

Unsymmetrical Dirhenium Complexes That Contain $[\text{Re}_2]^{6+}$ and $[\text{Re}_2]^{5+}$ Cores Complexed by Tridentate Ligands with P_2O and P_2N Donor Sets

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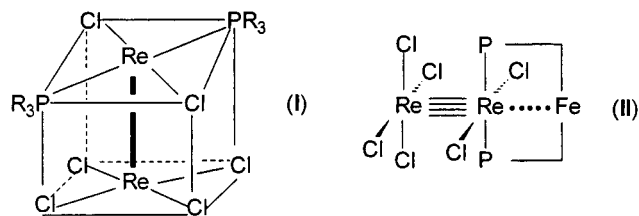
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The quadruply bonded dirhenium(III) complex $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ reacts with tridentate ligands that contain essentially planar P,O,P donor sets to afford the complexes $\text{Re}_2\text{Cl}_6(\eta^3\text{-L}_1)$ (**3**) ($\text{L}_1 = \text{bis}[2\text{-}(\text{diphenylphosphino})\text{phenyl}]\text{ether}$) and $(n\text{-Bu}_4\text{N})[\text{Re}_2\text{Cl}_7(\eta^1\text{-L}_2)]$ (**4**) ($\text{L}_2 = 4,6\text{-bis}(\text{diphenylphosphino})\text{dibenzofuran}$). Spectroscopic and electrochemical data support the unsymmetrical structure $\text{Cl}_4\text{ReReCl}_2(\eta^3\text{-L}_1)$ in the case of **3**, while **4** contains monodentate P-bound L_2 ; both complexes contain $\text{Re}^4\text{-Re}$ bonds. The synthon $\text{cis-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ reacts with ligands L_1 , L_2 , 2,6-bis(diphenylphosphinomethyl)pyridine (L_3), bis[2-(diphenylphosphino)ethyl]amine (L_4), and *N,N*-bis[2-(diphenylphosphino)ethyl]trimethylacetamide (L_5) to give the paramagnetic complexes $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_4(\eta^3\text{-L}_n)$ (**5–9**) with $\text{Re}^{3.5}\text{-Re}$ bonds. The lability of the μ -acetato ligands in **5–9** has been demonstrated by the reactions of compounds **5** ($n = 1$) and **7** ($n = 3$) with 4- $\text{Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{H}$, 2- $\text{Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{H}$, and quinoline-4-carboxylic acid to give complexes **10–12** (from **5**) and **13–15** (from **7**), respectively. These products contain uncoordinated donor atoms that can be used to produce mixed-metal assemblies. Compounds **5** and **7** also react with terephthalic acid ($1,4\text{-C}_6\text{H}_4(\text{CO}_2\text{H})$) to give $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_1)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (**16**) and $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_3)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (**17**) in which electronic coupling between the paramagnetic sets of dirhenium units is very weak. Single-crystal X-ray structure determinations have been carried out on complexes **5–8**, **11**, **12**, and **14–16**.

Introduction

The genesis of the present study was our recent discovery of the first example of a 1,3- $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ type isomer (**I**) as encountered in the Re-Re quadruply bonded complex $\text{Cl}_4\text{-ReReCl}_2(\text{dppf})$, where $\text{dppf} = 1,1'\text{-bis}(\text{diphenylphosphino})\text{-ferrocene}$ (**II**).¹ The search for a “missing” isomer of this



type had been stimulated by the earlier work of Cotton and others on the synthetic and structural chemistry of a variety of isomers of dirhenium complexes of the general type

$[\text{Re}_2\text{Cl}_{6-x}(\text{PR}_3)_{2+x}]^n$ ($x = 0, 1, \text{ or } 2; n = +2, +1, 0, \text{ or } -1$).^{2–7} Through our structural characterization of compound **II** we found that the $\text{Re-Re}\cdots\text{Fe}$ unit was linear although, as expected, the Fe center was at a nonbonding distance to the closest Re center ($\sim 3.5 \text{ \AA}$). Upon replacing the Cp_2Fe unit by a suitable donor ligand atom we reasoned that it should be possible to obtain unsymmetrical compounds (like **II**) in which the trans 1,3 arrangement of P donors is maintained but a significant bonding interaction would exist in one of the axial sites of the Re-Re bond. The stability of such an arrangement is of interest in light of the tendency of the $\text{Re}^4\text{-Re}$ bond to be cleaved by certain bidentate and

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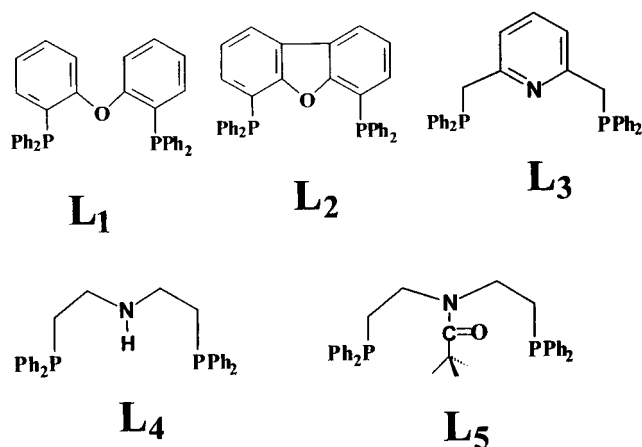
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Chart 1



tridentate phosphine donors.⁸ Accordingly, we have examined the reactions of an assortment of such ligands (see L_1 – L_5 in Chart 1) with the dirhenium(III) precursors (n -Bu₄N)₂Re₂Cl₈ (**1**) and *cis*-Re₂(μ -O₂CCH₃)₂Cl₄(H₂O)₂ (**2**). The studies involving the dirhenium(III) acetate complex **2** proved to be the most fruitful and led to a series of paramagnetic [Re₂]⁵⁺ core complexes, including ones in which two such units are coupled together. Some of these results have been the subject of a preliminary report.⁹

Experimental Section

The dirhenium complexes (n -Bu₄N)₂Re₂Cl₈ (**1**)¹⁰ and *cis*-Re₂(μ -O₂CCH₃)₂Cl₄(H₂O)₂ (**2**)¹¹ were prepared by standard literature procedures, as were the phosphine ligands L_1 – L_5 shown in Chart 1.^{12–15} Ligand L_4 was isolated as its HCl salt¹⁴ and used as such. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. All reactions were performed under an atmosphere of dinitrogen.

A. (i) Synthesis of Re₂Cl₆(η^3 - L_1) (3**).** A mixture of (n -Bu₄N)₂Re₂Cl₈ (**1**) (114 mg, 0.10 mmol) and bis[2-(diphenylphosphino)phenyl]ether (L_1) (108 mg, 0.20 mmol) was refluxed in 60 mL of ethanol for 2 h, the reaction mixture allowed to cool to 25 °C and filtered, and the red solid washed with ethanol (2 \times 5 mL) and diethyl ether (2 \times 5 mL); yield 98 mg (93%). Anal. Calcd for C₃₈H₃₄Cl₆O₂P₂Re₂ (i.e., **3**·EtOH): C, 39.02; H, 2.93; Cl, 18.19. Found: C, 39.69; H, 2.76; Cl, 18.10. The presence of lattice ethanol was confirmed by ¹H NMR spectroscopy.

(ii) Synthesis of (n -Bu₄N)[Re₂Cl₇(η^1 - L_2)] (4**).** The reaction of (n -Bu₄N)₂Re₂Cl₈ (**1**) (114 mg, 0.10 mmol) and 4,6-bis(diphenylphosphino)dibenzofuran (L_2) (107 mg, 0.20 mmol) in refluxing

ethanol (50 mL) for 12 h gave a green powder that was filtered off and washed with ethanol (2 \times 5 mL) and diethyl ether (2 \times 5 mL) and dried; yield 92 mg (61%). Anal. Calcd for C₅₂H₆₂Cl₇NOP₂Re₂: C, 45.27; H, 4.53; Cl, 17.73. Found: C, 44.43; H, 4.43; Cl, 17.83. The use of longer reaction times produced this same product.

B. Synthesis of Complexes of the Type Re₂(μ -O₂CCH₃)Cl₄(η^3 - L), where L = Bis[2-(diphenylphosphino)phenyl]ether (L_1), 4,6-Bis(diphenylphosphino)dibenzofuran (L_2), 2,6-Bis(diphenylphosphinomethyl)pyridine (L_3), Bis[2-(diphenylphosphino)ethyl]amine (L_4), or *N,N*-Bis[2-(diphenylphosphino)ethyl]trimethylacetamide (L_5). **(i) Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_1) (**5**).** A mixture of *cis*-Re₂(μ -O₂CCH₃)₂Cl₄(H₂O)₂ (**2**) (67 mg, 0.10 mmol) and L_1 (108 mg, 0.20 mmol) was refluxed in 60 mL of ethanol for 16 h, the reaction mixture allowed to cool to 25 °C, and the yellow-brown crystalline product filtered off and washed with ethanol (2 \times 5 mL) and diethyl ether (2 \times 5 mL); yield 59 mg (53%). Anal. Calcd for C₃₈H₃₁Cl₄O₃P₂Re₂: C, 41.05; H, 2.79. Found: C, 41.14; H, 2.79.

(ii) Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_2) (6**).** A procedure similar to B(i) was used with 107 mg (0.20 mmol) of L_2 in place of L_1 and a reaction time of 3 days; yield 54 mg (49%). Anal. Calcd for C₃₈H₂₉Cl₄O₃P₂Re₂: C, 41.13; H, 2.63. Found: C, 41.11; H, 2.69.

(iii) Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_3) (7**).** The reaction between **2** (67 mg, 0.10 mmol) and 2,6-bis(diphenylphosphinomethyl)pyridine (L_3) (95 mg, 0.20 mmol) was carried out in refluxing ethanol for 4 h as described in B(i); yield 89 mg (85%). Anal. Calcd for C₃₃H₃₀Cl₄NO₂P₂Re₂: C, 37.79; H, 2.88. Found: C, 38.37; H, 2.98. Recrystallization from 1,2-dichloroethane/benzene gave **7** as brown crystals of composition **7**·C₆H₆.

(iv) Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_4) (8**).** A procedure identical to B(iii) was used with the salt bis(diphenylphosphinoethyl)amine hydrochloride (L_4 ·HCl) (100 mg, 0.22 mmol) in place of L_3 ; yield 82 mg (81%). Anal. Calcd for C₃₀H₃₂Cl₄NO₂P₂Re₂: C, 35.51; H, 3.18. Found: C, 35.67; H, 3.26.

Compound **8** was also obtained by the reaction of Re₂(μ -O₂CCH₃)₄Cl₂ with an excess of L_4 ·HCl in refluxing ethanol for 2 weeks; yield 36%. This procedure is not a convenient one and was not pursued further with other ligands.

(v) Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_5) (9**).** The use of L_5 (105 mg, 0.20 mmol) in place of L_4 ·HCl afforded compound **9** after a reaction time of 2 days; yield 63 mg (57%). This product was recrystallized from dichloromethane/diethyl ether to give brown microcrystals. Anal. Calcd for C₃₆H₄₂Cl₆NO₃P₂Re₂ (i.e., **9**·CH₂Cl₂): C, 36.53; H, 3.58. Found: C, 35.77; H, 3.27.

C. Carboxylate-Exchange Reactions of Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_1) (5**) and Re₂(μ -O₂CCH₃)Cl₄(η^3 - L_3) (**7**).** Since all reactions were carried out with the use of essentially identical procedures, details of representative reactions only are given.

(i) Synthesis of Re₂(μ -O₂CC₆H₄-4-PPh₂)Cl₄(η^3 - L_1) (10**).** A mixture of **5** (111 mg, 0.10 mmol) and 4-Ph₂PC₆H₄CO₂H (36 mg, 0.12 mmol) was refluxed in 50 mL of ethanol for 3 days. The reaction mixture was cooled to 25 °C and filtered and the yellow powder washed with ethanol (2 \times 5 mL) and diethyl ether (2 \times 5 mL); yield 100 mg (74%). Recrystallization from dichloromethane/diethyl ether gave yellow microcrystals. Anal. Calcd for C₅₆H₄₄Cl₆O₃P₃Re₂ (i.e., **10**·CH₂Cl₂): C, 46.61; H, 3.07. Found: C, 45.91; H, 2.93.

(ii) Synthesis of Re₂(μ -O₂CC₆H₄-2-PPh₂)Cl₄(η^3 - L_1) (11**).** The use of 2-Ph₂PC₆H₄CO₂H and the same procedure as C(i) afforded **11** in crystalline form; yield 22%. Anal. Calcd for C₅₅H₄₂Cl₄O₃P₃Re₂: C, 48.64; H, 3.12. Found: C, 46.64; H, 3.07. Although the C microanalysis of this complex was consistently low, the composition of this product was confirmed by X-ray crystallography.

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(iii) **Synthesis of $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_{10}\text{H}_6\text{N})\text{Cl}_4(\eta^3\text{-L}_1)$ (**12**).** The title complex was obtained as insoluble red crystals from the reaction between **5** and quinoline-4-carboxylic acid for 2 days using the procedure described in C(i); yield 61%. Anal. Calcd for $\text{C}_{46}\text{H}_{34}\text{Cl}_4\text{NO}_3\text{P}_2\text{Re}_2$: C, 45.10; H, 2.80. Found: C, 44.93; H, 2.75.

(iv) **Synthesis of $\text{Re}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-4-PPH}_2)\text{Cl}_4(\eta^3\text{-L}_3)$ (**13**).** The use of **7** (105 mg, 0.10 mmol) in place of **5** and a procedure similar to C(i) give the desired product; yield 76%. Anal. Calcd for $\text{C}_{50}\text{H}_{41}\text{Cl}_4\text{NO}_2\text{P}_3\text{Re}_2$: C, 46.37; H, 3.19. Found: C, 46.00; H, 3.30.

(v) **Synthesis of $\text{Re}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-PPH}_2)\text{Cl}_4(\eta^3\text{-L}_3)$ (**14**).** A procedure similar to C(i) gave **14** as insoluble yellow crystals; yield 36%. Anal. Calcd for $\text{C}_{52}\text{H}_{47}\text{Cl}_4\text{NO}_3\text{P}_3\text{Re}_2$ (i.e., **14**·EtOH): C, 46.57; H, 3.53. Found: C, 46.03; H, 3.15.

(vi) **Synthesis of $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_{10}\text{H}_6\text{N})\text{Cl}_4(\eta^3\text{-L}_3)$ (**15**).** The title complex was obtained as red crystals with the use of a procedure similar to C(i); yield 57%. Anal. Calcd for $\text{C}_{43}\text{H}_{39}\text{Cl}_4\text{N}_2\text{O}_3\text{P}_2\text{Re}_2$ (i.e., **15**·EtOH): C, 42.76; H, 3.25. Found: C, 42.51; H, 3.02.

(vii) **Synthesis of $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_1)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (**16**).** A mixture of **5** (111 mg, 0.10 mmol) and terephthalic acid (8.3 mg, 0.05 mmol) was refluxed in 50 mL of *n*-butanol for 12 h. The cooled reaction mixture was filtered, and the brown powder was washed with ethanol (2 × 5 mL) and diethyl ether (2 × 5 mL); yield 84 mg (74%). Anal. Calcd for $\text{C}_{80}\text{H}_{60}\text{Cl}_8\text{O}_6\text{P}_4\text{Re}_4$: C, 42.34; H, 2.66. Found: 41.23; H, 3.10.

This complex was also obtained by an alternative procedure. A solution of **5** (111 mg, 0.10 mmol) in acetonitrile (40 mL) was treated with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.20 mL) and the mixture stirred at room temperature for 24 h. The clear green solution that resulted was treated with a solution of disodium terephthalate (11 mg, 0.05 mmol) in ethanol (5 mL), the mixture was stirred at room temperature for another 24 h and filtered, and the volume of the filtrate was reduced to about 10 mL. Benzene (10 mL) was added, and the slow evaporation of the solvents over a period of days gave brown crystals; yield 36 mg (31%).

(viii) **Synthesis of $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_3)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (**17**).** The reaction of **7** (105 mg, 0.10 mmol) with terephthalic acid (8.3 mg, 0.05 mmol) was carried out in refluxing *n*-propanol for 1 week; yield 78 mg (73%). Anal. Calcd for $\text{C}_{70}\text{H}_{58}\text{Cl}_8\text{N}_2\text{O}_4\text{P}_4\text{Re}_4$: C, 39.22; H, 2.73. Found: C, 39.14; H, 2.82.

D. Single-Crystal X-ray Crystallography. Single crystals of **5**, **6**, **8**, **11**, **12**, **14**, and **15** were harvested directly from the reaction mixtures. Crystals of **7** were obtained by recrystallization from 1,2-dichloroethane/benzene while suitable crystals of **16** were grown from a mixed acetonitrile/benzene/ethanol solvent system. Subsequent structure analysis showed that several of the single crystals chosen for the structure analyses contained solvent molecules; these particular crystals were of compositions **7**· C_6H_6 , **14**·EtOH, **15**·EtOH, and **16**·2EtOH.

The crystals were mounted on glass fibers in random orientations. The data collections were carried out at 150(±1) K with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The key crystallographic data are given in Table 1.

The structures of **6** and **8** were solved by using the structure solution program SHELXS-97¹⁶ while the structures of **5**, **7**, **11**, **12**, and **14–16** were solved with the use of the structure solution program PATTY in DIRDIF92.¹⁷ The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms bound to carbon were placed in calculated

positions according to idealized geometries with C–H = 0.95 Å and $U(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK¹⁸ was applied. The final refinements were performed by the use of the program SHELXL-97.¹⁹ For **12** the absolute structure was determined by refinement. The enantiomer chosen had a Flack parameter²⁰ of –0.017(7). Crystallographic drawings were done using the program ORTEP.²¹

The structure solutions and refinements of all nine compounds proceeded without significant problems. The C and O atoms of the solvent molecules present in the structures of **7** and **14–16** were refined with anisotropic thermal parameters. Unidentified and disordered solvent molecules were present in the crystals of **11** and **16**, but in neither case could the disorder be adequately modeled. Accordingly, these molecules were removed with the squeeze option in PLATON.²² In the cases of **6** and **11**, two independent dirhenium molecules are present in the asymmetric unit.

Full structural details for the nine compounds are provided in the Supporting Information. The most important bond distances and bond angles are given in the captions to Figures 1–9, which show the ORTEP representations of the structures.

E. Physical Measurements. Infrared spectra were recorded in the region 4000–400 cm^{-1} as KBr pellets and from 700 to 150 cm^{-1} as Nujol mulls on a Perkin-Elmer 2000 FT-IR spectrometer. Electronic absorption spectra were recorded with use of a Cary 300 spectrophotometer, while ¹H and ³¹P{¹H} NMR spectra were obtained on a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The ³¹P{¹H} spectra were recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. Cyclic voltammetric measurements were carried out with use of a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{\text{p,a}} + E_{\text{p,c}})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Differential pulsed voltammetric (DPV) measurements and magnetic data were recorded in the Laboratory of Professor Kim R. Dunbar at Texas A&M University. Conductivity measurements were obtained with the use of a YSI model 35 conductance meter.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

The reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (**1**) with bis[2-(diphenylphosphino)phenyl]ether (**L**₁) and 4,6-bis(diphenylphosphino)dibenzofuran (**L**₂) (see Chart 1) afford the red complex $\text{Re}_2\text{Cl}_6(\eta^3\text{-L}_1)$ (**3**) and the green complex $(n\text{-Bu}_4\text{N})[\text{Re}_2\text{Cl}_7(\eta^1\text{-L}_2)]$ (**4**), respectively. Compound **3** is formally very

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Table 1. Crystallographic Data for the Dirhenium Complexes of Composition $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_1)$ (5), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_2)$ (6), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_3)$ (7), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_4)$ (8), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_5)$ (9), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_6)$ (10), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_7)$ (11), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_8)$ (12), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_9)$ (13), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{10})$ (14), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{11})$ (15), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{12})$ (16), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{13})$ (17), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{14})$ (18), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{15})$ (19), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{16})$ (20), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{17})$ (21), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{18})$ (22), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{19})$ (23), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{20})$ (24), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{21})$ (25), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{22})$ (26), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{23})$ (27), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{24})$ (28), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{25})$ (29), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{26})$ (30), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{27})$ (31), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{28})$ (32), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{29})$ (33), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{30})$ (34), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{31})$ (35), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{32})$ (36), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{33})$ (37), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{34})$ (38), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{35})$ (39), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{36})$ (40), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{37})$ (41), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{38})$ (42), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{39})$ (43), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{40})$ (44), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{41})$ (45), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{42})$ (46), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{43})$ (47), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{44})$ (48), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{45})$ (49), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{46})$ (50), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{47})$ (51), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{48})$ (52), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{49})$ (53), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{50})$ (54), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{51})$ (55), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{52})$ (56), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{53})$ (57), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{54})$ (58), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{55})$ (59), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{56})$ (60), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{57})$ (61), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{58})$ (62), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{59})$ (63), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{60})$ (64), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{61})$ (65), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{62})$ (66), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{63})$ (67), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{64})$ (68), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{65})$ (69), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{66})$ (70), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{67})$ (71), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{68})$ (72), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{69})$ (73), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{70})$ (74), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{71})$ (75), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{72})$ (76), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{73})$ (77), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{74})$ (78), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{75})$ (79), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{76})$ (80), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{77})$ (81), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{78})$ (82), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{79})$ (83), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{80})$ (84), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{81})$ (85), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{82})$ (86), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{83})$ (87), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{84})$ (88), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{85})$ (89), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{86})$ (90), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{87})$ (91), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{88})$ (92), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{89})$ (93), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{90})$ (94), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{91})$ (95), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{92})$ (96), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{93})$ (97), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{94})$ (98), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{95})$ (99), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{96})$ (100), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{97})$ (101), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{98})$ (102), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{99})$ (103), $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_{100})$ (104).

	5	6	7	8	11	12	14	15	16
formula	$\text{C}_{38}\text{H}_{31}\text{Cl}_4\text{O}_3\text{P}_2\text{Re}_2$	$\text{C}_{38}\text{H}_{29}\text{Cl}_4\text{O}_3\text{P}_2\text{Re}_2$	$\text{C}_{39}\text{H}_{36}\text{Cl}_4\text{NO}_2\text{P}_2\text{Re}_2$	$\text{C}_{30}\text{H}_{32}\text{Cl}_4\text{NO}_2\text{P}_2\text{Re}_2$	$\text{C}_{35}\text{H}_{42}\text{Cl}_4\text{O}_3\text{P}_3\text{Re}_2$	$\text{C}_{46}\text{H}_{34}\text{Cl}_4\text{NO}_3\text{P}_3\text{Re}_2$	$\text{C}_{52}\text{H}_{47}\text{Cl}_4\text{NO}_3\text{P}_3\text{Re}_2$	$\text{C}_{43}\text{H}_{39}\text{Cl}_4\text{N}_2\text{O}_3\text{P}_2\text{Re}_2$	$\text{C}_{84}\text{H}_{72}\text{Cl}_8\text{O}_8\text{P}_4\text{Re}_2$
fw	1111.83	1109.81	1126.89	1014.76	1358.08	1224.95	1341.09	1207.96	2361.83
space group	$P1$ (No. 2)	$P1$ (No. 2)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$P1$ (No. 2)	$P2_12_12_1$ (No. 19)	$P1$ (No. 2)	$P1$ (No. 2)	$P2_1/n$ (No. 14)
a , Å	10.0629(2)	10.9609(2)	25.6460(4)	13.3060(2)	17.1912(2)	12.7371(3)	11.4143(4)	10.4099(2)	11.4902(2)
b , Å	11.2949(3)	17.2743(3)	9.0831(3)	23.8348(2)	18.4794(2)	14.5258(4)	14.7078(6)	14.5099(3)	23.3097(5)
c , Å	17.2694(5)	20.0145(4)	16.0974(8)	20.5660(3)	20.5209(3)	22.7450(4)	15.8257(9)	15.7034(3)	17.3837(3)
α , deg	98.1017(11)	101.3326(9)	93.3707(10)	90	109.6286(7)	90	80.8470(19)	80.8470(12)	90
β , deg	99.9442(10)	95.3235(8)	90	90	104.2938(6)	90	83.683(2)	85.1213(11)	92.2112(13)
γ , deg	103.8370(17)	92.3179(10)	90	90	102.6112(7)	90	68.953(3)	78.6255(9)	90
V , Å ³	1849.95(17)	3693.0(2)	3743.3(3)	6522.4(2)	5616.7(3)	4208.2(3)	2444.0(3)	2096.01(10)	4652.5(3)
Z	2	4	4	8	4	4	2	2	2
ρ_{calc} , g/cm ⁻³	1.996	1.999	1.999	2.065	1.606	1.933	1.822	1.914	1.686
μ , mm ⁻¹	7.041	6.959	7.976	4.680	4.680	6.201	5.377	6.223	5.606
$R(F_o)^a$	0.038	0.047	0.047	0.035	0.042	0.039	0.053	0.041	0.046
$R_w(F_o^2)^b$	0.077	0.086	0.078	0.078	0.099	0.077	0.116	0.082	0.109
GOF	1.004	0.949	0.990	1.048	0.880	1.035	0.984	0.982	0.945

$$^a R = \sum |F_o| - |F_c| / \sum |F_o| \text{ with } F_o^2 > 2\sigma(F_o^2), \text{ } ^b R_w = \left[\sum w(F_o^2 - |F_c^2|)^2 / \sum w|F_o^2|^2 \right]^{1/2}$$

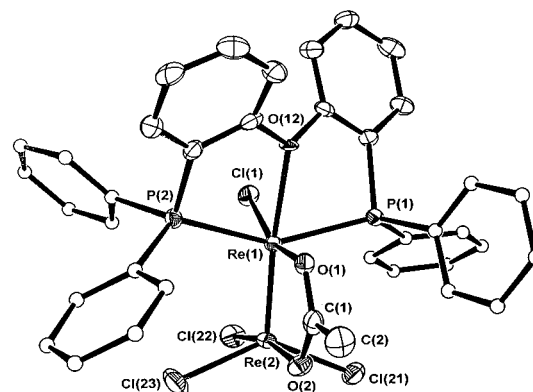


Figure 1. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_1)$ (5). Thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2454(3), $\text{Re}(1)\text{-O}(1)$ 2.089(4), $\text{Re}(1)\text{-O}(12)$ 2.351(3), $\text{Re}(1)\text{-Cl}(1)$ 2.3731(15), $\text{Re}(2)\text{-O}(2)$ 2.091(4), $\text{Re}(2)\text{-Cl}(22)$ 2.3230(16), $\text{Re}(2)\text{-Cl}(23)$ 2.3006(16), $\text{Re}(2)\text{-Cl}(21)$ 2.3095(16); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 149.84(5), $\text{O}(1)\text{-Re}(1)\text{-Cl}(1)$ 162.58(11), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 167.29(12), $\text{Cl}(23)\text{-Re}(2)\text{-Cl}(21)$ 136.10(6).

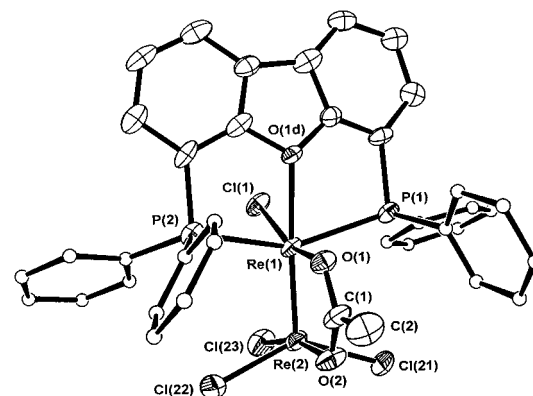


Figure 2. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\eta^3\text{-L}_2)$ (6). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2403(4), $\text{Re}(1)\text{-O}(1)$ 2.059(4), $\text{Re}(1)\text{-O}(1d)$ 2.285(4), $\text{Re}(1)\text{-Cl}(1)$ 2.3929(15), $\text{Re}(2)\text{-O}(2)$ 2.063(5), $\text{Re}(2)\text{-Cl}(23)$ 2.3407(19), $\text{Re}(2)\text{-Cl}(22)$ 2.306(2), $\text{Re}(2)\text{-Cl}(21)$ 2.3085(18); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 150.11(6), $\text{O}(1)\text{-Re}(1)\text{-Cl}(1)$ 162.86(13), $\text{O}(2)\text{-Re}(2)\text{-Cl}(23)$ 166.95(19), $\text{Cl}(22)\text{-Re}(2)\text{-Cl}(21)$ 139.12(7).

similar to the product obtained in the reaction between $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and 1,1'-bis(diphenylphosphino)ferrocene (dppf) that affords the unsymmetrical quadruply bonded complex $\text{Cl}_4\text{ReReCl}_2(\text{dppf})$,¹ while the salt **4** may well be related closely to the intermediate formed in the conversion of **1** to **3** which involves the sequential displacement of two Cl^- ligands.

All indications are that **3** is structurally very similar to $\text{Re}_2\text{Cl}_6(\text{dppf})$,¹ but with a weak axially bound O atom of the L_1 ligand in place of the unbound Fe atom of $\text{Re}_2\text{Cl}_6(\text{dppf})$ (see structure representation **II**). Like $\text{Re}_2\text{Cl}_6(\text{dppf})$, compound **3** is diamagnetic and shows a singlet at $\delta = +24.7$ in its $^31\text{P}\{^1\text{H}\}$ NMR spectrum (recorded in $(\text{CD}_3)_2\text{SO}$) downfield of that of the free ligand ($\delta = -21.0$ in $(\text{CD}_3)_2\text{SO}$). A cyclic voltammogram (CV) of a solution of **3** in 0.1 M $n\text{-Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ shows potentials at $E_{1/2}(\text{red}) = -0.02$ V and $E_{1/2}(\text{red}) \approx -1.35$ V vs Ag/AgCl , which is very similar to

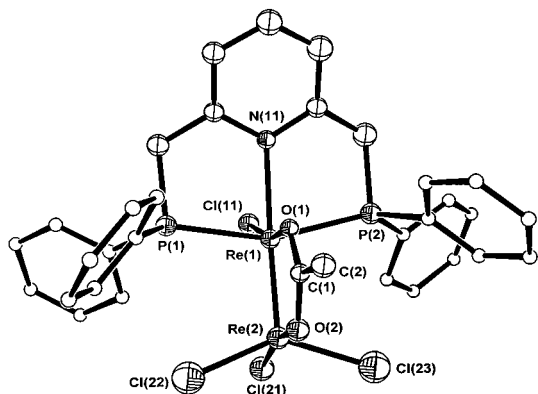


Figure 3. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{-Cl}_4(\eta^3\text{-L}_3)$ (**7**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2804(4), $\text{Re}(1)\text{-O}(1)$ 2.094(4), $\text{Re}(1)\text{-N}(11)$ 2.310(5), $\text{Re}(1)\text{-Cl}(11)$ 2.3715(16), $\text{Re}(2)\text{-O}(2)$ 2.053(5), $\text{Re}(2)\text{-Cl}(21)$ 2.3496(18), $\text{Re}(2)\text{-Cl}(22)$ 2.260(2), $\text{Re}(2)\text{-Cl}(23)$ 2.293(2); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 158.21(6), $\text{O}(1)\text{-Re}(1)\text{-Cl}(11)$ 164.27(14), $\text{O}(2)\text{-Re}(2)\text{-Cl}(21)$ 166.98(14), $\text{Cl}(22)\text{-Re}(2)\text{-Cl}(23)$ 137.50(8).

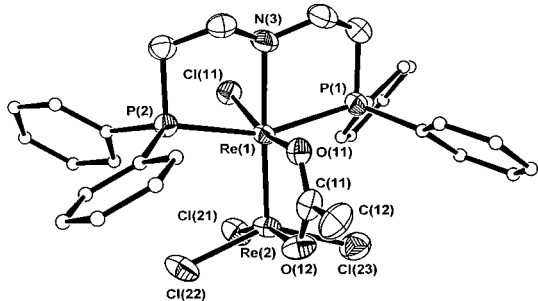


Figure 4. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{-Cl}_4(\eta^3\text{-L}_4)$ (**8**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2596(3), $\text{Re}(1)\text{-O}(11)$ 2.090(4), $\text{Re}(1)\text{-N}(3)$ 2.327(5), $\text{Re}(1)\text{-Cl}(11)$ 2.3954(13), $\text{Re}(2)\text{-O}(12)$ 2.058(4), $\text{Re}(2)\text{-Cl}(21)$ 2.3367(16), $\text{Re}(2)\text{-Cl}(22)$ 2.3094(16), $\text{Re}(2)\text{-Cl}(23)$ 2.3191(18); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 156.95(5), $\text{O}(11)\text{-Re}(1)\text{-Cl}(11)$ 164.85(11), $\text{O}(12)\text{-Re}(2)\text{-Cl}(21)$ 163.77(13), $\text{Cl}(22)\text{-Re}(2)\text{-Cl}(23)$ 143.65(6).

the dirhenium-based redox chemistry observed for $\text{Re}_2\text{Cl}_6(\text{dppf})$, with $E_{1/2} = -0.03$ V and $E_{p,c} \approx -1.5$ V vs Ag/AgCl .¹ Electronic absorption spectral measurements on dichloromethane solutions of $\text{Re}_2\text{Cl}_6(\text{dppf})$ and **3** show that they have their $\delta \rightarrow \delta^*$ transitions²³ at 834 nm ($\epsilon = 1408$) and 850 nm ($\epsilon = 1420$), respectively; the symmetrical dirhenium-(III) complex $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ has its $\delta \rightarrow \delta^*$ transition at 667 nm ($\epsilon = 1600$) with use of our experimental conditions. Further support for this close relationship comes from a comparison of their low-frequency IR spectra (recorded as Nujol mulls), which show very similar absorption patterns, with bands at 519 (s), 508 (m-s), 485 and 478 (s), and 346 (vs) cm^{-1} in the case of $\text{Re}_2\text{Cl}_6(\text{dppf})$ and 520 (s), 498 (m-s), 478 (m-s), and 342 (vs) cm^{-1} for **3**. The bands at ~ 345 cm^{-1} are assigned to $\nu(\text{Re}-\text{Cl})$. This conclusion was confirmed by a partial X-ray structure determination of a crystal of **3** grown from dichloromethane which showed it to be similar to $\text{Re}_2\text{Cl}_6(\text{dppf})$,¹ with a Re-Re quadruple bond

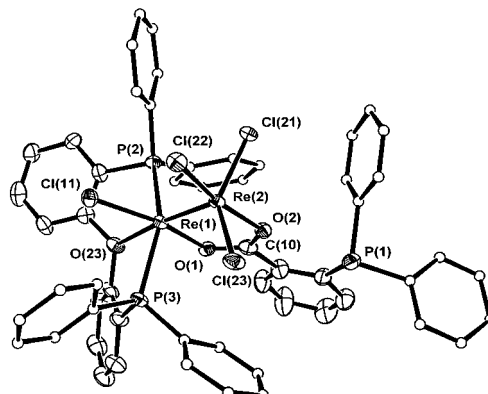


Figure 5. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-PPh}_2)\text{Cl}_4(\eta^3\text{-L}_1)$ (**11**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2390(3), $\text{Re}(1)\text{-O}(1)$ 2.069(4), $\text{Re}(1)\text{-O}(23)$ 2.378(4), $\text{Re}(1)\text{-Cl}$ 2.3707(17), $\text{Re}(2)\text{-O}(2)$ 2.077(4), $\text{Re}(2)\text{-Cl}(22)$ 2.3288(16), $\text{Re}(2)\text{-Cl}(23)$ 2.3010(18), $\text{Re}(2)\text{-Cl}(21)$ 2.3219(17); $\text{P}(2)\text{-Re}(1)\text{-P}(3)$ 149.65(16), $\text{O}(1)\text{-Re}(1)\text{-Cl}(11)$ 162.86(13), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 167.68(13), $\text{Cl}(23)\text{-Re}(2)\text{-Cl}(21)$ 138.92(6).

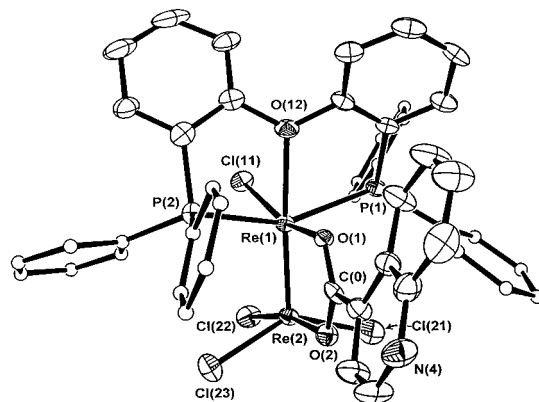


Figure 6. ORTEP²⁰ representation of the structure $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_{10}\text{H}_6\text{N})\text{-Cl}_4(\eta^3\text{-L}_1)$ (**12**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2536(4), $\text{Re}(1)\text{-O}(1)$ 2.090(5), $\text{Re}(1)\text{-O}(12)$ 2.360(4), $\text{Re}(1)\text{-Cl}(11)$ 2.3577(18), $\text{Re}(2)\text{-O}(2)$ 2.070(5), $\text{Re}(2)\text{-Cl}(22)$ 2.3227(18), $\text{Re}(2)\text{-Cl}(21)$ 2.260(2), $\text{Re}(2)\text{-Cl}(23)$ 2.316(2); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 151.53(7), $\text{O}(1)\text{-Re}(1)\text{-Cl}(11)$ 162.29(13), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 168.07(14), $\text{Cl}(21)\text{-Re}(2)\text{-Cl}(23)$ 139.37(9).

distance of 2.24 Å; unfortunately the $\text{C}_6\text{H}_4\text{OC}_6\text{H}_4$ fragment of the ligand L_1 did not refine satisfactorily and the result was unacceptable. We have not yet been able to grow a suitable single crystal of **3** for a full structure determination. However, the structural identity of **3** was further supported by its low-resolution mass spectrum (as determined by MALDI) which showed an intense peak at m/z ca. 1090 (calcd for $[\text{Re}_2\text{Cl}_5(\text{L}_1)]^+$, i.e., $[\text{M} - \text{Cl}]^+$, m/z 1088).

A solution of $(n\text{-Bu}_4\text{N})[\text{Re}_2\text{Cl}_7(\eta^1\text{-L}_2)]$ (**4**) in acetone (1.0×10^{-3} M) has a conductivity in accord with that expected for a 1:1 electrolyte ($\Lambda_m = 97 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The electronic absorption spectrum of a dichloromethane solution of **4** shows a $\delta \rightarrow \delta^*$ transition²³ at 695 nm ($\epsilon = 1710$), a value intermediate between those measured for $(n\text{-Bu}_4\text{N})_2\text{-Re}_2\text{Cl}_8$ and **3**. The ^1H NMR spectrum of **4** in $(\text{CD}_3)_2\text{SO}$ confirms the presence of $[n\text{-Bu}_4\text{N}]^+$, but these solutions decompose. However, freshly prepared solutions of **4** in $\text{CD}_2\text{-}$

(23) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, U.K., 1993.

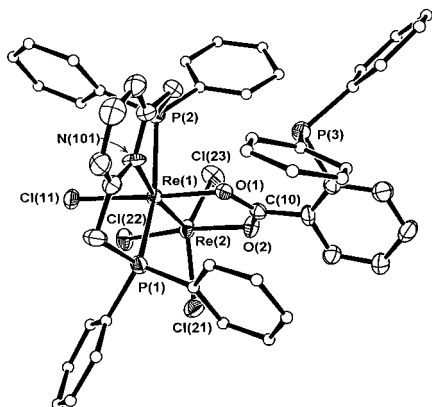


Figure 7. ORTEP²⁰ representation of the structure $\text{Re}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{-2-PPh}_2)\text{Cl}_4(\eta^3\text{-L}_3)$ (**14**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2651(4), $\text{Re}(1)\text{-O}(1)$ 2.120(5), $\text{Re}(1)\text{-N}(101)$ 2.331(6), $\text{Re}(1)\text{-Cl}(11)$ 2.374(2), $\text{Re}(2)\text{-O}(2)$ 2.043(6), $\text{Re}(2)\text{-Cl}(22)$ 2.343(2), $\text{Re}(2)\text{-Cl}(23)$ 2.301(2), $\text{Re}(2)\text{-Cl}(21)$ 2.313(2); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 152.58(7), $\text{O}(1)\text{-Re}(1)\text{-Cl}(11)$ 165.46(15), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 167.31(16), $\text{Cl}(23)\text{-Re}(2)\text{-Cl}(21)$ 135.28(9).

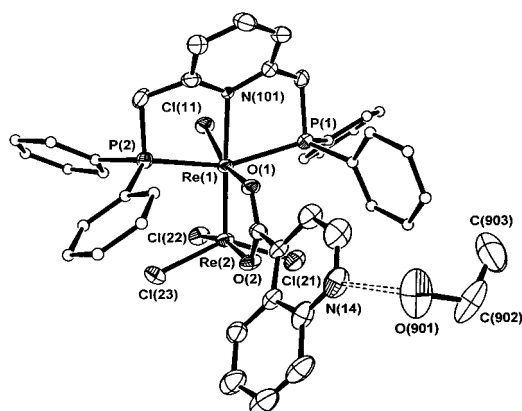


Figure 8. ORTEP²⁰ representation of the structure of $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_{10}\text{H}_6\text{N})\text{Cl}_4(\eta^3\text{-L}_3)$ (**15**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. The hydrogen-bonding interaction between the EtOH molecule and the N atom of the 4-quinoline carboxylate ligand is also shown (the H atom is omitted). Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2694(3), $\text{Re}(1)\text{-O}(1)$ 2.101(4), $\text{Re}(1)\text{-N}(101)$ 2.329(5), $\text{Re}(1)\text{-Cl}(11)$ 2.3667(14), $\text{Re}(2)\text{-O}(2)$ 2.061(4), $\text{Re}(2)\text{-Cl}(22)$ 2.3313(15), $\text{Re}(2)\text{-Cl}(21)$ 2.304(2), $\text{Re}(2)\text{-Cl}(23)$ 2.3177(18); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 155.89(6), $\text{O}(1)\text{-Re}(1)\text{-Cl}(11)$ 165.02(12), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 165.48(12), $\text{Cl}(21)\text{-Re}(2)\text{-Cl}(23)$ 137.91(6).

Cl_2 are quite stable and show two singlets with similar intensities in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta = +1.2$ and $\delta = -21.0$, the latter resonance being shifted a little upfield of that of the free ligand ($\delta = -16.7$ in CD_2Cl_2). The ^1H NMR spectrum in CD_2Cl_2 shows a complex set of phenyl H resonances in the region $\delta = +9.3$ to $\delta = +6.8$ and confirms the 1:1 stoichiometry of L_2 to $[\text{n-Bu}_4\text{N}]^+$. Upon allowing these solutions to stand, the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra slowly change and reveal the presence of a small amount of free ligand L_2 , an increase in the amount of $[\text{n-Bu}_4\text{N}]^+$ present relative to compound **4**, but no change in the relative intensities of the two singlets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. A quantity of $(\text{n-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ can be isolated upon workup of these “aged” solutions, so it is apparent that some decomposition of **4** to $(\text{n-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ and L_2 eventually

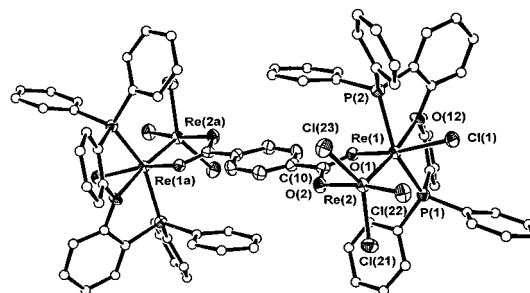


Figure 9. ORTEP²⁰ representation of the structure of the tetrarhenium complex $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_1)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (**16**). The thermal ellipsoids are drawn at the 50% probability level, except for the carbon atoms of the Ph_2P groups, which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (deg) are as follows: $\text{Re}(1)\text{-Re}(2)$ 2.2424(4), $\text{Re}(1)\text{-O}(1)$ 2.067(4), $\text{Re}(1)\text{-O}(12)$ 2.376(4), $\text{Re}(1)\text{-Cl}(1)$ 2.3672(18), $\text{Re}(2)\text{-O}(2)$ 2.064(5), $\text{Re}(2)\text{-Cl}(22)$ 2.3308(18), $\text{Re}(2)\text{-Cl}(21)$ 2.3033(18), $\text{Re}(2)\text{-Cl}(23)$ 2.3097(19); $\text{P}(1)\text{-Re}(1)\text{-P}(2)$ 149.78(6), $\text{O}(1)\text{-Re}(1)\text{-Cl}(1)$ 163.76(14), $\text{O}(2)\text{-Re}(2)\text{-Cl}(22)$ 166.39(15), $\text{Cl}(21)\text{-Re}(2)\text{-Cl}(23)$ 138.41(7).

occurs. This was also confirmed by monitoring the CV of a solution of **4** in 0.1 M TBAH- CH_2Cl_2 over a period of several hours. A freshly prepared solution shows an irreversible oxidation at $E_{\text{p,a}} = +1.25$ V and a reversible reduction at $E_{1/2} = -0.35$ V vs Ag/AgCl, behavior that is different from that seen in the CV of **3** (vide supra). When this solution is allowed to stand for several hours, processes that are characteristic of the $[\text{Re}_2\text{Cl}_8]^{2-}$ anion grow in at $E_{1/2} = +1.20$ V and $E_{1/2} = -0.87$ V vs Ag/AgCl,²⁴ although the majority species is still **4**. Interestingly, the CV of **4** resembles closely that reported for a solution of the salt $(\text{Ph}_4\text{As})[\text{Re}_2\text{Cl}_7(\text{PBU}^{\text{n}}\text{-Ph}_2)]$ in $(\text{n-Bu}_4\text{N})\text{BF}_4\text{-CH}_2\text{Cl}_2$ ($E_{1/2} = -0.34$ V vs SCE).²⁵ This observation, coupled with that of two singlets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**, indicating the presence of both free and bound P atoms in the L_2 ligand, implies that **4** may well involve η^1 -bound L_2 , so that it resembles structurally a compound of the type $[\text{Re}_2\text{Cl}_7(\text{PR}_3)]^-$ in only having eight donor atoms strongly bound to the $[\text{Re}_2]^{6+}$ core (i.e., $[\text{Cl}_4\text{ReReCl}_3(\text{P})]^-$).^{23,25-28} This type of compound is the logical intermediate in the formation of a compound such as **3**; the latter would be formed after the loss of an additional $[\text{Cl}]^-$ ligand and the coordination of the second P atom along with the more weakly bound axial O(ether) atom. The reason that the reaction of $(\text{n-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with L_2 terminates at this first stage may be related to the rigid nature of L_2 compared to the more flexible ligand L_1 . Note that **4** does not react further with an excess of L_2 even under forcing reaction conditions.

The reactions of $(\text{n-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with ligands L_3 and L_4 in refluxing ethanol gave insoluble brown and green products, respectively, but neither product was soluble in solvents without decomposition. Accordingly, they were not inves-

(24) Cameron, C. J.; Tetrack, S. M.; Walton, R. A. *Organometallics* **1984**, *3*, 240.

(25) Ferry, J.; Gallagher, J.; Cunningham, D.; McArdle, P. *Inorg. Chim. Acta* **1989**, *164*, 185.

(26) (a) McArdle, P.; Rabbitte, M.; Cunningham, D. *Inorg. Chim. Acta* **1995**, *229*, 95. (b) Ferry, J.; Gallagher, J.; Cunningham, D.; McArdle, P. *Inorg. Chim. Acta* **1990**, *172*, 79.

(27) Bakir, M.; Walton, R. A. *Polyhedron* **1987**, *6*, 1925.

(28) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **2001**, *40*, 5716.

tigated further, although we note that neither contains $[n\text{-Bu}_4\text{N}]^+$ as shown by ^1H NMR measurements on $(\text{CD}_3)_2\text{-SO}$ solutions.

The type of tridentate coordination of L_1 that we propose is present in **3**, is encountered in the paramagnetic $[\text{Re}_2]^{5+}$ complex $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_4(\eta^3\text{-L}_1)$ (**5**) which is formed by the reaction between *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (**2**) and L_1 in refluxing ethanol. Complexes analogous to **5** are formed when the ligands $\text{L}_2\text{--L}_5$ (see Chart 1) are used in place of **1**; this gives rise to compounds **6–9**. The reagent for the reduction process is probably the ethanol solvent, a conclusion that is supported by earlier work of Cotton and co-workers.²⁹ The crystal structures of **5–8** (Figures 1–4) show that they have the same structure, with Re–Re distances for the $\text{Re}^{3.5}\text{-Re}$ bonds in the range 2.2403(4)–2.2804(4) Å. The small variation in Re–Re distances probably reflects some differences in the strength of the axial Re–O and Re–N binding, the Re–Re distance with the pyridyl-containing ligand L_3 being the longest of the set. The parameters for the two dirhenium molecules present in the asymmetric unit of **6** are very similar; only one set of these parameters is given in the caption to Figure 2. In spite of the considerably greater flexibility of ligand L_1 compared to L_2 , we see little significant difference between the structural parameters of **5** and **6**, although the axial Re–O bond distance $\text{Re}(1)\text{-O}(1d)$ in **6** (2.285(4) Å) is a little shorter than is the comparable distance $\text{Re}(1)\text{-O}(12)$ of 2.351(3) Å in **5**. The nonplanarity of the C_6H_4 rings of L_1 in **5** is reflected by a dihedral angle of 55.1° , a value which is similar to that present in other complexes of L_1 that are discussed later.

The Re–P bond distances of **5–8**, which are not given in the captions to Figures 1–4, fall in the range 2.40–2.49 Å and seem to show only small variations with the Re– L_{ax} interaction. The compound with the shortest Re–P bond lengths (**6**) also shows the largest P–Re–P angle (158.21°).

The torsional angles that define the extent of rotation of the ligand sets about the Re–Re bonds are all less than 5° , signifying that the rotational geometries are very close to being fully eclipsed; for example, for **5** the angles $\text{Cl}(1)\text{-Re}(1)\text{-Re}(2)\text{-Cl}(22)$, $\text{P}(2)\text{-Re}(1)\text{-Re}(2)\text{-Cl}(23)$, $\text{O}(1)\text{-Re}(1)\text{-Re}(2)\text{-O}(2)$, and $\text{P}(1)\text{-Re}(1)\text{-Re}(2)\text{-Cl}(21)$ are 4.1° , 2.6° , 1.9° , and 0.0° , respectively.

As expected, compounds **5–9** give only broad poorly defined resonances in their ^1H NMR spectra and no resonances in the ^{31}P NMR spectra. The magnetic moment of **5**, which is $1.40 \mu_{\text{B}}$ at 300 K, is effectively constant down to ~ 4 K, and Curie law behavior is observed. A rising absorption in the electronic absorption spectrum of a dichloromethane solution of **5**, at the low-energy limit of our measurements (900 nm), signals the presence of the expected low-energy $\delta \rightarrow \delta^*$ transition for a complex of the $[\text{Re}_2]^{5+}$ core.²³

In accord with the structural similarity of compounds **5–9**, we observe very similar electrochemical behavior for this

Table 2. Cyclic Voltammetric Half-Wave Potentials for Dirhenium Complexes of Ligands $\text{L}_1\text{--L}_5$

compd no.	$E_{1/2}(\text{ox}), \text{V}^a$	$E_{1/2}(\text{red}), \text{V}^a$
5	+0.42	−1.03
6	+0.42	−1.00
7	+0.36	−1.09
8	+0.30	−1.10
9	+0.33	−1.11
10	+0.39	−1.02
11	+0.37	−1.06
12	+0.44	−0.97
13	+0.37	−1.06
14	+0.34	−1.10
15	+0.40	−1.01
16	+0.43 ^b	−1.00 ^b
17	+0.39 ^b	−1.05 ^b

^a Data are based upon single-scan cyclic voltammograms measured on 0.1 M TBAH– CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead electrode. The $E_{1/2}$ values are for one-electron processes with $i_{\text{p,a}} = i_{\text{p,c}}$. Values of ΔE_{p} , i.e., $E_{\text{p,a}} - E_{\text{p,c}}$, for the individual processes are in the range 60–120 mV. ^b These processes are broadened due to weak electronic coupling between the pairs of dirhenium units.

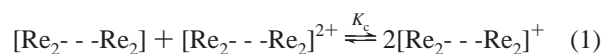
series of compounds. The cyclic voltammograms of 0.1 M TBAH– CH_2Cl_2 solutions show a one-electron oxidation and a one-electron reduction for each of the compounds, the $E_{1/2}$ values of which are listed in Table 2. Attempts to oxidize these compounds chemically to afford salts of the diamagnetic cations $[\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_4(\text{L}_n)]^+$ have not been successful.

Solid samples of **5–9** were quite stable in air for extended periods, and their solutions in polar solvents likewise showed little sign of decomposition when kept under dinitrogen. However, these compounds readily undergo carboxylate exchange reactions in refluxing alcohol solvents. This type of behavior was examined in detail in the case of the reactions of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_4(\eta^3\text{-L}_1)$ (**5**) and $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)\text{Cl}_4(\eta^3\text{-L}_3)$ (**7**) with 4- $\text{Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{H}$, 2- $\text{Ph}_2\text{PC}_6\text{H}_4\text{-CO}_2\text{H}$, quinoline-4-carboxylic acid, and terephthalic acid (1,4- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$). These reactions afforded complexes **10–17**, which are either of the type $\text{Re}_2(\mu\text{-O}_2\text{CAr})\text{Cl}_4(\eta^3\text{-L}_n)$ (where Ar = 4- $\text{Ph}_2\text{PC}_6\text{H}_4$, 2- $\text{Ph}_2\text{PC}_6\text{H}_4$, or 4- $\text{C}_{10}\text{H}_6\text{N}$ and $n = 1$ or 3) or of the type $[\text{Re}_2\text{Cl}_4(\eta^3\text{-L}_n)]_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)$ (where $n = 1$ or 3), the latter pair of compounds containing two $[\text{Re}_2]^{5+}$ units that are linked via a terephthalate bridge. The structural identity of this series of complexes was established by X-ray crystal structure determinations on **11**, **12**, **14**, **15**, and **16** (Figures 5–9). These compounds retain the same type of $\text{Re}(\mu\text{-O}_2\text{CR})\text{Cl}_4(\eta^3\text{-L}_n)$ structure that is present in **5** and **7**. The Re–Re distances are in the range 2.2390(3)–2.2694(3) Å and are very similar to the distances encountered for complexes **5–8**. The two molecules present in the asymmetric unit of **11** have essentially identical parameters; only one set of parameters is given in the caption to Figure 5. Like the set of complexes **5–8**, compounds **11**, **12**, and **14–16** all have essentially eclipsed rotational geometries (the relevant torsional angles (χ) are all less than 6°) and Re–P distances that fall in the very narrow range 2.41–2.45 Å. Other features of note include the presence of ethanol solvent molecules in the crystals of **14–16**. While the EtOH present in **16** does not interact with the coupled dirhenium units, an EtOH molecule is hydrogen-bonded to

(29) (a) Angaridis, P.; Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Polyhedron* **2001**, *20*, 755. (b) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **1999**, *38*, 3384.

the Cl atom (Cl(11)) of one of the Re–Cl bonds of **14**, and to the N atom of the quinoline carboxylate ligand of **15**; the latter of these interactions is depicted in Figure 8. The parameters for these hydrogen-bonded interactions are as follows: **14**, Cl(11)⋯H(901) 2.722(3) Å and Cl(11)⋯H(901)–O(901) 168.1(6)°; **15**, N(14)⋯H(901) 2.051(7) Å and N(14)⋯H(901)–O(901) 173.0(6)°. In the structure of complex **16**, in which there are two dirhenium units coupled through a terephthalate bridge, the deviation from planarity of the [Re₂O₂CC₆H₄CO₂Re₂] unit is reflected by the torsional angles O(1)–C(10)–C(11)–C(16) and O(2)–C(10)–C(11)–C(12), which have values of 11.4(10)° and 13.3(10)°, respectively.

The cyclic voltammetric properties of **10–15** resemble closely those of **5–9** (Table 2). While the potentials for the tetrarhenium complexes **16** and **17** are very similar to those of all the complexes listed in Table 2, each of the processes ($E_{1/2}(\text{ox})$ and $E_{1/2}(\text{red})$) differ in showing clear evidence for broadening due to electronic coupling between the pairs of [Re₂]⁵⁺ dirhenium units that are present in these compounds. However, we were unable to resolve the pairs of sequential one-electron redox processes and estimate that $\Delta E_{1/2}$ is <40 mV for both $E_{1/2}(\text{ox})$ and $E_{1/2}(\text{red})$. Accordingly, the value for the comproportionation constant K_c for the equilibrium represented in eq 1,



where

$$K_c = \exp(\Delta E_{1/2}/25.69)$$

is very small, well less than the value of 100 that is typically the order of magnitude expected for a weakly coupled valence trapped system.^{30–32} This result is in accord with the evidence reported by Chisholm and co-workers³⁰ that terephthalate is at best a poor linker ligand for electronic coupling, and relates to our recent findings concerning the linking of symmetrical [Re₂Cl₄(μ -dppm)₂]⁺ and [Re₂Cl₂(μ -dppm)₂]²⁺ units via terephthalate and related ligands.³³ Support for the conclusion that electronic coupling in **16** and **17** is at most very weak comes from a study of the temperature range magnetic properties of **16** (from 300 to 2

K), which show the absence of a significant antiferromagnetic interaction between the [Re₂]⁵⁺ units.³⁴ The magnetic moment of **16** is 2.80 μ_B at 300 K.

Concluding Remarks

The use of the tridentate P,O,P and P,N,P ligands **L₁–L₅** (Chart 1) provides new types of unsymmetrical [Re₂]⁶⁺ and [Re₂]⁵⁺ complexes. The compound Re₂Cl₆(η^3 -**L₁**) (**3**), which is formed from (*n*-Bu₄N)₂Re₂Cl₈ and is formally a quadruply bonded Re(IV)Re(II) complex, resembles closely Re₂Cl₆(dppf) (dppf = 1,1'-bis(diphenylphosphino)ferrocene).¹ However, unlike Re₂Cl₆(dppf), compound **3** contains a weak axial ligand coordination although this does not significantly affect its spectroscopic properties compared to those of Re₂Cl₆(dppf). Ligand **L₂**, which is a rigid variant of **L₁**, reacts with (*n*-Bu₄N)₂Re₂Cl₈ to afford the stable salt (*n*-Bu₄N)[Re₂Cl₇(η^1 -**L₂**)] (**4**), which we believe contains P-bound η^1 -ligand coordination and would very likely have a structure similar to that of the intermediate (*n*-Bu₄N)[Re₂Cl₇(η^1 -**L₁**)] that is presumably formed in the conversion of (*n*-Bu₄N)₂Re₂Cl₈ to **3**. The five-ligand set **L₁–L₅** reacts with *cis*-Re₂(μ -O₂-CCH₃)₂Cl₄(H₂O)₂ to afford paramagnetic complexes of the type Re₂(μ -O₂-CCH₃)Cl₄(η^3 -**L_n**) (**5–9**), all of which involve the nonbridging tridentate coordination of **L_n** to one of the Re atoms. The lability of the acetate ligand in these complexes toward carboxylates that contain other donor sites (i.e., 4-Ph₂PC₆H₄, 2-Ph₂PC₆H₄, and 4-C₁₀H₆N) provides a route to systems that have the potential to be used to obtain new types of mixed-metal assemblies. These studies are currently underway. The exchange of terephthalate for acetate shows that the μ -terephthalate bridged paramagnetic tetrarhenium complexes **16** and **17** can easily be obtained. Other dicarboxylic acids, which can also serve as linkers between dirhenium units and are of different lengths and involve different degrees of conjugation, will be used to develop this chemistry further.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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