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Synthesis, Characterization, and Molecular Structure of a Novel Triply Bonded Dirhenium(II) Complex That Contains Three Intramolecular Phosphine Bridging Ligands: $Re_2Cl_4(\mu\text{-}Me_2PCH_2PMe_2)_3$

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The reactions of bis(dimethylphosphino)methane (dmpm) with $(n\text{-}Bu_4N)_2Re_2Cl_8$ in methanol and with $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ in ethanol–toluene afford two means of preparing red crystalline $Re_2Cl_4(\mu\text{-dmpm})_3$. Its $^{31}P\{^1H\}$ NMR spectrum (in $CDCl_3$) shows the presence of inequivalent dmpm ligands (δ −21.56 and −36.92 with an intensity ratio of 2:1), and its electrochemical properties (cyclic voltammetry in 0.1 M TBAH–CH_2Cl_2) reveal the existence of two accessible redox processes (both correspond to oxidations) at $E_{1/2} = +0.53$ V and $E_{p,a} = +1.30$ V vs. Ag/AgCl. The structural identity of this complex has been confirmed by X-ray crystal structure determinations on batches of crystals obtained by using both preparative methods. For crystals prepared from $(n\text{-}Bu_4N)_2Re_2Cl_8$ (A) the crystal data are as follows: space group *Pbca*; $a = 15.432$ (6) Å; $b = 29.245$ (8) Å; $c = 12.985$ (4) Å; $V = 5860$ (6) Å^3; $Z = 8$. For crystals prepared from $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (B) the crystal data are as follows: space group $P2_1/c$; $a = 14.870$ (10) Å; $b = 13.203$ (5) Å; $c = 15.348$ (7) Å; $\beta = 103.10$ (4)°; $V = 2935$ (5) Å^3; $Z = 4$. The molecules in the two forms are essentially identical, but structure B is more accurate. For structure B we have Re–Re = 2.3157 (4) Å. The Re_2 unit is bridged by three dmpm ligands, and each Re atom also has one equatorial and one axial Cl ligand. The rotational conformation is staggered, and there is a twofold axis passing through the methylene carbon atom of one dmpm ligand and the midpoint of the Re–Re bond. The unique dmpm ligand has a helical sense opposite to that of the other two, thus making interconversion of the enantiomers by simple internal rotation about the Re–Re bond impossible.

Introduction

The triply bonded complex $Re_2Cl_4(\mu\text{-dppm})_2$ (dppm = $Ph_2PCH_2PPh_2$) possesses a structure in which the two dppm ligands form intramolecular bridges spanning the Re–Re bond. The resulting two fused five-membered rings assume twist–boat conformations, thereby leading to a completely staggered arrangement of the substituents on the two rhenium atoms.[2] This structure contrasts with the fully eclipsed rotational geometry encountered with the quadruply bonded dimolybdenum(II) analogues $Mo_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br).[3,4] In view of the rich reaction chemistry that is associated with $Re_2Cl_4(\mu\text{-dppm})_2$,[5-10] we have attempted to prepare the analogous complex that contains the $Me_2PCH_2PMe_2$ ligands (abbreviated dmpm) with a view to examining its properties and comparing them to those of $Re_2Cl_4(\mu\text{-dppm})_2$ and the recently characterized dirhenium(II) complex $\alpha\text{-}Re_2Cl_4(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[2] To our surprise we find that all attempts have to date led to the tris complex $Re_2Cl_4(\mu\text{-dmpm})_3$. This is the first example of a multiply bonded dimetal complex in which three intramolecular phosphine bridging ligands are present. The synthesis, structural characterization, and properties of this novel complex are reported.

Experimental Section

Starting Materials. The complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$[11] and $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$[12] were prepared according to literature methods. The $Me_2PCH_2PMe_2$ (dmpm) ligand was purchased from Strem Chemicals. Solvents used in the preparation and workup of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed in an atmosphere of dry nitrogen by using standard procedures.

Preparation of $Re_2Cl_4(\mu\text{-dmpm})_3$. (A) From $(n\text{-}Bu_4N)_2Re_2Cl_8$. To a methanol (5 mL) suspension of $(Bu_4N)_2Re_2Cl_8$ (0.03 g, 0.03 mmol) was added 1 mL of a 2 M solution of dmpm in Et_2O. The solution immediately turned red, and the blue solid, $(Bu_4N)_2Re_2Cl_8$, soon disappeared. After ca. 10 min at room temperature, a small amount of a fine white precipitate was observed. The methanol solution was filtered and solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2, and X-ray quality crystals were obtained by slow evaporation of the CH_2Cl_2 solution in air or under nitrogen.

(B) From $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$. A quantity of $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (0.20 g, 0.17 mmol) was placed in a 1:1 mixture (by volume) of ethanol–toluene (20 mL), and dmpm (0.57 mL, 0.51 mmol) was added. The reaction mixture was refluxed for 16 h to yield a bright red solution. After the solution was cooled, the ethanol was evaporated under a stream of nitrogen. Addition of hexane (~25 mL) to the solution yielded a pink solid. It was recrystallized from chloroform–hexane, washed with hexane, and dried in vacuo; yield 0.11 g, 69%. Anal. Calcd for $C_{15}H_{42}Cl_4P_6Re_2$: C, 19.52; H, 4.60; Cl, 15.37. Found: C, 19.11; H, 4.89; Cl, 15.41.

Single Crystals of $Re_2Cl_4(\mu\text{-dmpm})_3$. Suitable single crystals of this complex were obtained for batches prepared by both method A and method B. Crystals of the complex prepared by procedure B were grown from a $CDCl_3$ solution (which had been used for NMR spectral measurements) to which an equal volume of hexane had been added. As the solution evaporated slowly, red crystals deposited on the bottom of the flask.

X-ray Crystal Structure Analyses. The crystal structure analyses of reaction products A and B were conducted routinely with procedures that have been described elsewhere.[13] Crystals of both products were found to have the same composition; however, product A crystallized in the orthorhombic space group *Pbca*, while B was monoclinic, with space group $P2_1/c$. Table I gives the dimensions of the unit cells and other crystallographic parameters for the two structures.

In addition to the usual data collection and reduction procedures, absorption corrections[13b] were applied to both data sets, based on azimuthal scans of several reflections with χ near 90°. In the case of A,

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Table I. Crystal Data for the Orthorhombic (A) and Monoclinic (B) Forms of $Re_2Cl_4(\mu\text{-dmpm})_3$

	A	B
formula	$Re_2Cl_4P_6C_{15}H_{42}$	$Re_2Cl_4P_6C_{15}H_{42}$
fw	922.57	922.57
space group	*Pbca*	$P2_1/c$
syst abs	$(0kl)$: $k \neq 2n$ $(h0l)$: $l \neq 2n$ $(hk0)$: $h \neq 2n$	$(0k0)$: $k \neq 2n$ $(h0l)$: $l \neq 2n$
a, Å	15.432 (6)	14.870 (10)
b, Å	29.245 (8)	13.203 (5)
c, Å	12.985 (4)	15.348 (7)
β, deg	90	103.10 (4)
V, Å^3	5860 (6)	2935 (5)
Z	8	4
d_{calcd}, g/cm^3	2.09	2.09
cryst size, mm	0.30 × 0.30 × 0.05	0.32 × 0.30 × 0.09
μ(Mo Kα), cm^{-1}	94.1	94.1
data collcn instrum	Syntex P$\bar{1}$	Enraf-Nonius CAD-4F
radiation (monochromated. in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)
orientation reflcns: no.; range (2θ), deg	14; 18–26	25; 11–45
scan method	ω–2θ	ω-scans
data collcn range (2θ), deg	2.5–56.0	4.0–55.0
no. of unique data,	2185	5528
with $F_o^2 > 3\sigma(F_o^2)$	1343	4333
no. of params refined	169	244
transmissn factors: max, min	obsd 1.00, 0.55	obsd 1.00, 0.37
R^a	0.0494	0.0372
$R_w{}^b$	0.0594	0.0494
quality-of-fit indicator^c	1.107	1.351
largest shift/esd, final cycle	0.14	0.05
largest peak, e/Å^3	1.3 (see text)	2.0 (see text)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observn} - N_{params})]^{1/2}$.

a further absorption correction was based on the method of Walker and Stuart.[13c]

Both structures were solved by Patterson methods. The final least-squares refinements of the structures of A and B had data-to-parameter ratios of 7.9 and 17.8, respectively. The final residuals are given in Table I.

A difference Fourier map following the refinement of B had a peak of maximum density 2.0 e/Å^3, well outside of contact distances to any of the atoms of the $Re_2Cl_4(\mu\text{-dmpm})_3$ molecule. We could not refine any model for this area of the cell. Contoured sections of the difference map in this area (available as supplementary material) show that this peak is as much as 2 Å in breadth in some directions. This part of the unit cell could be populated by disordered solvent molecules, but since we also observe negative difference density in the same region it is also possible that series-termination effects are responsible for these anomalies. We observed a similar peak in the final difference map of A. The maximum density in this case was only 1.3 e/Å^3. Contoured sections of this map are also available as supplementary material.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on an IBM Instruments IR 32 Fourier transform (4000–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on an IBM Instruments 9420 (900–300 nm) UV–visible spectrophotometer. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed by using a Bioanalytical Systems Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder. An X-band ESR spectrum of a frozen dichloromethane solution of Re_2Cl_4 (μ-dmpm)$_3$ was recorded at −160 °C with the use of a Varian E-109 spectrometer. No signal was observed in accord with the diamagnetic character of this complex. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances were referenced internally to the impurity in the deuterated solvent (δ 7.27 for $CDCl_3$).

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for the Orthorhombic Form (A) of $Re_2Cl_4(\mu\text{-dmpm})_3{}^a$

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.2205 (1)	0.39152 (4)	0.56579 (8)	2.29 (2)
Re(2)	0.1468 (1)	0.34946 (4)	0.44343 (8)	2.53 (3)
Cl(1)	0.3253 (8)	0.4264 (3)	0.7062 (6)	4.3 (3)
Cl(2)	0.1956 (9)	0.4720 (3)	0.5188 (6)	5.7 (4)
Cl(3)	0.0420 (9)	0.3143 (3)	0.3066 (6)	6.0 (4)
Cl(4)	0.2532 (8)	0.2978 (3)	0.3689 (6)	4.1 (3)
P(1)	0.3468 (9)	0.4022 (3)	0.4538 (6)	3.7 (3)
P(2)	0.2608 (9)	0.3221 (3)	0.6523 (6)	3.7 (3)
P(3)	0.1025 (9)	0.4081 (3)	0.6833 (7)	5.1 (4)
P(4)	0.1999 (9)	0.3965 (3)	0.2988 (6)	4.4 (4)
P(5)	0.1076 (9)	0.2819 (3)	0.5433 (6)	4.0 (4)
P(6)	0.019 (1)	0.3901 (3)	0.4788 (7)	5.2 (4)
C(1)	0.319 (3)	0.409 (1)	0.321 (2)	4.4 (8)*
C(2)	0.407 (3)	0.455 (1)	0.473 (3)	6 (1)*
C(3)	0.447 (4)	0.361 (1)	0.443 (3)	8 (1)*
C(4)	0.150 (3)	0.452 (1)	0.255 (2)	4.9 (8)*
C(5)	0.199 (3)	0.366 (1)	0.170 (2)	5.2 (9)*
C(6)	0.169 (3)	0.279 (1)	0.667 (2)	5.4 (9)*
C(7)	0.288 (3)	0.328 (1)	0.792 (2)	4.3 (8)*
C(8)	0.361 (4)	0.287 (1)	0.620 (3)	8 (1)*
C(9)	0.116 (3)	0.228 (1)	0.478 (2)	4.8 (9)*
C(10)	−0.006 (4)	0.269 (1)	0.596 (3)	7 (1)*
C(11)	−0.000 (4)	0.417 (2)	0.603 (4)	12 (2)*
C(12)	0.115 (3)	0.462 (1)	0.754 (3)	6 (1)*
C(13)	0.059 (3)	0.371 (1)	0.784 (3)	7 (1)*
C(14)	−0.090 (4)	0.358 (1)	0.477 (3)	7 (1)*
C(15)	−0.015 (4)	0.439 (1)	0.393 (3)	8 (1)*

[a] Starred values denote isotropically refined values. *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

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

Results and Discussion

(a) Synthesis of $Re_2Cl_4(\mu\text{-dmpm})_3$ and Its Spectroscopic and Electrochemical Properties. Two synthetic strategies afforded the title complex, namely, the reduction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ by dmpm in methanol and a ligand displacement reaction utilizing the prereduced complex $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ in an ethanol–toluene solvent. Crystallographic analyses (vide infra) confirmed that these products were structurally identical and that the tris complex with dmpm, rather than the expected bis product, had been formed. This had in fact been anticipated on the basis of microanalytical data and the spectroscopic and electrochemical properties of this complex. These characterization studies were carried out on the product that was prepared by using the synthetic procedure in which $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ was reacted with dmpm.

(b) Structural Results. The atomic positional parameters for forms A and B are listed in Tables II and III, respectively. The two molecular structures are nearly identical, and the numbering schemes in the two cases have been matched. Therefore, analogous bonds and angles have identical designations and can be listed in parallel columns, as in Tables IV and V.

While there are some statistically significant differences between bond lengths and angles for A and B there are none that would appear to be of any chemical significance. The two forms contain the same molecules packed differently, and packing forces evidently cause some real but chemically irrelevant differences. Because the structure was obtained more accurately for form B, discussion of the structure will be based on those results. Figures 1 and 2 show two views of the molecular structure.

The molecule has no crystallographically imposed symmetry, but comes close to having C_2 symmetry. Presumably the free molecule would display this symmetry fully. Each molecule is thus chiral, but in both crystal forms there are equal numbers of the two enantiomorphs. The twofold axis passes through the carbon atom C(1) and the midpoint of the Re–Re bond. Rotation about this axis interchanges the P(3)–C(11)–P(6) ligand and the

Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for the Monoclinic Form (B) of $Re_2Cl_4(\mu\text{-dmpm})_3$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re(1)	0.19863 (2)	0.05789 (3)	0.28994 (2)	2.411 (6)
Re(2)	0.28229 (2)	−0.06468 (3)	0.23472 (2)	2.388 (6)
Cl(1)	0.1295 (2)	0.1918 (2)	0.3858 (2)	4.60 (6)
Cl(2)	0.1016 (2)	0.1434 (2)	0.1599 (2)	4.54 (6)
Cl(3)	0.3493 (2)	−0.2040 (2)	0.1428 (2)	4.80 (6)
Cl(4)	0.4464 (2)	−0.0238 (2)	0.2949 (2)	4.61 (6)
P(1)	0.3000 (2)	0.1958 (2)	0.2631 (2)	3.88 (6)
P(2)	0.2772 (2)	0.0184 (2)	0.4407 (2)	3.61 (6)
P(3)	0.0561 (2)	−0.0339 (2)	0.2903 (2)	3.49 (5)
P(4)	0.3065 (2)	0.0454 (2)	0.1139 (2)	3.98 (6)
P(5)	0.3135 (2)	−0.1802 (2)	0.3613 (2)	3.69 (6)
P(6)	0.1418 (2)	−0.1474 (2)	0.1637 (2)	2.97 (5)
C(1)	0.321 (1)	0.1788 (9)	0.1497 (8)	6.8 (3)
C(2)	0.246 (1)	0.3223 (8)	0.2553 (9)	6.5 (4)
C(3)	0.4149 (9)	0.230 (1)	0.327 (1)	6.7 (4)
C(4)	0.223 (1)	0.055 (1)	0.0055 (7)	6.5 (3)
C(5)	0.4132 (9)	0.019 (1)	0.0750 (8)	6.3 (3)
C(6)	0.350 (1)	−0.095 (1)	0.4602 (9)	9.3 (4)
C(7)	0.2152 (9)	0.014 (1)	0.5306 (7)	5.8 (3)
C(8)	0.367 (1)	0.112 (1)	0.4977 (9)	7.7 (4)
C(9)	0.4196 (9)	−0.257 (1)	0.376 (1)	7.3 (4)
C(10)	0.237 (1)	−0.269 (1)	0.3953 (9)	8.1 (4)
C(11)	0.0576 (7)	−0.1555 (9)	0.2372 (7)	4.5 (2)
C(12)	−0.0490 (7)	0.026 (1)	0.2253 (9)	5.7 (3)
C(13)	0.0134 (9)	−0.069 (1)	0.3902 (8)	7.2 (4)
C(14)	0.1475 (8)	−0.2823 (8)	0.1343 (8)	4.7 (3)
C(15)	0.0705 (9)	−0.104 (1)	0.0597 (8)	5.6 (3)

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

P(2)–C(6)–P(5) ligand, as can be most easily seen in Figure 2, where the axis runs vertically.

This structure has several curious features. One is that there are bridging dmpm ligands with helicities of both senses within the same molecule. For example, in the molecule depicted in Figures 1 and 2, the P(1)–C(1)–P(4) ligand has a negative (counterclockwise) helicity while the other two dmpm ligands have positive helicities. This means that the two enantiomorphic forms of the molecule cannot be interconverted by a simple internal twisting about the Re–Re bond, as is the case, for example, with molecules of the β-$M_2X_4(dppe)_2$ type or $Re_2Cl_4(dppm)_2$. Thus, it might be possible to separate the enantiomorphs, perhaps by their different solubilities in a chiral solvent, and measure their chiroptical properties.

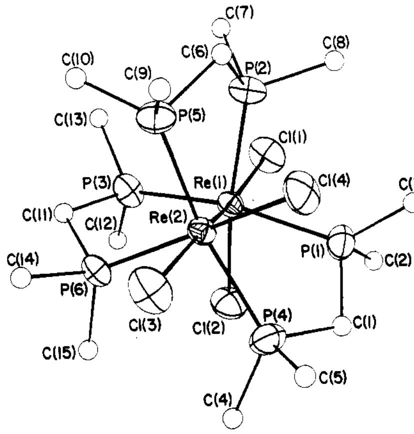

Figure 1. ORTEP drawing of $Re_2Cl_4(\mu\text{-dmpm})_3$, showing the structure and atom-labeling scheme. Parameters for this plot were taken from the monoclinic structure (B). The structure of A is almost identical. Carbon atoms are represented as circles of arbitrary radius. Other atoms are given as their 35% probability ellipsoids.

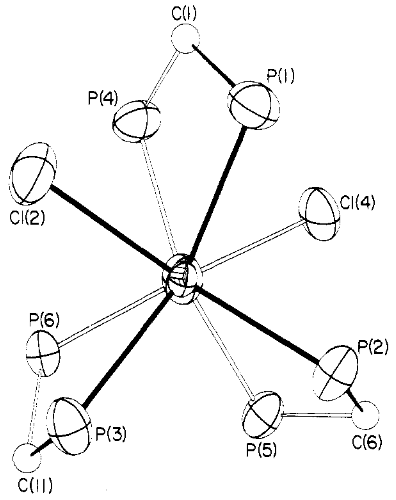

Figure 2. View of the core of the $Re_2Cl_4(\mu\text{-dmpm})_3$ molecule along the Re–Re vector, showing the conformations of the three bridging ligands. The sizes and shapes of the atoms do not represent crystallographic displacement parameters.

The compound contains a triple bond of the $\sigma^2\pi^4\delta^2\delta^{*2}$ (d^5–d^5) type between the rhenium atoms, and the bond length, 2.3157 (4) Å, is consistent with this. This bond is longer than the triple bonds in other Re_2^{4+} species (which are typically about 2.24 Å) but this may be attributed to the presence of the two axial Re–Cl bonds, whereas species such as $Re_2Cl_4(PEt_3)_4$ and $Re_2Cl_4(dppm)_2$ have no axial ligands. The two axial Re–Cl bonds, whose average length is 2.650 ± 0.002 Å, are, as expected, much longer than the equatorial Re–Cl bonds, which have an average length of 2.461 ± 0.004 Å. Nevertheless, they are short enough, and hence strong

Table IV. Bond Distances (Å) and Their Estimated Standard Deviations for the Orthorhombic (A) and Monoclinic (B) Forms of $Re_2Cl_4(\mu\text{-dmpm})_3$[a]

		dist				dist	
atom 1	atom 2	A	B	atom 1	atom 2	A	B
Re(1)	Re(2)	2.309 (2)	2.3157 (4)	P(2)	C(7)	1.87 (3)	1.83 (1)
Re(1)	Cl(1)	2.641 (9)	2.652 (2)	P(2)	C(8)	1.90 (5)	1.88 (1)
Re(1)	Cl(2)	2.461 (8)	2.457 (2)	P(3)	C(11)	1.91 (6)	1.803 (9)
Re(1)	P(1)	2.45 (1)	2.457 (2)	P(3)	C(12)	1.83 (4)	1.83 (1)
Re(1)	P(2)	2.403 (8)	2.402 (2)	P(3)	C(13)	1.82 (4)	1.85 (1)
Re(1)	P(3)	2.43 (1)	2.442 (2)	P(4)	C(1)	1.90 (5)	1.84 (1)
Re(2)	Cl(3)	2.61 (1)	2.647 (2)	P(4)	C(4)	1.89 (4)	1.84 (1)
Re(2)	Cl(4)	2.43 (1)	2.465 (2)	P(4)	C(5)	1.89 (3)	1.85 (1)
Re(2)	P(4)	2.468 (9)	2.446 (2)	P(5)	C(6)	1.87 (4)	1.87 (1)
Re(2)	P(5)	2.440 (8)	2.430 (2)	P(5)	C(9)	1.78 (3)	1.84 (1)
Re(2)	P(6)	2.35 (1)	2.390 (2)	P(5)	C(10)	1.91 (6)	1.79 (1)
P(1)	C(1)	1.79 (3)	1.85 (1)	P(6)	C(11)	1.82 (6)	1.869 (9)
P(1)	C(2)	1.82 (4)	1.85 (1)	P(6)	C(14)	1.92 (6)	1.844 (9)
P(1)	C(3)	1.97 (5)	1.82 (1)	P(6)	C(15)	1.88 (4)	1.80 (1)
P(2)	C(6)	1.90 (5)	1.83 (1)				

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

Table V. Bond Angles (deg) and Their Estimated Standard Deviations for the Orthorhombic (A) and Monoclinic (B) Forms of $Re_2Cl_4(\mu\text{-dmpm})_3$[a]

			angle					angle	
atom 1	atom 2	atom 3	A	B	atom 1	atom 2	atom 3	A	B
Re(2)	Re(1)	Cl(1)	169.1 (2)	167.63 (6)	Cl(4)	Re(2)	P(5)	82.9 (4)	81.06 (9)
Re(2)	Re(1)	Cl(2)	105.2 (3)	106.80 (6)	Cl(4)	Re(2)	P(6)	163.5 (4)	163.64 (8)
Re(2)	Re(1)	P(1)	92.9 (2)	93.19 (6)	P(4)	Re(2)	P(5)	159.8 (3)	160.84 (9)
Re(2)	Re(1)	P(2)	89.9 (2)	90.94 (6)	P(4)	Re(2)	P(6)	98.4 (4)	100.90 (9)
Re(2)	Re(1)	P(3)	99.7 (3)	101.09 (5)	P(5)	Re(2)	P(6)	95.6 (4)	93.83 (8)
Cl(1)	Re(1)	Cl(2)	84.1 (3)	85.10 (8)	Re(1)	P(1)	C(1)	114 (2)	107.9 (4)
Cl(1)	Re(1)	P(1)	82.8 (4)	85.90 (8)	Re(1)	P(1)	C(2)	116 (1)	114.0 (4)
Cl(1)	Re(1)	P(2)	81.1 (3)	77.01 (8)	Re(1)	P(1)	C(3)	126 (1)	129.1 (4)
Cl(1)	Re(1)	P(3)	87.0 (4)	83.35 (8)	C(1)	P(1)	C(2)	99 (2)	102.2 (6)
Cl(2)	Re(1)	P(1)	81.7 (4)	78.06 (9)	C(1)	P(1)	C(3)	101 (2)	101.3 (6)
Cl(2)	Re(1)	P(2)	164.7 (3)	161.94 (8)	C(2)	P(1)	C(3)	98 (2)	98.8 (6)
Cl(2)	Re(1)	P(3)	81.2 (4)	83.10 (9)	Re(1)	P(2)	C(6)	114 (1)	118.4 (4)
P(1)	Re(1)	P(2)	100.3 (4)	98.00 (9)	Re(1)	P(2)	C(7)	116 (1)	121.1 (4)
P(1)	Re(1)	P(3)	160.9 (3)	159.02 (9)	Re(1)	P(2)	C(8)	124 (1)	116.4 (4)
P(2)	Re(1)	P(3)	94.0 (4)	97.06 (9)	C(6)	P(2)	C(7)	97 (2)	103.4 (6)
Re(1)	Re(2)	Cl(3)	169.2 (3)	168.30 (6)	C(6)	P(2)	C(8)	106 (2)	97.5 (7)
Re(1)	Re(2)	Cl(4)	105.8 (3)	106.15 (6)	C(7)	P(2)	C(8)	94 (2)	95.5 (6)
Re(1)	Re(2)	P(4)	93.6 (3)	92.62 (6)	Re(1)	P(3)	C(11)	108 (2)	110.0 (3)
Re(1)	Re(2)	P(5)	100.8 (2)	99.63 (6)	Re(1)	P(3)	C(12)	114 (2)	114.8 (4)
Re(1)	Re(2)	P(6)	90.6 (3)	89.99 (5)	Re(1)	P(3)	C(13)	128 (1)	126.0 (4)
Cl(3)	Re(2)	Cl(4)	84.4 (4)	83.77 (8)	C(11)	P(3)	C(12)	104 (2)	103.5 (5)
Cl(3)	Re(2)	P(4)	84.7 (4)	82.59 (9)	C(11)	P(3)	C(13)	99 (2)	101.3 (5)
Cl(3)	Re(2)	P(5)	83.7 (3)	87.87 (8)	C(12)	P(3)	C(13)	101 (2)	98.5 (6)
Cl(3)	Re(2)	P(6)	79.1 (4)	80.51 (8)	Re(2)	P(4)	C(1)	109 (1)	111.6 (3)
Cl(4)	Re(2)	P(4)	79.6 (3)	81.41 (9)	Re(2)	P(4)	C(4)	125 (1)	122.7 (4)
Re(2)	P(4)	C(5)	114 (1)	114.7 (4)	Re(2)	P(6)	C(11)	122 (2)	112.8 (3)
C(1)	P(4)	C(4)	105 (2)	102.3 (6)	Re(2)	P(6)	C(14)	119 (1)	118.0 (4)
C(1)	P(4)	C(5)	103 (2)	102.9 (6)	Re(2)	P(6)	C(15)	120 (2)	122.7 (4)
C(4)	P(4)	C(5)	98 (1)	100.1 (6)	C(11)	P(6)	C(14)	95 (3)	99.6 (5)
Re(2)	P(5)	C(6)	112 (1)	103.9 (4)	C(11)	P(6)	C(15)	99 (2)	102.3 (5)
Re(2)	P(5)	C(9)	116 (1)	116.5 (4)	C(14)	P(6)	C(15)	97 (2)	98.0 (5)
Re(2)	P(5)	C(10)	125 (1)	128.7 (4)	P(1)	C(1)	P(4)	110 (2)	111.4 (5)
C(6)	P(5)	C(9)	109 (2)	98.6 (7)	P(2)	C(6)	P(5)	105 (2)	107.9 (7)
C(6)	P(5)	C(10)	99 (2)	104.0 (8)	P(3)	C(11)	P(6)	107 (3)	107.5 (5)
C(9)	P(5)	C(10)	94 (2)	100.6 (6)					

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

enough, to cause a significant lengthening of the Re–Re bond.

The Re–P bonds are of three different types under C_2 symmetry but can also be classified into only two types according to whether they are trans to another Re–P bond or trans to a Re–Cl bond. There are four of the former with a mean length of 2.444 [6] Å and two of the latter with a mean length of 2.396 [5] Å. The difference is statistically significant, 0.048 [8] Å, and may be attributed to the greater structural trans effect of the phosphine ligands.

(c) General Characterization. This red crystalline, diamagnetic complex is soluble in solvents such as $CHCl_3$, CH_2Cl_2, and acetonitrile; it forms a nonconducting solution in the latter solvent. Its Nujol mull IR spectrum (4000–600 cm^{-1}) shows bands that can be attributed only to the presence of coordinated dmpm, thereby ruling out its formulation as the mixed-ligand complex $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_2$ (dmpm).[14]

The electrochemical properties of $Re_2Cl_4(\mu\text{-dmpm})_3$ show the existence of two redox processes, each of which corresponds to an oxidation, as is found for $Re_2X_4(LL)_2$ complexes (LL represents a bridging phosphine ligand) that possess a staggered rotational geometry.[5,15,16] Its cyclic voltammogram (measured in 0.1 M TBAH–CH_2Cl_2) displays a one-electron couple at $E_{1/2}$ = +0.53 V and an irreversible process at $E_{p,a}$ = +1.30 V vs. Ag/AgCl (Figure 3). However, both couples are ca. +0.3 V more positive than those that characterize $Re_2Cl_4(LL)_2$, where LL = $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, or $Et_2PCH_2CH_2PEt_2$.[5,15,16] Some differences are seen between the electronic absorption spectrum of $Re_2Cl_4(\mu\text{-dmpm})_3$ (λ_{max} at 488 nm (ϵ ~150) in CH_2Cl_2)[17] and the related spectra of $Re_2Cl_4(dppm)_2$,[5] β-$Re_2Cl_4(dppe)_2$,[18] and β-$Re_2Cl_4(depe)_2$[16] (depe = $Et_2PCH_2CH_2PEt_2$), all of which exhibit two or three bands in the region 700–400 nm.

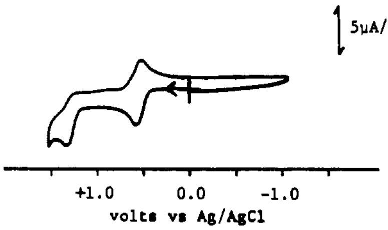

Figure 3. Cyclic voltammogram of $Re_2Cl_4(\mu\text{-dmpm})_3$ in 0.1 M TBAH–CH_2Cl_2.

The NMR spectra are consistent with the molecular structure found in the crystal. The $^{31}P\{^1H\}$ spectrum in $CDCl_3$ solution exhibits two broad structureless resonances in a 2:1 intensity ratio at δ values of −21.56 and −36.92. On pure symmetry considerations, as already noted, there are three sets of phosphorus atoms, but chemically they may be classified as those trans to other P atoms (four) and those trans to Cl atoms (two). Presumably, the ^{31}P NMR spectrum reflects this latter classification. It is not certain why both of these resonances are broad and featureless. Possibly the molecule engages in some slow dynamical process that wipes out fine structure which might otherwise be expected.

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(14) Complexes of the type $Re_2Cl_4(PR_3)_2(LL)$ (LL = $Ph_2PCH_2PPh_2$ or $Ph_2PNHPPh_2$) constitute a well-characterized group of compounds that can be prepared by the reaction of $Re_2Cl_4(PR_3)_4$ with LL; see: Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Chem. Soc.* **1986**, *108*, 953.

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The ^1H spectrum ($CDCl_3$, room temperature) is rather complex and displays six broad singlets at δ 2.36, 2.21, 2.07, 1.92, 1.59, and 1.55 (of approximately equal intensity) in accord with the six pairs of inequivalent methyl groups that are seen to be present in the molecular structure. The absence of splitting by the ^{31}P nuclei is a phenomenon for which there are several precedents, though no simple explanation. In $Mo_2Cl_4(dmpm)_2$[19] the CH_3 resonances appear as singlets, and a similar observation has been made for $Mn_2(CO)_6(dmpm)_2$.[20] Other examples of small or nondetectable ^{31}P–^1H coupling of this sort will be found in other reports.[21,22] The methylene ^1H resonances are seen as an AB pattern centered at δ 4.40 (J_{AB} = 13.4 Hz) and a broad peak at δ 3.95, in an intensity ratio of 2:1. The absence of an AB pattern in the second resonance may be due to a slow motion of the unique methylene group from side to side. Unfortunately, the solubility of this compound is too low to permit low-temperature NMR studies.

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Registry No. $Re_2Cl_4(\mu\text{-dmpm})_3$, 103852-11-5; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$, 52359-07-6.

Supplementary Material Available: Tables of torsion angles and anisotropic displacement parameters for both structures and figures showing contoured Fourier sections from both structures (10 pages); tables of observed and calculated structure factors for both structures (35 pages). Ordering information is given on any current masthead page.

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Quadruply Bonded $Mo_2I_4(dppe)_2$ (dppe = Bis(diphenylphosphino)ethane): Twisted and Eclipsed Rotational Conformations and Their Significance

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The structural characterizations of two crystallographic forms of β-$Mo_2I_4(dppe)_2$ are reported, and the relationship between the degree of torsional twist that the molecules exhibit in the solid state and the energy of the $\delta \rightarrow \delta^*$ transition is discussed. The title compound can be prepared by reaction of the quadruply bonded $Mo_2(\mu\text{-}O_2CCH_3)_4$ with Me_3SiI in toluene in the presence of 2 equiv of dppe and can be crystallized from many solvents. A solution of the compound in dichloromethane–methanol produces green monoclinic crystals of the dichloromethane solvate β-$Mo_2I_4(dppe)_2\cdot{}^2/_3CH_2Cl_2$ (**1**), in which there are twisted molecules, **1a**, located on a general position, and eclipsed molecules, **1b**, which reside on crystallographic inversion centers. The crystal belongs to the space group $P2_1/n$ with unit cell dimensions a = 13.600 (4) Å, b = 17.755 (5) Å, c = 30.30 (1) Å, β = 98.74 (2)°, V = 8426 (4) Å^3, and Z = 6. The asymmetric unit is defined by 1.5 molecular formulas of $Mo_2I_4(dppe)_2$ and one CH_2Cl_2 molecule. The structure is unusual in that **1a** possesses a mean torsional twist angle of χ = 27.9° and **1b** assumes the fully eclipsed orientation with an average χ = 0°, where χ is the angle of internal rotation away from the eclipsed conformation. A significant difference exists in the degree of Mo–Mo interaction for **1a** and **1b** as is evident from the Mo–Mo bond distances of 2.180 (4) and 2.129 (5) Å for the cocrystallized molecules **1a** and **1b**, respectively. A second crystal of $Mo_2I_4(dppe)_2$ was grown from a dichloromethane–toluene mixture and is designated as β'-$Mo_2I_4(dppe)_2\cdot C_7H_8$ (**2**). The β' form crystallizes in the monoclinic $P2_1/n$ space group with the following unit cell dimensions: a = 12.015 (2) Å, b = 25.048 (4) Å, c = 19.407 (4) Å, β = 95.3 (2)°, V = 5814 (2) Å^3, and Z = 4. The midpoints of the Mo–Mo bonds reside on a set of general positions. The molecule is internally rotated by an average value of χ = 25.7°, and the Mo–Mo distance is 2.179 (3) Å. The variation in δ overlap in the three different types of molecules **1a**, **1b**, and **2** was effectively probed by recording the visible spectra of the samples in the solid state. Two distinct bands are observed at 670 nm (14 900 cm^{-1}) and at 920 nm (10 900 cm^{-1}) in the spectrum of β-$Mo_2I_4(dppe)_2\cdot{}^2/_3CH_2Cl_2$ and are assigned to the $\delta \rightarrow \delta^*$ ($A_{1g} \rightarrow A_{1u}$) transitions of molecules **1b** (χ = 0°) and **1a** (χ = 27.9°), respectively; the intensity ratio is in approximate accord with the ratio of the δ/δ overlap integrals. The solid-state visible spectrum of β'-$Mo_2I_4(dppe)_2\cdot C_7H_8$ contains only one band at λ_{max} = 878 nm (11 400 cm^{-1}), in agreement with the results of the X-ray structure, which shows that only one type of molecule is present. Dichloromethane solution spectra of both β and β' forms are identical, with the $\delta \rightarrow \delta^*$ transition being located at 860 nm (11 600 cm^{-1}). The electronic absorption properties of **1** and **2** as well as the results of $^{31}P\{^1H\}$ NMR spectroscopy and cyclic voltammetry studies are discussed.

Introduction

Compounds of the type $Mo_2X_4(LL)_2$, where X = Cl or Br and LL is a bridging bidentate phosphine $R_2P(CH_2)_nPR_2$, have been interesting subjects for structural and spectroscopic studies.[1-7] X-ray crystallographic data for those with n = 1, i.e., the bis(diphenylphosphino)methane complexes, $Mo_2X_4(dppm)_2$ (X = Cl[8], Br[4], I[9]), have shown that the ligands adopt a fully eclipsed orientation across the two metal centers, with the dppm ligands in a trans bridging disposition. In the case of n = 2, as in $Mo_2X_4(dmpe)_2$ or $Mo_2X_4(dppe)_2$ (X = Cl, Br; dmpe = bis(dimethylphosphino)ethane, dppe = bis(diphenylphosphino)ethane), the molecules exhibit various degrees of torsional twist about the Mo–Mo axis, resulting from the conformational preference of the fused, six-membered rings that are present in these β-$Mo_2X_4(LL)_2$ molecules.

It can be shown from the angular parts of the orbital wave functions that the strength of the δ component of a quadruple bond should vary with cos (2χ), where χ is the angle of internal rotation away from the eclipsed conformation (χ = 0°).[10] Extensive studies conducted in this group, based upon data from 10 related, structurally characterized compounds, have shown that the Mo–Mo distance in the $Mo_2X_4(LL)_2$ class of molecules varies linearly with cos (2χ).[4,7] An analysis of the variation in $\delta \rightarrow \delta^*$ transition energy with δ-bond strength (measured by Mo–Mo bond length)

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