

Complexes of the Type $M_2X_4(LL)(LL')$ That Contain Mixed Intramolecular Phosphine Ligand Bridges. Synthesis and Characterization of $\beta\text{-Re}_2\text{Cl}_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ and Related Species

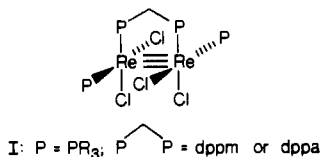
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The violet dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$, $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$, and $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$, where $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\text{dppa} = \text{Ph}_2\text{PNHPPH}_2$, $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, and $\text{arphos} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$, have been prepared by the reaction of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{LL})$, where $\text{LL} = \text{dppm}$ or dppa , with dppe or arphos in refluxing 1-butanol. Alternative synthetic strategies for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ involve the reaction of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ with 2 equiv of dppm and 1 equiv of dppe and the reaction of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with dppe . The spectroscopic and electrochemical properties of these three mixed phosphine ligand complexes are in accord with their possessing structures in which the two bidentate ligands assume a bridging transoid disposition to one another. This has been confirmed by a single-crystal X-ray structure analysis on crystals of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ grown from CH_2Cl_2 solution. This complex crystallizes in the monoclinic space group $P2_1/n$ with the following unit-cell dimensions: $a = 16.985(4) \text{ \AA}$, $b = 13.070(6) \text{ \AA}$, $c = 22.787(4) \text{ \AA}$, $\beta = 107.94(2)^\circ$, $V = 4813(5) \text{ \AA}^3$, and $Z = 4$. The structure was refined to $R = 0.061$ ($R_w = 0.080$) for 3807 data with $F^2 > 3.0\sigma(F^2)$. The structure is similar to that of $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$ and displays the same sort of disorder. It involves a trans arrangement of intramolecular dppm and dppe bridges and is the first that has been determined in which a multiply bonded dimetal complex contains two different intramolecular phosphine bridges. There is a staggered rotational geometry about the short Re-Re bond (2.237(1) \AA) with average Cl-Re-Re-Cl and P-Re-Re-P torsional angles of 57.6° and 48.9° , respectively.

Introduction

Our isolation and characterization of the mixed phosphine ligand complexes $\text{Re}_2\text{Cl}_4(\text{PR}_3)_2(\text{LL})$ (I), where $\text{PR}_3 = \text{PMe}_3, \text{PEt}_3,$



or PMe_2Ph and $\text{LL} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) or $\text{Ph}_2\text{PNHPPH}_2$ (dppa),¹⁻³ has led us to explore the substitutional lability of the monodentate phosphine ligands PR_3 toward various neutral bidentate ligands. In the case of the bidentates $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ (arphos), we have isolated complexes of the type $\text{Re}_2\text{Cl}_4(\text{LL})(\text{LL}')$ that contain mixed intramolecular phosphine ligand bridges. These constitute the first examples of their kind for multiply bonded dimetal complexes that possess the stoichiometry $\text{M}_2\text{X}_4\text{L}_4$, where $\text{M} = \text{Mo}, \text{W},$ or Re and $\text{X} = \text{halide}$.⁴ The present report addresses the synthesis and characterization of these species, including details of the X-ray crystal structure of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$.

Experimental Section

Starting Materials. The dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$, $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$, $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppa})$, $\text{Re}_2\text{Cl}_4(\text{dppm})_2$, and $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ were prepared as described in the literature.^{1,5-7} All solvents and reagents were obtained from commercial sources and were used without further purification. Solvents were dried by using standard techniques and deoxygenated by a nitrogen purge.

Reaction Procedures. All reactions were performed under a dry nitrogen atmosphere by using standard vacuum line techniques.

A. Reactions of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$. (i) **Reactions with dppm or dppa .** When $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ was combined in a 1:2 ratio with either dppm or dppa in refluxing 1-butanol, no reaction was observed to occur.

(ii) **Reaction with dppe .** A mixture of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ (0.204 g, 0.194 mmol) and dppe (0.157 g, 0.394 mmol) was suspended in 20 mL of 1-butanol. The mixture was refluxed for 48 h, and the resulting violet precipitate was filtered off, washed with 1-butanol and diethyl ether, and dried under vacuum; yield 0.217 g (83%). Anal. Calcd for $\text{C}_{51}\text{H}_{52}\text{Cl}_4\text{O}_3\text{P}_4\text{Re}_2$ (i.e., $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})\cdot 3\text{H}_2\text{O}$): C, 45.33; H, 3.89; Cl, 10.49. Found: C, 45.43; H, 4.00; Cl, 10.13. The presence of waters of crystallization was apparent from IR spectroscopy ($\nu(\text{O-H})$ at ~ 3300 (m-w, br) cm^{-1} for a Nujol mull) and ^1H NMR spectroscopy on a CD_2Cl_2 solution of the complex ($\delta +1.60$ showing the correct integration).

(iii) **Reaction with arphos .** $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ (0.055 g, 0.052 mmol) was combined with arphos (0.027 g, 0.061 mmol) in 10 mL of 1-butanol. The mixture was refluxed for 3 days to give a violet precipitate that was filtered off, washed with 1-butanol and diethyl ether, and dried under vacuum; yield 0.034 g (49%). Anal. Calcd for $\text{C}_{51}\text{H}_{46}\text{AsCl}_4\text{P}_3\text{Re}_2$ (i.e., $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$): C, 45.67; H, 3.46. Found: C, 45.46; H, 3.62.

B. Reactions of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppa})$. (i) **Reaction with dppm or dppa .** When $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppa})$ was combined in a 1:2 ratio with either dppm or dppa in refluxing 1-butanol, no reaction took place.

(ii) **Reaction with dppe .** A mixture of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppa})$ (0.068 g, 0.065 mmol) and dppe (0.028 g, 0.070 mmol) was suspended in 10 mL of 1-butanol and the mixture refluxed for 46 h. Workup of the reaction product was carried out as in A(ii); yield 0.047 g (56%). Anal. Calcd for $\text{C}_{50}\text{H}_{47}\text{Cl}_4\text{NOP}_4\text{Re}_2$ (i.e., $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})\cdot \text{H}_2\text{O}$): C, 45.63; H, 3.61. Found: C, 45.60; H, 4.31.

(iii) **Reaction with arphos .** Attempts to prepare $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{arphos})$ through the reaction of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppa})$ with arphos in refluxing 1-butanol led to the isolation of mixtures.

C. Reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$. (i) **Reaction with PMe_3 .** A quantity of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.070 g, 0.055 mmol) was suspended in 10 mL of 1-butanol, and PMe_3 (0.2 mL, 2.0 mmol) was added by syringe. The mixture was refluxed for 12 h, and the pale violet precipitate was filtered off, washed with 1-butanol and diethyl ether, and dried in vacuo; yield 0.024 g (42%). The product was shown to be $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ on the basis of its spectroscopic and electrochemical properties.¹

(ii) **Reaction with dppe .** $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.075 g, 0.058 mmol) was reacted with dppe (0.048 g, 0.120 mmol) for 3 days in refluxing 1-butanol (10 mL). The reaction mixture was cooled and the violet precipitate filtered off, washed with 1-butanol and diethyl ether, and dried in vacuo; yield 0.031 g (41%). The product was shown to be $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ through a comparison of its properties with samples prepared as described in A(ii).

(iii) **Reaction with $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$.** A mixture of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ (0.058 g, 0.071 mmol) and $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.085 g, 0.066 mmol) was refluxed in 1-butanol (10 mL) for 1.5 days. The resulting silver-gray precipitate was filtered off, washed with 1-butanol and diethyl ether, and

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- For a recent review dealing with multiply bonded dimetal complexes of this type that contain intramolecular phosphine ligand bridges, see: Price, A. C.; Walton, R. A., submitted for publication in *Polyhedron*.
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- In the case of the synthesis of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$, the use of 1-butanol as solvent in place of toluene increased the product yield to 85% and reduced the reaction time to 1 day.

Table I. Crystallographic Data and Data Collection Parameters for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})^a$

formula	$\text{Re}_2\text{Cl}_4\text{P}_4\text{C}_{51}\text{H}_{46}$
fw	1297.0
space group	$P2_1/n$
a , Å	16.985 (4)
b , Å	13.070 (6)
c , Å	22.787 (4)
β , deg	107.94 (2)
V , Å ³	4813 (5)
Z	4
d_{calc} , g cm ⁻³	1.790
cryst dimens, mm	0.35 × 0.15 × 0.05
temp, °C	23.0
radiatn (wavelength)	Mo K α (0.71073 Å)
monochromator	graphite
linear abs coeff, cm ⁻¹	54.85
abs correctn applied	empirical ^b
cryst radius, cm	0.015
diffractometer	Enraf-Nonius CAD4
scan method	θ - 2θ
h, k, l limits	0 to +18, 0 to +14, -24 to +23
2θ range, deg	3.00-45.00
scan width, deg	0.80 + 0.35 tan θ
takeoff angle, deg	5.00
programs used	Enraf-Nonius SDP
F_{000}	2520.0
ρ factor used in weighting	0.070
unique data	6613
data with $I > 3.0\sigma(I)$	3807
no. of variables	329
largest shift/esd in final cycle	0.24
R^c	0.061
R_w^d	0.080
goodness of fit ^e	1.768

^aNumbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. ^bFlack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* 1977, A33, 890. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. ^eGoodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

dried in vacuo; yield 0.048 g (69%). The product was shown to be $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$.

D. Reactions of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$. (i) **Reaction with dppe.** A mixture of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ (0.085 g, 0.104 mmol) and dppe (0.084 g, 0.211 mmol) was suspended in 10 mL of 1-butanol and refluxed for 48 h. The resulting violet precipitate was filtered off, washed with 1-butanol and diethyl ether, and dried under vacuum; yield 0.070 g (51%). The product was shown to be $\text{Re}_2\text{Cl}_4(\text{dppe})_2$. This reaction does not proceed when it is carried out in benzene or toluene.

(ii) **Reaction with dppm and dppe.** A small quantity of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ (0.052 g, 0.064 mmol) was placed in a reaction vessel with dppm (0.056 g, 0.146 mmol) and dppe (0.025 g, 0.063 mmol), and 10 mL of 1-butanol was added. The mixture was heated, and after 1.5 days the resulting violet precipitate was filtered off, washed with 1-butanol and diethyl ether, and dried in vacuo; yield 0.042 g (51%). The spectroscopic and electrochemical properties of this product showed it to be $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$.

(iii) **Reaction with dpma and dppe.** A procedure similar to D(ii) but using a mixture of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ (0.060 g, 0.073 mmol), dpma (0.062 g, 0.161 mmol), and dppe (0.061 g, 0.153 mmol) gave a low yield of $\text{Re}_2\text{Cl}_4(\text{dpma})(\text{dppe})$; yield 0.012 g (13%).

X-ray Structure Determination. Violet crystals of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ were obtained by slow evaporation of a dichloromethane solution in an NMR tube. A single crystal of dimensions 0.35 × 0.15 × 0.05 mm was mounted on a glass fiber with epoxy resin. The crystal was indexed, and data were collected on an Enraf-Nonius CAD 4 diffractometer equipped with a graphite monochromator and a standard-focus molybdenum X-ray tube. The crystal data and information relating to data collection and structure refinement are listed in Table I. Further details of the crystal data collection and reduction methods are described elsewhere.⁸

The structure was refined in the monoclinic space group $P2_1/n$. The space group was uniquely determined by the extinctions $h,0,l$ ($h + l =$

$2n + 1$) and $0,k,0$ ($k = 2n + 1$). Three standard reflections were monitored after every hour of beam exposure during data collection and displayed no systematic variation in intensity. The cell constants suggested that this crystal was isostructural with that of $\text{Re}_2\text{Cl}_4(\text{dppe})_2$. Therefore, the structure reported herein was refined by using the Re, P, and Cl positions known for $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ and the same disorder model in which there are two Re_2 units perpendicular to one another.⁶ This type of disorder is commonly encountered for multiply bonded M_2L_8 types of complexes.⁹ All other atoms were found by using a least-squares refinement and difference Fourier maps. The Re, P, and Cl atoms were refined anisotropically, while the phenyl carbons were refined isotropically. Hydrogen atoms were not included in the final least-squares refinement. The occupancy of the major Re_2 orientation was 95.3% and that of the minor orientation 4.7%. The final difference Fourier map displayed no peaks of chemical significance. No evidence for a disorder between the dppm and dppe ligands was observed. The structure solution clearly shows a unique positioning of the ligands.

All calculations were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package. An empirical absorption correction was applied,¹⁰ and corrections for anomalous dispersion were applied to all of the anisotropically refined atoms. The least-squares program minimized the function $w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. Further details of the data set and the structure solution and refinement may be obtained from Dr. P. E. Fanwick. Table II lists the atomic positional parameters and their errors, while Table III lists selected intramolecular bond distances and angles. Tables listing thermal parameters (Table S1) and complete listings of bond distances (Table S2) and bond angles (Table S3) are available as supplementary material, as well as a figure (Figure S1) which shows the full atomic numbering scheme.

Physical Measurements. Infrared spectra were recorded as Nujol mulls by 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 Hewlett-Packard Model 7035B x-y recorder. Dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte were utilized. $E_{1/2}$ values $[(E_{pa} + E_{pc})/2]$ were referenced against a Ag/AgCl electrode at room temperature and were uncorrected for junction potentials. ³¹P NMR and ¹H NMR spectra were recorded on CD_2Cl_2 solutions with a Varian XL-200 spectrometer.

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

Results and Discussion

(a) Synthesis and General Characterization of $\text{Re}_2\text{Cl}_4(\text{LL})(\text{LL}')$. The lability of the PMe_3 ligands in $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ is clearly demonstrated by the reaction of this complex with 2 equiv of dppe in refluxing 1-butanol to give $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$. Alternative synthetic methods were later developed. One of these involved the one-pot reaction of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ with 2 equiv of dppm and 1 equiv of dppe. This reaction probably proceeds through the intermediacy of the reactive species $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$. Another method involves the reaction of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with 2 equiv of dppe in 1-butanol.¹¹ This reaction is of interest because the alternative strategy of reacting $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ with dppm does not work. This presumably reflects the much greater stability of the six-membered Re-Re-P-C-P rings to ring opening compared to the five-membered Re-Re-P-C-P . This conclusion has been substantiated by studies on the reactivity of $[\text{Re}_2\text{Cl}_4(\text{dppe})_2]^{n+}$ ($n = 0$ or 1) toward nitriles and isocyanides.¹² In this same context, the greater reactivity of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ toward ligand substitution is demonstrated by its reaction with excess PMe_3 to give $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$, and its reaction with an equivalent of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_4$ in refluxing 1-bu-

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(9) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982.

(10) Flack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffraction, Theor. Gen. Crystallogr.* 1977, A33, 890.

(11) It should be noted that the reactions which give $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ all proceed in lower yield if only a single equivalent of the appropriate phosphine ligand is used.

(12) Anderson, L. B.; Tetrick, S. M.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* 1986, 55.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (\AA^2) for Non-Hydrogen Atoms and Their Estimated Standard Deviations^a

atom	x	y	z	B
Re(1)	-0.00272 (4)	0.30412 (5)	0.30237 (3)	3.74 (2)
Re(2)	0.05179 (5)	0.20501 (5)	0.24478 (3)	4.15 (2)
Re(3)	-0.028 (1)	0.283 (1)	0.2370 (9)	9.1 (6)
Re(4)	0.066 (1)	0.221 (1)	0.3167 (8)	7.7 (5)
Cl(1)	-0.0681 (3)	0.4558 (3)	0.2553 (2)	5.3 (1)
Cl(2)	0.0123 (3)	0.2411 (4)	0.4021 (2)	5.3 (1)
Cl(3)	0.1931 (3)	0.1644 (4)	0.2828 (2)	6.3 (1)
Cl(4)	-0.0441 (4)	0.1511 (4)	0.1512 (2)	7.0 (2)
P(1)	0.1158 (3)	0.4135 (4)	0.3445 (2)	4.4 (1)
P(2)	0.1023 (3)	0.3420 (4)	0.1927 (2)	5.0 (1)
P(3)	-0.1305 (3)	0.2084 (4)	0.2720 (3)	5.7 (1)
P(4)	0.0074 (3)	0.0524 (4)	0.2874 (2)	5.4 (1)
C(1)	0.143 (1)	0.488 (1)	0.2866 (8)	5.0 (4)
C(2)	0.180 (1)	0.423 (2)	0.2458 (9)	7.1 (6)
C(3)	-0.106 (1)	0.067 (2)	0.274 (1)	7.7 (7)
C(111)	0.090 (1)	0.508 (1)	0.3935 (7)	4.3 (4)*
C(112)	0.105 (1)	0.492 (2)	0.4561 (9)	6.7 (5)*
C(113)	0.084 (1)	0.562 (2)	0.495 (1)	7.2 (5)*
C(114)	0.050 (1)	0.652 (2)	0.4706 (9)	6.2 (5)*
C(115)	0.035 (1)	0.672 (2)	0.408 (1)	7.9 (6)*
C(116)	0.054 (1)	0.602 (2)	0.3710 (9)	6.7 (5)*
C(121)	0.216 (1)	0.369 (2)	0.3968 (8)	5.7 (4)*
C(122)	0.223 (1)	0.271 (2)	0.4211 (9)	6.3 (5)*
C(123)	0.296 (2)	0.241 (2)	0.464 (1)	8.9 (6)*
C(124)	0.361 (2)	0.314 (2)	0.482 (1)	9.2 (7)*
C(125)	0.363 (2)	0.408 (3)	0.453 (1)	12.0 (9)*
C(126)	0.284 (2)	0.436 (2)	0.409 (1)	10.0 (7)*
C(211)	0.160 (1)	0.289 (2)	0.1453 (9)	5.8 (4)*
C(212)	0.114 (1)	0.241 (2)	0.092 (1)	7.4 (5)*
C(213)	0.153 (1)	0.198 (2)	0.049 (1)	8.3 (6)*
C(214)	0.242 (1)	0.212 (2)	0.066 (1)	8.5 (6)*
C(215)	0.286 (2)	0.256 (2)	0.121 (1)	8.9 (7)*
C(216)	0.245 (1)	0.296 (2)	0.162 (1)	8.1 (6)*
C(221)	0.033 (1)	0.430 (1)	0.1376 (8)	5.2 (4)*
C(222)	-0.053 (1)	0.409 (2)	0.1159 (8)	5.8 (4)*
C(223)	-0.102 (1)	0.475 (2)	0.0703 (9)	6.9 (5)*
C(224)	-0.068 (1)	0.556 (2)	0.050 (1)	7.2 (5)*
C(225)	0.017 (2)	0.576 (2)	0.068 (1)	8.7 (6)*
C(226)	0.070 (1)	0.512 (2)	0.116 (1)	7.0 (5)*
C(311)	-0.194 (1)	0.230 (2)	0.318 (1)	7.3 (5)*
C(312)	-0.200 (1)	0.316 (2)	0.346 (1)	8.3 (6)*
C(313)	-0.260 (2)	0.355 (3)	0.381 (2)	13 (1)*
C(314)	-0.298 (2)	0.262 (3)	0.390 (1)	12.3 (9)*
C(315)	-0.300 (2)	0.171 (3)	0.365 (1)	12 (1)*
C(316)	-0.247 (2)	0.139 (3)	0.325 (1)	13 (1)*
C(321)	-0.209 (1)	0.223 (2)	0.1978 (9)	6.5 (5)*
C(322)	-0.227 (2)	0.316 (2)	0.169 (1)	9.9 (8)*
C(323)	-0.288 (1)	0.329 (2)	0.109 (1)	8.6 (6)*
C(324)	-0.331 (2)	0.250 (2)	0.081 (1)	9.6 (7)*
C(325)	-0.319 (2)	0.160 (4)	0.105 (2)	17 (1)*
C(326)	-0.265 (2)	0.145 (3)	0.168 (2)	15 (1)*
C(411)	0.052 (1)	0.008 (2)	0.3671 (9)	5.7 (4)*
C(412)	0.138 (1)	0.009 (2)	0.388 (1)	7.8 (6)*
C(413)	0.178 (2)	-0.030 (2)	0.452 (1)	10.0 (8)*
C(414)	0.129 (2)	-0.067 (2)	0.482 (1)	9.5 (7)*
C(415)	0.047 (2)	-0.070 (2)	0.464 (1)	10.4 (8)*
C(416)	0.004 (2)	-0.030 (2)	0.402 (1)	9.9 (7)*
C(421)	0.012 (1)	-0.067 (2)	0.2475 (9)	6.0 (5)*
C(422)	-0.038 (1)	-0.149 (5)	0.261 (1)	7.8 (6)*
C(423)	-0.025 (2)	-0.243 (2)	0.232 (1)	10.7 (8)*
C(424)	0.029 (2)	-0.255 (2)	0.203 (1)	8.9 (7)*
C(425)	0.073 (2)	-0.175 (2)	0.183 (1)	10.1 (8)*
C(426)	0.065 (1)	-0.075 (2)	0.213 (1)	8.1 (6)*

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. Atoms with an asterisk were refined isotropically.

tanol to give this same complex. However, no reaction was observed when $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ was reacted with $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ under these same conditions.

Two other mixed bidentate ligand complexes of this type were prepared, viz., $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$ and $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$. In each case, the superior synthetic method proved to be the

Table III. Important Bond Distances (\AA) and Angles (deg) for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})^a$

Bond Distances			
Re(1)-Re(2)	2.237 (1)	P(1)-C(121)	1.85 (2)
Re(1)-Cl(1)	2.362 (4)	P(2)-C(2)	1.83 (2)
Re(1)-Cl(2)	2.357 (4)	P(2)-C(211)	1.81 (2)
Re(1)-P(1)	2.415 (5)	P(2)-C(221)	1.84 (2)
Re(1)-P(3)	2.415 (5)	P(3)-C(3)	1.90 (3)
Re(2)-Cl(3)	2.348 (5)	P(3)-C(311)	1.74 (3)
Re(2)-Cl(4)	2.357 (5)	P(3)-C(321)	1.81 (2)
Re(2)-P(2)	2.444 (6)	P(4)-C(3)	1.86 (2)
Re(2)-P(4)	2.437 (6)	P(4)-C(411)	1.83 (2)
P(1)-C(1)	1.81 (3)	P(4)-C(421)	1.83 (2)
P(1)-C(111)	1.81 (2)	C(1)-C(2)	1.53 (4)
Bond Angles			
Cl(1)-Re(1)-Cl(2)	128.9 (2)	Re(2)-P(2)-C(221)	122.9 (7)
Cl(1)-Re(1)-P(1)	84.3 (2)	C(2)-P(2)-C(211)	102 (1)
Cl(1)-Re(1)-P(3)	92.8 (2)	C(2)-P(2)-C(221)	105.6 (9)
Cl(2)-Re(1)-P(1)	89.7 (2)	C(221)-P(2)-C(221)	100.6 (9)
Cl(2)-Re(1)-P(3)	85.2 (2)	Re(1)-P(3)-C(3)	108.9 (7)
P(1)-Re(1)-P(3)	170.6 (2)	Re(1)-P(3)-C(311)	114.6 (7)
Cl(3)-Re(2)-Cl(4)	127.5 (2)	Re(1)-P(3)-C(321)	123.6 (8)
Cl(3)-Re(2)-P(2)	82.7 (2)	C(3)-P(3)-C(311)	109 (1)
Cl(3)-Re(2)-P(4)	94.3 (2)	C(3)-P(3)-C(321)	103 (1)
Cl(4)-Re(2)-P(2)	91.7 (2)	C(311)-P(3)-C(321)	97 (2)
Cl(4)-Re(2)-P(4)	84.5 (2)	Re(2)-P(4)-C(3)	106.3 (7)
P(2)-Re(2)-P(4)	172.2 (2)	Re(2)-P(4)-C(411)	124.5 (7)
Re(1)-P(1)-C(1)	113.4 (5)	Re(2)-P(4)-C(421)	115.8 (8)
Re(1)-P(1)-C(111)	108.6 (6)	C(3)-P(4)-C(411)	107 (2)
Re(1)-P(1)-C(121)	124.1 (7)	C(3)-P(4)-C(421)	102.1 (9)
C(1)-P(1)-C(111)	104.1 (9)	C(411)-P(4)-C(421)	98.9 (9)
C(1)-P(1)-C(121)	104.6 (9)	P(1)-C(1)-C(2)	113 (1)
C(111)-P(1)-C(121)	99.6 (8)	P(2)-C(2)-C(1)	112 (1)
Re(2)-P(2)-C(2)	113.1 (7)	P(3)-C(3)-P(4)	108 (2)
Re(2)-P(2)-C(211)	110.2 (7)		

^a Data are for the major orientation only. Numbers in parentheses are estimated standard deviations in the least significant digits.

reaction of $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{LL})$, where LL = dppm or dppe, with 2 equiv of the appropriate bidentate ligand in refluxing 1-butanol. $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$ is the product when $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ is reacted with arphos, whereas the reaction between $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppe})$ and dppe leads to the isolation of $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$.^{13,14}

The Nujol mull IR spectra of these violet complexes show bands that can be attributed to the presence of both of the respective bidentate phosphine ligands. The solution electronic absorption spectra (measured in CH_2Cl_2) very closely resemble those reported for other complexes of this type,² with λ_{max} at ca. 520 nm ($\epsilon \approx 500 \text{ M}^{-1} \text{ cm}^{-1}$) and a shoulder to lower energy at ca. 600 nm. These similarities are also reflected by the electrochemical properties of these complexes. As expected for complexes that possess the triply bonded $\sigma^2\pi^4\delta^2\delta^{*2}$ ground-state configuration,^{9,15} solutions of the $\text{Re}_2\text{Cl}_4(\text{LL})(\text{LL}')$ complexes in 0.1 M TBAH- CH_2Cl_2 exhibit two reversible one-electron oxidations in their cyclic voltammogram. The $E_{1/2}$ values for these processes [$E_{1/2} = +0.32$ and $+0.96$ V vs. Ag/AgCl for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$, $E_{1/2} = +0.31$ and $+0.88$ V vs. Ag/AgCl for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$, and $E_{1/2} = +0.35$ and $+1.00$ V vs. Ag/AgCl for $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$] are typical of data obtained previously for $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ ¹⁶ and $\text{Re}_2\text{Cl}_4(\text{dppm})_2$.³

- (13) Note that all attempts to prepare the mixed-ligand complexes $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppa})$ by reacting $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{LL})$, where LL = dppm or dppe, with an excess of dppe or dppm were unsuccessful. This is in accord with the observation that no reaction occurs between $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppm})$ and dppe or between $\text{Re}_2\text{Cl}_4(\text{PMe}_3)_2(\text{dppe})$ and dppa. All attempts by us to prepare dimolybdenum(II) analogues such as $\text{Mo}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ have failed. Reactions that have been tried include $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4 + \text{dppm}$ and dppe , $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4 + \text{Me}_3\text{SiCl} + \text{dppm}$ and dppe , $\text{Mo}_2\text{Cl}_4(\text{dppm})_2 + \alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$, $\text{Mo}_2\text{Cl}_4(\text{dppa})_2 + \text{dppe}$, and $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2 + \text{dppm}$; Qi, J.-S.; Walton, R. A., unpublished observations (1985).
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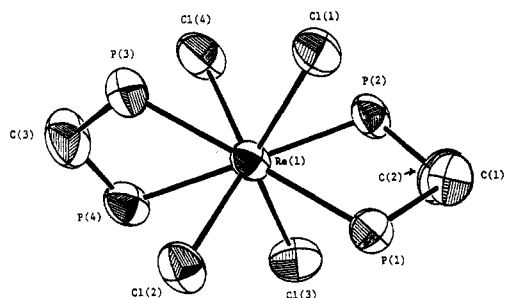


Figure 1. ORTEP representation of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ as viewed down the Re-Re axis. One rhenium (Re(2)) has been obscured by the other. Phenyl rings have been omitted, and atoms are given as their 50% probability ellipsoids.

The implication of the preceding results is that the complexes $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$, $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$, and $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$ possess structures in which the two bidentate ligands assume a bridging transoid disposition to one another. This is confirmed by an X-ray structure analysis of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ (vide infra). The NMR spectra are in keeping with this structure. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of CD_2Cl_2 solutions of $\text{Re}_2\text{Cl}_4(\text{LL})(\text{dppe})$, where LL = dppm or dppa, are very similar in appearance; each displays two complex multiplets in an AA'BB' pattern, where J_{AB} represents the largest coupling constant for the trans phosphorus interaction. These patterns are centered at δ ca. +3.0 and ca. -5.7 for $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ and at δ ca. +37.5 and ca. +3.5 for $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$. The appearance of each subspectrum reflects the fact that J_{AB} is the largest coupling constant because the chemically different phosphorus atoms are located trans to one another.¹⁷ This pattern contrasts with that for other complexes which exhibit an AA'BB' pattern where the trans phosphorus atoms are chemically equivalent; i.e., $J_{\text{AA}'}$ and $J_{\text{BB}'}$ are the largest coupling constants.

The ^1H NMR spectra of the complexes (recorded in CD_2Cl_2) are very similar. In the case of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ and $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$, these spectra support the bulk complexes as being best formulated as hydrates (δ +1.60—see Experimental Section), and all three complexes show the expected resonances due to the phenyl protons (between δ +7.0 and δ +8.5). The spectra of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ and $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{arphos})$ display a multiplet associated with the bridgehead methylene protons of the dppm ligand at δ ca. +5.5, while the spectrum of $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$ contains a broad singlet at δ +6.4 which we attribute to the unique amine proton of the dppa ligand. All three spectra also have multiplets associated with the dppe or arphos methylene protons at δ ca. +3.2 and ca. +2.8.

(b) **The Crystal Structure of $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$.** A single-crystal X-ray structure analysis of this compound shows it to be

closely allied to the complexes $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ ⁵ and $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$.⁶ The structure solution showed this complex to be isostructural crystallographically with $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$ and to possess the same sort of disorder.^{5,9} The same basic structural unit is present in all three complexes in which the phosphine ligands adopt an intramolecular bridging mode with a transoid disposition to one another. The pertinent structural data for this complex are listed in Tables I-III, and an ORTEP view of the molecule (major orientation) is shown in Figure 1. The major orientation is denoted as Re(1)Re(2) and the minor orientation as Re(3)Re(4).

This is the first example of a multiply bonded dimetal complex in which two *different* intramolecular phosphine bridges are present. The complex possesses a staggered rotational geometry which accords with this being a Re(II)-Re(II) compound in which the $\text{Re}\equiv\text{Re}$ triple bond ($\sigma^2\pi^4\delta^2\delta^*2$ configuration) imposes no electronic barrier to rotation. The Re-Re bond distance of 2.237 (1) Å is slightly shorter than that of $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$ (2.244 (1) Å)⁶ but not significantly different from the distance reported for $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (2.234 (3) Å).⁵ The structure is also closely akin to that of the recently characterized complex $\beta\text{-Re}_2\text{Cl}_4(\text{depe})_2$ ($\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$) for which the Re-Re distance is 2.211 (1) Å.¹⁸

The staggered rotational conformation about the Re-Re bond is similar for all three complexes. In the case of $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$ and $\beta\text{-Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ the pairs of torsional angles Cl(1)-Re-Re-Cl(4), Cl(2)-Re-Re-Cl(3) and P(1)-Re-Re-P(2), P(3)-Re-Re-P(4) average to 59.6° and 52.4°, respectively, for the former complex and to 57.6° and 48.9°, respectively, for the latter mixed-phosphine species. These values are in turn similar to those reported for $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ of 56° and 47°, respectively.⁵ The Re-Cl and Re-P bond lengths are normal and are similar to those found in the structures of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ ⁵ and $\beta\text{-Re}_2\text{Cl}_4(\text{dppe})_2$.⁶

In contrast to dimolybdenum(II) compounds, rotation about the Re-Re bond of the analogous dirhenium(II) complexes should not lead to a change in the formal metal-metal bond order—it remains a triple bond. In accord with this, it has been found that an excellent inverse linear relationship exists between the Mo-Mo bond length of $\text{Mo}_2\text{X}_4(\text{LL})_2$ compounds and $\cos 2\chi$, where χ is the average torsional angle. For dirhenium(II) complexes of this type no such simple relationship exists on the basis of data reported in this paper and that described elsewhere.^{5,6,18}

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table S1), bond distances (Table S2), and bond angles (Table S3) and a figure showing the full atomic numbering scheme (Figure S1) (8 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

(17) For $\text{Re}_2\text{Cl}_4(\text{dppm})(\text{dppe})$ we have $J_{\text{AB}} = 237.4$ Hz, $J_{\text{AA}'} = 79.1$ Hz, $J_{\text{AB}'} = 2.2$ Hz, and $J_{\text{BB}'} = -11.1$ Hz, while $\text{Re}_2\text{Cl}_4(\text{dppa})(\text{dppe})$ has $J_{\text{AB}} = 244.0$ Hz, $J_{\text{AA}'} = 76.4$ Hz, $J_{\text{AB}'} = 0.3$ Hz, and $J_{\text{BB}'} = -12.3$ Hz.

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