metal multiple bond, and their chirality.[1–3,5] In the case of the complexes where M = Mo or W, the related α-isomers, in which the phosphine ligands are chelating and there is an eclipsed rotational geometry, have also been isolated in some instances.[1–3]

We now report the first cases of dirhenium(II) complexes of this type which have been isolated in both their α- and β-isomeric forms [the phosphine ligands are $Et_2PCH_2CH_2PEt_2$(depe) and *cis*-$Ph_2PCH{=}CHPPh_2$(dppee)]. In the case of β-$Re_2X_4(Ph_2PCH{=}CHPPh_2)_2$ (X = Cl or Br), these complexes constitute the first examples of complexes of this type which contain both C═C and M≡M units within the same fused decaline-like ring system.

EXPERIMENTAL

Starting materials

Samples of the complexes $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$,[6] $Re_2Cl_4(PEt_3)_4$,[7] $Re_2X_4(P\text{-}n\text{-}Pr_3)_4$ (X = Cl or Br)[7]

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* Author to whom correspondence should be addressed.

and α-$Re_2Cl_4(dmpe)_2$[8] were prepared, according to the literature methods, from $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br)[9,10] and the appropriate phosphine in alcohol solution. The $Me_2PCH_2CH_2PMe_2$(dmpe), depe and dppee ligands were purchased from Strem Chemicals. In the case of depe, a 0.606 M solution in toluene was used. The $LiBEt_3H$ reagent was obtained from Aldrich as a 1.0 M solution in THF. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction procedures

All reactions were performed in a nitrogen atmosphere using standard vacuum line techniques. Chromatographic separations were performed on a silica gel column (60–200-mesh, Davidson Grade 62).

(A) *Preparation of* $Re_2X_4(depe)_2$. (i) β-$Re_2Cl_4(depe)_2$. A quantity of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (0.30 g, 0.26 mmol) was suspended in 20 cm^3 of a 1 : 1 mixture (by volume) of toluene and ethanol, and then treated with depe (1.29 cm^3, 0.78 mmol). This reaction mixture was refluxed for 20 h, cooled to room temperature, and ethanol (~ 15 cm^3) was added. The purple crystalline product which precipitated from the purple-brown solution was collected by filtration, washed with ethanol and hexane, then dried *in vacuo*: yield 0.140 g (70%). Found: C, 25.8; H, 5.3. Calc. for $C_{20}H_{48}Cl_4P_4Re_2$: C, 25.9; H, 5.2%.

(ii) α-$Re_2Br_4(depe)_2$. The preparation of this complex involved refluxing a mixture of $Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (0.465 g, 0.35 mmol) and depe (1.75 cm^3, 1.1 mmol) in 20 cm^3 of a 1 : 1 mixture (by volume) of toluene and ethanol for 24 h. The reaction mixture was cooled, filtered, and the dark green crystalline solid collected. The purple-brown filtrate was set aside [see A(iii)]. The green product was washed with ethanol and hexane and dried *in vacuo*; yield 0.262 g (68%). Found: C, 22.0; H, 4.4. Calc. for $C_{20}H_{48}Br_4P_4Re_2$: C, 21.7; H, 4.4%.

(iii) β-$Re_2Br_4(depe)_2$. Addition of 20 cm^3 of ethanol to the purple-brown filtrate obtained from A(ii) yielded a purple solid. This was collected, washed with ethanol and hexane and dried *in vacuo*; yield 0.032 g (8%). The identity of this product was based upon its electrochemical and spectroscopic properties (*vide infra*).

(B) *Preparation of* $Re_2X_4(dppee)_2$. (i) α-$Re_2Cl_4(dppee)_2$. A mixture comprising $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.20 g, 0.175 mmol), dppee (0.60 g, 1.51 mmol), and 10 cm^3 of methanol, to which eight drops of conc. HCl had been added, was refluxed for 24 h. The resulting reaction mixture was cooled to room temperature and filtered to give a green solid and yellow filtrate. The solid was washed with methanol until the washings were colorless, and then with hexanes and finally diethyl ether. It was purified by chromatography (silica gel column with CH_2Cl_2 as eluent) and recrystallized from CH_2Cl_2–diethyl ether; yield 0.035 g (15%). Found: C, 47.9; H, 3.7; Cl, 11.0. Calc. for $C_{52}H_{44}Cl_4P_4Re_2$: C, 47.8; H, 3.4; Cl, 10.8%.

The reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppee in refluxing ethanol (4 days) likewise gave α-$Re_2Cl_4(dppee)_2$ in low yield. Work-up of the yellow filtrate from this reaction, and that from the analogous reaction in methanol–conc. HCl (*vide supra*), gave *trans*-$[ReCl_2(dppee)_2]Cl \cdot nH_2O$ as a second product.[11] The reaction of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ (0.10 g, 0.10 mmol) with dppee (0.26 g, 0.67 mmol) in refluxing ethanol (10 cm^3) for 4 days gave a green-yellow solid which was filtered off, washed with hexanes and diethyl ether, and dried. This product was washed with CH_2Cl_2 to give a green extract [shown to be α-$Re_2Cl_4(dppee)_2$]; the remaining orange-yellow solid was shown to be *trans*-$ReCl_2(dppee)_2$.*

(ii) β-$Re_2Cl_4(dppee)_2$. A mixture of $Re_2Cl_4(PEt_3)_4$ (0.15 g, 0.152 mmol), dppee (0.18 g, 0.454 mmol) and 10 cm^3 of benzene was refluxed for 2 days. The reaction mixture was cooled to room temperature and filtered. A light brown solid was collected, and washed with benzene, methanol, hexanes and diethyl ether. The product was purified by chromatography (silica gel column with CH_2Cl_2 as eluent) and recrystallized from CH_2Cl_2–diethyl ether: yield 0.09 g (45%). Found: C, 47.7; H, 3.4. Calc. for $C_{52}H_{44}Cl_4P_4Re_2$: C, 47.8; H, 3.4%.

β-$Re_2Cl_4(dppee)_2$ was isolated in 35% yield when $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ was used in place of $Re_2Cl_4(PEt_3)_4$ in the above procedure.

(iii) α-$Re_2Br_4(dppee)_2$. The reaction between $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.10 g, 0.067 mmol) and dppee (0.23 g, 0.580 mmol) in 10 cm^3 of methanol that contained eight drops of conc. HBr (48%) was carried out with a procedure similar to that described in B(i) and a reaction time of 2 days. The green insoluble product was found to be the bis-CH_2Cl_2 solvate: yield 0.02 g (20%). Found: C, 39.1; H, 2.9. Calc. for $C_{54}H_{48}Br_4Cl_4P_4Re_2$: C, 39.2; H, 2.9%. The presence and amount of CH_2Cl_2 was confirmed by ^1H NMR spectroscopy in $(CD_3)_2SO$ ($\delta = +5.76$).

The filtrate from this reaction was evaporated to low volume to afford orange crystals of $[ReBr_2(dppee)_2]Br \cdot H_2O$: yield 0.036 g (22%).[11]

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* The identity of *trans*-$ReCl_2(dppee)_2$ has been established by an X-ray structure analysis[11] and its independent preparation from the one-electron reduction of *trans*$[ReCl_2(dppee)_2]Cl$.

(iv) β-$Re_2Br_4(dppee)_2$. The reaction between $Re_2Br_4(PR)_3)_4$ (R = Et or n-Pr) and dppee in refluxing benzene gave brown β-$Re_2Br_4(dppee)_2$ in yields of 35–50% when a procedure similar to B(ii) was used. Purification was affected by chromatography (silica gel column with CH_2Cl_2 as eluent) and recrystallization from CH_2Cl_2–diethyl ether. Found: C, 42.2; H, 3.2. Calc. for $C_{52}H_{44}Br_4P_4Re_2$: C, 42.1; H, 3.0%.

(C) *Reactions of the* $Re_2X_4(depe)_2$ *complexes.* (i) β-$[Re_2Cl_4(depe)_2]PF_6$. The neutral species β-$Re_2Cl_4(depe)_2$ was oxidized by suspending a quantity of it (0.10 g, 0.11 mmol) in 4 cm^3 of CH_3CN. The suspension was chilled, and a stoichiometric quantity of $NOPF_6$ (0.021 g, 0.12 mmol) added. Following the addition of $NOPF_6$, all of the solid dissolved to yield a red-violet solution. The solution was warmed to room temperature and stirred for 30 min. It was filtered to remove any trace amounts of unreacted $NOPF_6$ and diethyl ether was added to the filtrate. The resulting red-violet solid was collected by filtration, washed with diethyl ether and dried *in vacuo*: yield 0.085 g (74%). Found: C, 22.3; H, 4.7. Calc. for $C_{20}H_{48}Cl_4F_6P_5Re_2$: C, 22.4; H, 4.5%. Addition of an excess of $NOPF_6$ produced the dark purple, air-sensitive dication $[Re_2Cl_4(depe)_2](PF_6)_2$ as evidenced by its electrochemical properties.

(ii) β-$[Re_2Cl_3(depe)_2(NCMe)](PF_6)_2$. The preparation of this complex involved dissolving β-$[Re_2Cl_4(depe)_2]PF_6$ [see C(i)] (0.10 g, 0.093 mmol) and $TlPF_6$ (0.032 g, 0.093 mmol) in 5 cm^3 of acetone and adding 1 cm^3 of CH_3CN. When the reaction mixture was stirred for 12 h, a white precipitate of TlCl formed in the purple-colored reaction medium. This mixture was filtered to remove the TlCl, and diethyl ether was added to the filtrate to precipitate a purple-brown solid. This was collected, washed with diethyl ether and dried *in vacuo*: yield 0.085 g (75%). Found: C, 22.0; H, 4.7. Calc. for $C_{22}H_{51}Cl_3F_{12}NP_6Re_2$: C, 21.6; H, 4.2%.

(iii) β-$[Re_2Cl_3(depe)_2(NCMe)]PF_6$. The reduction of $[Re_2Cl_3(depe)_2(NCMe)](PF_6)_2$ [C(ii)] was accomplished by placing a quantity of it (0.075 g, 0.061 mmol) in 5 cm^3 of THF and adding a solution of $LiBEt_3H$ in THF (0.10 cm^3). The violet suspension turned green-brown within 5 min of stirring the reaction mixture at room temperature. Stirring was continued for a total of 30 min, and diethyl ether added to the green-brown solution to precipitate a light green solid. This solid was collected and recrystallized from CH_2Cl_2–diethyl ether and dried *in vacuo*: yield 0.048 g (73%). Found: C, 24.7; H, 4.8. Calc. for $C_{22}H_{51}Cl_3F_6NP_5Re_2$: C, 24.5; H, 4.8%.

(D) *Reactions of the* $Re_2X_4(dppee)_2$ *complexes.* (i) β-$[Re_2Cl_4(dppee)_2]PF_6$. A mixture of β-$Re_2Cl_4(dppee)_2$ (0.15 g, 0.115 mmol) and $NOPF_6$ (0.022 g, 0.125 mmol) was dissolved in 10 cm^3 of CH_3CN and then stirred for 30 min at room temperature. The solution was reduced in volume and diethyl ether was added to precipitate the product. A pale blue solid was filtered off, washed with hexanes and diethyl ether, and dried *in vacuo*: yield 0.14 g (84%). Found: C, 43.4; H, 3.2. Calc. for $C_{52}H_{44}Cl_4F_6P_5Re_2$: C, 43.0; H, 3.0%.

(ii) $[Re_2Br_4(dppee)_2]PF_6$. A procedure similar to D(i) produced a purple solid; yield 97%. Found: C, 39.0; H, 3.0. Calc. for $C_{52}H_{44}Br_4F_6P_5Re_2$: C, 38.3; H, 2.7%.

(iii) β-$[Re_2Cl_3(dppee)_2(NCMe)](PF_6)_2$. A mixture of β-$[Re_2Cl_4(dppee)_2]PF_6$ (0.09 g, 0.062 mmol) and $TlPF_6$ (0.02 g, 0.06 mmol) was dissolved in 10 cm^3 of CH_3CN. The reaction mixture was stirred at room temperature for 4 h and then evaporated to dryness. The residue was dissolved in CH_2Cl_2 and filtered into a flask containing diethyl ether. The purple insoluble product was filtered off, washed with hexanes and diethyl ether, and dried *in vacuo*: yield 0.075 g (81%). Found: C, 41.9; H, 3.4; Cl, 5.9. Calc. for $C_{54}H_{47}Cl_3F_{12}P_6Re_2$: C, 40.5; H, 3.0; Cl, 6.6%.

(iv) β-$[Re_2Br_3(dppee)_2(NCMe)](PF_6)_2$. A procedure identical to D(iii) produced a purple solid: yield 93%. Found: C, 38.1; H, 3.0. Calc. for $C_{54}H_{47}Br_3F_{12}P_6Re_2$: C, 37.4; H, 2.7%.

(v) *cis*-$ReCl_4(dppee)$. α-$Re_2Cl_4(dppee)_2$ (0.05 g, 0.038 mmol), 5 cm^3 of CH_2Cl_2, and 10 cm^3 of CCl_4 were refluxed for 2 days. The reaction mixture was cooled to room temperature, the solvent evaporated, and the resulting orange residue was extracted into CH_2Cl_2, filtered, and diethyl ether added to the filtrate to crystallize *cis*-$ReCl_4(dppee)$: yield 0.03 g (54%). Found: C, 42.8; H, 3.2; Cl, 19.2. Calc. for $C_{26}H_{22}Cl_4P_2Re$: C, 43.1; H, 3.1; Cl, 19.6%.

When β-$Re_2Cl_4(dppee)_2$ was used in place of the α-isomer, this same mononuclear Re(IV) complex *cis*-$ReCl_4(dppee)$ was isolated in 88% yield.

(vi) *cis*-$ReBr_4(dppee)$. A quantity of β-$Re_2Br_4(dppee)_2$ (0.05 g, 0.034 mmol), was suspended in 10 cm^3 of CH_2Cl_2 and treated with 2 drops of liquid Br_2. This mixture was then stirred at room temperature for 18 h. The solvent was evaporated and the resulting dark red residue was worked-up as described in D(v): yield 0.06 g (98%). Found: C, 34.9; H, 2.7. Calc. for $C_{26}H_{22}Br_4P_2Re$: C, 34.6; H, 2.5%.

Physical measurements

IR spectra were recorded as Nujol mulls using an IBM IR/32 Fourier transform spectrometer (4000–

400 cm^{-1}). Electronic absorption spectra were recorded as CH_2Cl_2 solutions on Cary 17D and IBM 9420 spectrophotometers. Electrochemical experiments were performed by using a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett–Packard Model 7035B x–y recorder. CH_2Cl_2 solutions containing 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte were utilized. $E_{1/2}$ values $[(E_{p,a}+E_{p,c})/2]$ were referenced against an Ag-AgCl electrode at room temperature and were uncorrected for junction potentials. ^{31}P NMR and ^{1}H NMR spectra were recorded with use of a Varian XL-200 spectrometer. The ^{31}P NMR spectra were referenced to H_3PO_4 as an internal standard while for the ^{1}H NMR spectra resonances were referenced internally to the residual protons of the incompletely deuterated solvents.

Analytical procedures

Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University microanalytical laboratory.

RESULTS AND DISCUSSION

Preparation and characterization of $Re_2X_4(depe)_2$ (X = Cl *or* Br)

The complex β-$Re_2Cl_4(depe)_2$ was first prepared and structurally characterized by Cotton and coworkers.[12] However, the reported method for its synthesis produced the desired compound in 20% yield. In order to explore the reaction chemistry of this complex, an improved synthetic route was desirable. We found that by using $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ in place of $(n\text{-}Bu_4N)_2Re_2Cl_8$ and refluxing this, in the presence of depe, in a mixed-solvent system (to enhance the solubility of the starting dirhenium complex), the yield of β-$Re_2Cl_4(depe)_2$ was increased to *ca* 70%. The bromide analogue β-$Re_2Br_4(depe)_2$ could also be isolated using reaction conditions similar to those employed in the preparation of the chloride derivative. The β-isomer, however, was formed in very low yield (< 10%), while the major product of the reaction was α-$Re_2Br_4(depe)_2$. The α-form is insoluble in the reaction mixture and crystallizes during the course of the reaction. This is the first time that α- and β-isomers of a dirhenium(II) complex of this type have been isolated although both isomers are known for certain dimolybdenum(II) and ditungsten(II) species.[1–4]

The identification of the new species α- and β-$Re_2Br_4(depe)_2$* was based upon a comparison of their electrochemical and spectroscopic properties (Table 1) with the related behavior of the structurally characterized complexes α-$Re_2Cl_4(dmpe)_2$,[8] α-$Re_2Cl_4(dppp)_2$ [dppp = $Ph_2P(CH_2)_3PPh_2$],[13] β-$Re_2Cl_4(depe)_2$[12] and β-$Re_2Cl_4(dppe)_2$[dppe = $Ph_2P(CH_2)_2PPh_2$].[14–16] In the case of α-$Re_2Cl_4(dmpe)_2$ and β-$Re_2Cl_4(depe)_2$, these data have not been reported previously and so are included here for the first time (see Table 1). The cyclic voltammograms (CVs) of solutions of these complexes in 0.1 M TBAH–CH_2Cl_2 revealed the presence of two accessible one-electron oxidations (Fig. 1); this property is characteristic of the triply bonded Re_2^{4+} core.[2,17] Oxidation of β-$Re_2Cl_4(depe)_2$ to the paramagnetic monocation was achieved by using 1 equivalent of $NOPF_6$ as the oxidizing agent. Attempts to carry out the analogous oxidation of α-$Re_2Br_4(depe)_2$ led to its decomposition. The oxidized species β-$[Re_2Cl_4(depe)_2]PF_6$ possesses electrochemical processes at $E_{1/2} = +0.08$ V(red) and $E_{1/2} = +0.88$ V(ox) vs Ag–AgCl (Fig. 1). The X-band ESR spectrum of the monocation, as measured at −160°C in CH_2Cl_2,

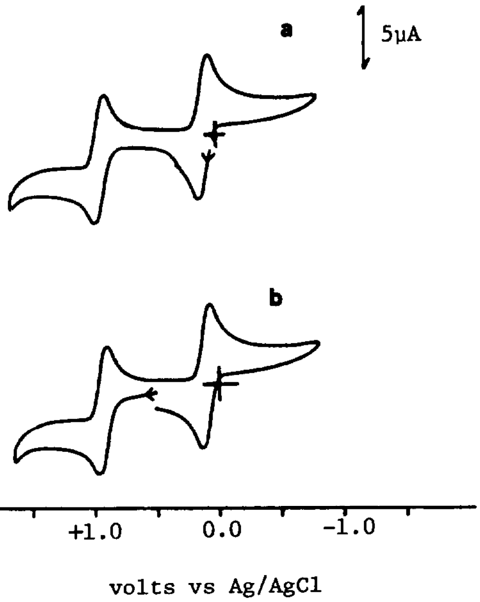

Fig. 1. Cyclic voltammograms (recorded at v = 200 mV s^{-1} using a Pt-bead electrode) for 0.1 M TBAH–CH_2Cl_2 solutions of: (a) β-$Re_2Cl_4(depe)_2$, and (b) β-$[Re_2Cl_4(depe)_2]PF_6$.

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*The structure of α-$Re_2Br_4(depe)_2$ has recently been confirmed by a single-crystal X-ray structure analysis with data collected at −150°C. The structure [space group $I4_1/acd$, with a = 13.466(2) Å and c = 36.619(7) Å] is disordered and the Re—Re distance is 2.202(6) Å (L. F. Falvello, unpublished results).

Table 1. Electrochemical properties and electronic absorption spectra

	Half-wave potentials[a]		Electronic absorption spectrum[b]	
Complex	$E_{1/2}$(ox 1)	$E_{1/2}$(ox 2)	λ (nm) (ε)	Reference
β-Re_2Cl_4(depe)$_2$	+0.08	+0.88	~ 580sh, 492 (200), 438 (180)	[f]
α-Re_2Br_4(depe)$_2$	+0.02	+1.07[c]	842 (130), 545 (150)	[f]
β-Re_2Br_4(depe)$_2$	+0.13	+0.89	505 (200), 442 (200)	[f]
α-Re_2Cl_4(dppee)$_2$	+0.30	+1.05	825m, 613m, 445sh[e]	[f]
β-Re_2Cl_4(dppee)$_2$	+0.24	+1.13	~ 640sh, 474 (300)	[f]
α-Re_2Br_4(dppee)$_2$	+0.33	~ +1.0[d]	842m, 618m, 465sh[e]	[f]
β-Re_2Br_4(dppee)$_2$	+0.34	+1.15	~ 650sh, ~ 575sh, 475m-s[e]	[f]
α-Re_2Cl_4(dmpe)$_2$	+0.21	+1.10[c]	874 (190), 563 (100)	[f]
α-Re_2Cl_4(dppp)$_2$	—	—	820m-s, 642m, 568w, 432s[e]	13
β-Re_2Cl_4(dppe)$_2$	+0.23	+1.04	625sh, 525 (335), 500sh	15, 16

[a] In V vs Ag–AgCl for 0.1 m TBAH–CH_2Cl_2 solutions recorded at $v = 200$ mV s^{-1}. In the case of the reversible couples, the ΔE_p values ($= E_{p,a} - E_{p,c}$) are in the range 90–130 mV.

[b] Spectra recorded in CH_2Cl_2 unless otherwise stated; ε values are given in parentheses.

[c] $E_{p,a}$ value.

[d] Approximate value since for $E_{p,a} = +1.08$ V and $E_{p,c} = +0.90$ V, $i_{p,a} > i_{p,c}$.

[e] Recorded as Nujol mull. Relative intensities of bands are signified by w = weak, m = medium and s = strong.

[f] This work.

displayed a broad signal between 1000 and 4000 G which is centered at $g = 2.1$. In the presence of an excess of $NOPF_6$, the second oxidation can be accessed to yield the dark purple air-sensitive dication. This species was characterized by cyclic voltammetry in 0.1 M TBAH–CH_2Cl_2 solution; the processes at $E_{1/2} = +0.08$ V and $E_{1/2} = +0.88$ V correspond to reductions.

While β-Re_2Cl_4(depe)$_2$ did not react with CH_3CN, its oxidized congener β-[Re_2Cl_4(depe)$_2$]PF_6 did so to give [Re_2Cl_3(depe)$_2$(NCMe)](PF_6)$_2$ when $TlPF_6$ was present. This behavior resembles that observed in the case of the formation of the dppe analogues [Re_2X_3(dppe)$_2$(NCMe)](PF_6)$_2$ (X = Cl or Br).[18] The CV of the paramagnetic dication exhibits $E_{1/2} = +0.35$ V(red) and $E_{p,a} = +1.55$ V vs Ag–AgCl. In this depe-bridged system, the potentials are shifted by at least 1 V to more positive values compared to the dppe analogue.[18] Thus, while the irreversible reduction at ~ −1.5 V in the CV of [Re_2X_3(dppe)$_2$(NCMe)](PF_6)$_2$ is apparently shifted to a potential below the solvent limit in the CV of [Re_2Cl_3(depe)$_2$(NCMe)](PF_6)$_2$, an additional oxidation is not accessible (at +1.55 V). These differences presumably reflect the greater σ-donor ability of depe compared to dppe. The complex behaves as a 2:1 electrolyte in acetone ($\Lambda_M = 170$ Ω^{-1} cm^2 mol^{-1}), in accord with its formulation as a dication. The paramagnetism of this species is evidenced by its ESR spectrum measured at −160°C in CH_2Cl_2 ($g \simeq 2.1$). The electronic absorption spectrum of [Re_2Cl_3(depe)$_2$(NCMe)](PF_6)$_2$ in CH_2Cl_2 has λ_{max} at 1275 nm (ε = 150), 640 nm(sh), 486 nm (ε = 700) and 424 nm (ε = 900).

The dication [Re_2Cl_3(depe)$_2$(NCMe)](PF_6)$_2$ could be reduced chemically to [Re_2Cl_3(depe)$_2$(NCMe)]PF_6 by the use of $LiBEt_3H$ in THF solution. The electrochemistry of the resulting monocation displays $E_{1/2} = +0.35$ V(ox), as well as $E_{p,a} = +1.55$ V vs Ag–AgCl. The conductivity of a 1×10^{-3} M acetone solution is consistent with the formulation as a 1:1 salt ($\Lambda_M = 120$ Ω^{-1} cm^2 mol^{-1}). Its electronic absorption spectrum, recorded in CH_2Cl_2 solution exhibits λ_{max} at 645 nm (ε = 120), 506 nm (ε = 200) and a shoulder at 400 nm, while the IR spectrum (Nujol mull) possesses a weak ν(CN) mode at 2269 cm^{-1} due to the coordinated MeCN ligand. Its ^{31}P–{^1H} NMR spectrum, measured in $(CD_3)_2CO$ solution, is similar to that of [Re_2X_3(dppe)$_2$(NCMe)]PF_6,[18] namely two apparent triplets at δ −4.81 and −5.02 which are the components of an AA′BB′ pattern.

Preparation and characterization of Re_2X_4(dppee)$_2$ (X = Cl *or* Br)

The phosphine ligand dppee reacts with $(n\text{-}Bu_4N)_2Re_2Cl_8$ in refluxing methanol–conc. HCl or ethanol, and with $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ in refluxing ethanol, to give the green isomer α-$Re_2Cl_4(dppee)_2$ in yields of *ca* 15%. Work-up of the yellow filtrate and washings from the reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dppee gave *trans*-$[ReCl_2(dppee)_2]Cl \cdot nH_2O$ as an additional reaction product, while *trans*-$ReCl_2(dppee)_2$ is a by-product of the reaction of $Re_2Cl_6(P\text{-}n\text{-}Bu_3)_2$ with dppee. The green bromo analogue α-$Re_2Br_4(dppee)_2$ was formed (yield *ca* 20%) upon heating $(n\text{-}Bu_4N)_2Re_2Br_8$ with an excess of dppee in methanol–conc. HBr (48%) for 2 days. Orange crystalline *trans*-$[ReBr_2(dppee)_2]Br$ was isolated from this reaction filtrate. Upon heating the dirhenium(II) species $Re_2X_4(PR_3)_4$ (X = Cl or Br, R = Et or *n*-Pr) with dppee in benzene, the brown β-isomers of $Re_2X_4(dppee)_2$ precipitated and were isolated in yields of 35–50%.

As shown in Table 1, the distinction between the α- and β-isomers is best seen in the differences between their electronic absorption spectra. The most prominent lowest-energy band is either at ~ 850 nm (α-forms) or at ~ 500 nm (β-forms), with weak lower-energy shoulders also apparent in some of the latter spectra. A further difference is apparent in the case of the low-frequency Nujol mull IR spectra of the chloride complexes in which α-$Re_2Cl_4(dppee)_2$ has ν(Re—Cl) modes at 314s, 282s and 260w cm^{-1}, while for β-$Re_2Cl_4(dppee)_2$ the corresponding bands are at 333s, 320m and 304m cm^{-1}. These data can be compared with that reported for α-$Re_2Cl_4(dppp)_2$ [ν(Re—Cl) at 307s, 292sh and 270m cm^{-1}][13] and β-$Re_2Cl_4(dppe)_2$ [ν(Re—Cl) at 333vs and 303m-s cm^{-1}].[15] These conclusions are further substantiated by differences in the $^{31}P\text{-}\{^1H\}$ NMR spectra of the pairs of α- and β-$Re_2X_4(dppee)_2$ compounds. For the α-isomers, a singlet is observed at δ +29.6 (CD_2Cl_2 solvent) for X = Cl, and at δ +25.9 ($(CD_3)_2SO$ solvent) for X = Br; these chemical shifts are characteristic of five-membered rings formed by chelating phosphines.[5,19] On the other hand, the β-isomers display singlets which are shifted upfield to δ +5.6 (CD_2Cl_2 solvent) and δ −0.2 (CD_2Cl_2 solvent) for X = Cl and Br, respectively. This shift is typical of the greater shielding associated with six-membered rings compared to their five-membered analogues.[19] The ^1H NMR spectra [recorded in CD_2Cl_2 or $(CD_3)_2SO$] showed the expected phenyl resonances along with an AA′XX′ pattern centered between δ +8.2 and +8.8 for the olefinic protons of the dppee ligand.

Although we were able to grow single crystals of β-$Re_2Cl_4(dppee)_2$ for an X-ray structure analysis, a satisfactory structure solution was thwarted by poor crystal quality. While we have not yet been able to obtain better crystals, the preliminary structure analysis is sufficient to clearly define the major structural details of this molecule.*

The reactivity of β-$Re_2X_4(dppee)_2$ towards $NOPF_6$ in CH_3CN resembled that found for β-$Re_2X_4(depe)_2$ (*vide supra*). Oxidation occurred to give β-$[Re_2X_4(dppee)_2]PF_6$ which displayed the expected electrochemical properties (see Table 1), with a one-electron oxidation at $E_{1/2} \simeq +1.1$ V and a one-electron reduction at $E_{1/2} \simeq +0.3$ V vs Ag–AgCl. These complexes behaved as 1 : 1 electrolytes in CH_3CN ($\Lambda_M \sim 125\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $C_M = 1.5 \times 10^{-4}$ M) and had Nujol mull IR spectra with ν(P—F) of PF_6^- at *ca* 850 cm^{-1}. Like their depe analogues, these salts react with acetonitrile in the presence of $TlPF_6$ to give $[Re_2X_3(dppee)_2(NCMe)](PF_6)_2$ whose properties resemble closely those of $[Re_2X_3(depe)_2(NCMe)](PF_6)_2$ (*vide supra*) and $[Re_2X_3(dppe)_2(NCMe)](PF_6)_2$.[18]†

Cleavage of β-$Re_2X_4(dppee)_2$ to give the mononuclear rhenium(IV) complexes *cis*-$ReX_4(dppee)$ occurred upon reaction with CCl_4 (X = Cl) or Br_2 (X = Br). These orange (X = Cl) or dark red (X = Br) colored complexes are almost certainly close structural analogues of *cis*-$ReCl_4(dppe)$.[20] In the case of *cis*-$ReCl_4(dppee)$, its low-frequency IR spectrum showed a pattern for the ν(Re—Cl) modes at 345m, 326s and 305s cm^{-1} that is very characteristic of a *cis*-MCl_4L_2 geometry [i.e. *cis*-$ReCl_4(dppe)$ has ν(Re—Cl) at 346m, 331s and 305s cm^{-1}].[20] Like other complexes of type *cis*-$ReCl_4(LL)$, where LL = dppe, dppm or arphos,[17]

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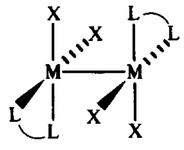
* Crystal data for β-$Re_2Cl_4(dppee)_2$ at 22°C: monoclinic space group $P2_1/n$, $a = 16.684(7)$, $b = 12.869(7)$, $c = 9.766(3)$ Å; $\beta = 106.69(3)°$, $V = 4706(7)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.843$ g cm^{-3}. A preliminary structure analysis was based upon 6458 reflections of which 5431 have $F_o^2 > 5\sigma(F_o^2)$. Like the crystal structures of other multiply bonded dimetal complexes, β-$Re_2Cl_4(dppee)_2$ exhibits a disorder in which there are two orientations of the M_2 unit within the polyhedron defined by the eight donor atoms. The Re—Re distance of 2.24(1) Å (for the major orientation, 76%) is typical of that seen in other complexes that contain Re≡Re bonds.[9,12–14] The staggered rotational geometry about the Re—Re bond is similar to that in β-$Re_2Cl_4(dppe)_2$. In the case of β-$Re_2Cl_4(dppee)_2$ the pairs of Cl—Re—Re—Cl and P—Re—Re—P torsional angles average to approximately 62 and 59°, respectively, while for β-$Re_2Cl_4(dppe)_2$ the corresponding values are 59.6 and 52.4°.[14]

† For example, the CVs of solutions of $[Re_2X_3(dppee)_2(NCMe)](PF_6)_2$ in 0.1 M TBAH–CH_2Cl_2 are as follows: X = Cl, $E_{1/2}(red) = +0.58$ V and $E_{p,c} = -1.67$ V vs Ag–AgCl; X = Br, $E_{1/2}(red) = +0.67$ V and $E_{p,c} \simeq -1.55$ V vs Ag–AgCl. Solutions of these complexes in CH_3CN had $\Lambda_M \simeq 230\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $C_M = 1.2 \times 10^{-4}$ M.

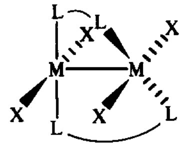
cis-ReX_4(dppee) display a very accessible one-electron reduction in the CVs of their solutions in 0.1 M TBAH–CH_2Cl_2 with $E_{1/2} = +0.13$ V (X = Cl) and $E_{1/2} = +0.21$ V (X = Br) vs Ag–AgCl.

Concluding remarks

The preparation of $Re_2X_4(depe)_2$ and $Re_2X_4(dppee)_2$ is the first time that the α- and β-pairs of the type $M_2X_4(bidentate)_2$ (see **I** and **II**) have been isolated for dirhenium(II), although such pairs are known in the case of the isostructural (but not isoelectronic) dimolybdenum(II) and ditungsten(II) cores.[1–4] In contrast to the much studied dimolybdenum(II) complexes of this type,[1,2] we find no evidence for α- $\rightleftharpoons$ β-isomerization in CH_2Cl_2 solutions of these complexes. This surprising result is under further investigation in view of the facility with which this isomerization occurs in the case of α- and β-isomers of $Mo_2X_4(LL)_2$ and the current interest in the mechanism of such transformations.[21,22]

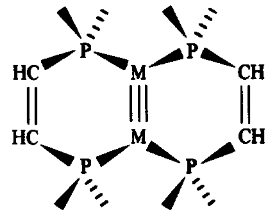


I



II

The complexes β-$Re_2X_4(dppee)_2$ are of special interest for they establish the stability of the fused ring system depicted below, and point to the existence of other complexes of this class.*



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* The α- and β-isomers of $Mo_2X_4(dppee)_2$ (X = Cl, Br or I) have now been isolated (M. Bakir, F. A. Cotton, C. Simpson and R. A. Walton, unpublished results).