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Two Reactions of $[Re_2Cl_8]^{2-}$ with Diphosphines that lead to Re–Re Bond Cleavage

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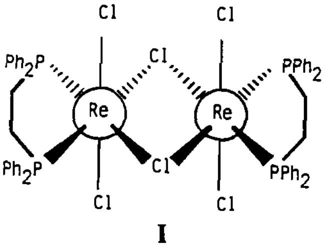
Abstract

Reactions of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with the diphosphines $Et_2PCH_2CH_2PEt_2$ (depe) and $(p\text{-}MeC_6H_4)_2PCH_2CH_2P(p\text{-}C_6H_4Me)_2$ (dtpe) were carried out under mild conditions with the hope of obtaining $Re_2Cl_6(diphos)_2$ type products. On the contrary, in both cases the only isolated products contained mononuclear Re^{III} cations of the type $[trans\text{-}ReCl_2(diphos)_2]^+$. The following two compounds and their crystallographic characterizations are described: **1**: $[ReCl_2(dtpe)_2]Cl\cdot 3CH_2Cl_2$, yellow, space group $P\bar{1}$, $a = 17.326(2)$, $b = 18.002(2)$, $c = 11.1931(9)$ Å, $\alpha = 102.861(7)$, $\beta = 105.345(7)$, $\gamma = 81.111(8)^\circ$, $Z = 2$. **2**: $[ReCl_2(depe)_2]_2[Re_2Cl_8]$, olive green, space group *Pbca*, $a = 23.069(3)$, $b = 24.036(3)$, $c = 14.818(2)$ Å, $Z = 4$. The cations in each case have *trans* structures and bond lengths within the expected ranges. The $[Re_2Cl_8]^{2-}$ ion has the expected structure and shows the typical form of disorder, with 74% major and 26% minor orientations of the Re_2 unit.

Introduction

In 1975 Walton and coworkers [1] reported that the reaction of $[Re_2Cl_8]^{2-}$ with dppe, $Ph_2PCH_2CH_2PPh_2$, afforded a product with structure **I** in which



I

the Re–Re distance was very long (3.81 Å). This, coupled with the fact that the compound is paramagnetic, led them to conclude that no Re–Re bond exists in this molecule. This behavior was, and continues to be, considered surprising when compared with that of numerous other edge-sharing bioctahedral complexes [2], including some with exactly the same constitution and structure [3, 4] wherein M–M bonds are clearly present according to magnetic and structural evidence. It has occasioned several critical discussions [2, 5].

The motivation for the work reported here was to see if this seemingly anomalous character would be general for all $Re_2Cl_6(diphos)_2$ compounds, where diphos is used as a generic abbreviation for all ligands of the type $R_2PCH_2CH_2PR_2$, or whether the Walton compound is (for some unidentified reason) exceptional. We therefore chose two other ligands of the same class, namely $(p\text{-}CH_3C_6H_4)_2PCH_2CH_2P(p\text{-}CH_3C_6H_4)_2$ (dtpe) and $(C_2H_5)_2PCH_2CH_2P(C_2H_5)_2$ (depe) and caused them to react with $(n\text{-}Bu_4N)_2Re_2Cl_8$ under mild conditions, with the hope that $Re_2Cl_6(diphos)_2$ products could be isolated and characterized.

Experimental

Reactions

Reaction of dtpe

To a solution of 0.10 g (0.088 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$ in 15 ml of CH_2Cl_2 was added a solution of 0.10 g (0.219 mmol) of 1,2-bis(di-*p*-tolyl)phosphinoethane in 10 ml of acetone (under Ar). Upon gentle mixing, the originally aqua-blue solution became yellow–green. The solution was placed in a Schlenk tube under Ar, and layered with 20 ml of hexane. After one week, yellow crystals of compound **1** appeared on the walls of the tube.

Reaction of depe

To a solution of 0.10 g (0.088 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$ in 20 ml of CH_2Cl_2 were added 40 mg (0.19 mmol) of 1,2-bis(diethylphosphino)ethane under Ar. The solution was stirred at room temperature for 1 h, during which time the color changed from aqua-blue to olive green. The CH_2Cl_2 solution

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TABLE I. Crystallographic Data for $[ReCl_2(dtpe)_2]Cl \cdot 3CH_2Cl_2$ and $[ReCl_2(depe)_2]_2[Re_2Cl_8] \cdot 4CH_2Cl_2$

Formula	$ReCl_9P_4C_{63}H_{70}$	$Re_4Cl_{20}P_8C_{44}H_{104}$
Formula weight	1456.43	2335.0
Space group	$P\bar{1}$	$Pbca$, No. 61
a (Å)	17.326(2)	23.069(3)
b (Å)	18.002(2)	24.036(3)
c (Å)	11.1931(9)	14.818(2)
α (°)	102.861(7)	
β (°)	105.345(7)	
γ (°)	81.111(8)	
V (Å^3)	3265(1)	8216(3) 5691(5)
Z	2	4
D_{calc} (g/cm^3)	1.481	1.887
Crystal size (mm)	0.1 × 0.1 × 0.4	0.2 × 0.2 × 0.4
μ(Mo Kα) (cm^{-1})	23.909	68.0
Data collection instrument	Rigaku AFC5	CAD-4S
Radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
Orientation reflections, number, range (2θ)	25, 20–30°	25, 20° < 2θ < 32°
Temperature (°C)	19	19
Scan method	ω–2θ	ω–2θ
Data collection range, 2θ (°)	3–50	0–45
No. unique data, total	8137	5311
with $F_o^2 > 3\sigma(F_o^2)$		2800
Number of parameters refined	695	353
Transmission factors, max./min.	1.00/0.865	0.999/0.669
R [a]	0.0531	0.0422
R_w [b]	0.0746	0.0508
Quality-of-fit indicator [c]	1.452	1.308
Largest shift/e.s.d., final cycle	0.02	0.05
Largest peak (e/Å^3)	1.09	1.04

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

was transferred to a Schlenk tube and layered with 20 ml of dry, distilled hexane. Within one week, olive green crystals of compound **2** grew on the walls of the tube. Yield 0.072 g (41%).

X-ray Crystallography

Compound 1

Since crystals of the complex rapidly lost lattice solvent upon removal from the mother liquor, a slender crystal of approximate dimensions 0.1 × 0.1 × 0.4 mm was mounted in a glass capillary filled with the liquid. Crystal alignment and data collection procedures followed those previously described from this laboratory [6]. Important data collection parameters appear in Table I. The position of the Re atom was obtained by direct methods. All other non-hydrogen atoms, including three molecules of CH_2Cl_2, were located through alternate least-squares refinement cycles and difference Fourier maps. Full-matrix least-squares refinement of 695 parameters fit to 8137 data converged with discrepancy indices of $R = 0.0531$ and $R_w = 0.0746$.

Compound 2

A block-shaped crystal of dimensions 0.2 × 0.4 × 0.4 mm was mounted on a glass fiber and coated with a thin layer of epoxy cement. Determination of the crystallographic cell and data collection procedures were carried out in a manner typical for this laboratory, and have been described previously [6]. Important data collection parameters appear in Table I. Atomic positions of the two independent Re atoms were provided by direct methods. The remaining non-hydrogen atoms were located by alternate least-squares refinement and difference Fourier techniques. Following location of the major $[Re_2Cl_8]^{2-}$ unit, a peak appeared corresponding to a minor orientation of the Re_2 unit within the Cl_8 cage. Further least-squares cycles included refinement of the ratio of the two disordered Re sites. Disorder of the Re_2 unit within the $[Re_2Cl_8]^{2-}$ ion has been reported previously [7a]. Full-matrix refinement of all non-hydrogen atoms (including two lattice CH_2Cl_2 molecules) resulted in convergence of the discrepancy indices to $R = 0.0422$ and $R_w = 0.0508$, with the occupancies of the major and minor Re sites being 0.74 and 0.26, respectively.

Results

In each of the reactions, the isolated and characterized crystalline product was not the desired $Re_2Cl_6(diphos)_2$ type of molecule. Instead, in both reactions a $[\textit{trans}\text{-}ReCl_2(diphos)_2]^+$ cation was formed. The atomic positional parameters for compounds **1** and **2** are listed in Tables II and III, respectively. The details of each structure will now be discussed.

Compound 1

The $[ReCl_2(dtpe)_2]^+$ cation is shown in Fig. 1, and distances and angles are listed in Tables IV and V. No crystallographic symmetry is required, but the core group of atoms, $ReCl_2P_4$, has D_{2h} symmetry. It lacks D_{4h} symmetry because the P–Re–P angles differ appreciably depending on whether they are within the chelate rings or between them. The ReP_4 set of atoms is coplanar within experimental error and the Cl–Re–Cl chain is practically linear. The two Re–Cl distances are equal within the uncertainties at 2.310(3) Å. The four Re–P distances have a mean value of 2.489(4) Å.

A point of interest, because it is unusual, is the environment of the separate chloride ion, Cl(3), in this structure. As might be expected from its relatively large thermal displacement parameter, it is not closely constrained. Its nearest neighbors are six carbon atoms, or perhaps the H atoms attached thereto; since no H atoms were found, this remains uncertain. Three of these carbon atoms are those of the CH_2Cl_2 molecules, namely, C(100), C(200) and C(300), which are at distances of 3.57, 3.37 and 3.66 Å, respectively. The other three carbon atoms are C(35) and C(39), both *m*-carbon atoms on *p*-tolyl rings, which are at distances of 3.64 and 3.76 Å, respectively, and C(47), which is an *o*-carbon atom of a *p*-tolyl ring, at a distance of 3.93 Å. The disposition of these carbon atoms about Cl(3) is crudely describable as a very distorted octahedron.

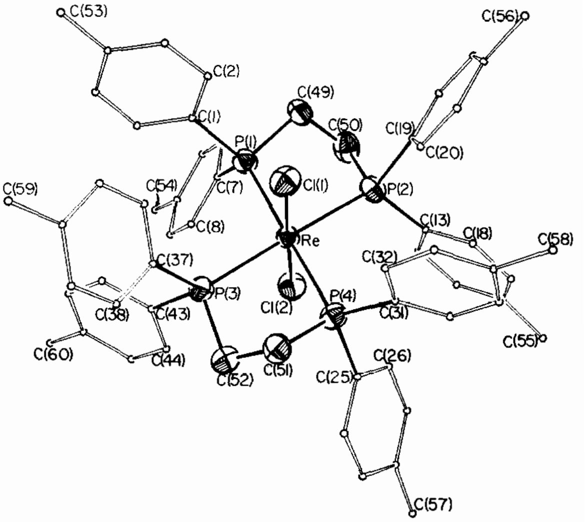

Fig. 1. An ORTEP drawing of the $[ReCl_2(dtpe)_2]^+$ ion in compound 1. The central atoms are represented by their thermal displacement ellipsoids drawn at the 40% level. All tolyl carbon atoms are drawn arbitrarily small for clarity.

TABLE II. Positional and Isotropic Equivalent Thermal Parameters for $[ReCl_2(dtpe)_2]Cl\cdot 3CH_2Cl_2$ [a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Re	0.21811(2)	0.25913(2)	0.45061(3)	2.411(8)
Cl(1)	0.1577(1)	0.2404(1)	0.6010(2)	3.73(6)
Cl(2)	0.2789(1)	0.2737(1)	0.2980(2)	3.58(6)
Cl(3)	0.7273(3)	0.3226(2)	0.9611(4)	8.6(1)
P(1)	0.3202(1)	0.1499(1)	0.4973(2)	2.96(5)
P(2)	0.1509(1)	0.1548(1)	0.2882(2)	2.94(5)
P(3)	0.2876(1)	0.3650(1)	0.6061(2)	2.81(5)
P(4)	0.1150(1)	0.3680(1)	0.4054(2)	2.91(5)
C(1)	0.3544(5)	0.1348(5)	0.6592(8)	3.3(2)
C(2)	0.3032(6)	0.1062(5)	0.7123(9)	4.0(3)
C(3)	0.3288(7)	0.0976(6)	0.8372(9)	4.5(3)
C(4)	0.4041(7)	0.1167(6)	0.912(1)	5.3(3)
C(5)	0.4548(7)	0.1443(6)	0.858(1)	4.9(3)
C(6)	0.4300(6)	0.1533(6)	0.7315(9)	4.3(3)
C(7)	0.4125(5)	0.1375(5)	0.4429(8)	3.3(2)
C(8)	0.4494(6)	0.2008(5)	0.445(1)	4.1(3)
C(9)	0.5215(6)	0.1929(6)	0.407(1)	4.5(3)
C(10)	0.5556(6)	0.1211(6)	0.3610(9)	4.2(3)
C(11)	0.5174(6)	0.0578(5)	0.358(1)	4.6(3)
C(12)	0.4482(6)	0.0646(5)	0.399(1)	4.3(3)
C(13)	0.1082(5)	0.1700(5)	0.1274(8)	3.2(2)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C(14)	0.1570(5)	0.1678(5)	0.0459(8)	3.7(2)
C(15)	0.1213(7)	0.1875(6)	−0.0722(9)	4.5(3)
C(16)	0.0380(6)	0.2090(6)	−0.1119(9)	4.5(3)
C(17)	−0.0070(6)	0.2109(7)	−0.027(1)	4.9(3)
C(18)	0.0261(6)	0.1906(6)	0.0904(9)	4.2(3)
C(19)	0.0728(5)	0.1088(5)	0.3179(8)	3.3(2)
C(20)	0.0183(6)	0.1515(6)	0.3856(9)	4.0(3)
C(21)	−0.0450(6)	0.1184(6)	0.400(1)	4.6(3)
C(22)	−0.0540(6)	0.0410(7)	0.349(1)	5.1(3)
C(23)	0.0011(8)	−0.0023(7)	0.282(1)	6.5(4)
C(24)	0.0633(7)	0.0325(6)	0.268(1)	5.9(4)
C(25)	0.1149(5)	0.4124(5)	0.2737(8)	3.4(2)
C(26)	0.1169(6)	0.3670(5)	0.1568(8)	3.9(2)
C(27)	0.1144(6)	0.4006(6)	0.052(1)	4.7(3)
C(28)	0.1104(6)	0.4802(7)	0.068(1)	5.0(3)
C(29)	0.1110(8)	0.5245(7)	0.185(1)	6.4(4)
C(30)	0.1115(8)	0.4922(6)	0.288(1)	5.4(3)
C(31)	0.0087(5)	0.3573(5)	0.3895(8)	3.4(2)
C(32)	−0.0158(6)	0.3497(5)	0.4954(9)	3.8(2)
C(33)	−0.0941(6)	0.3352(6)	0.484(1)	4.8(3)
C(34)	−0.1488(6)	0.3315(6)	0.362(1)	5.2(3)
C(35)	−0.1237(6)	0.3401(7)	0.261(1)	5.0(3)
C(36)	−0.0448(6)	0.3527(6)	0.275(1)	4.3(3)
C(37)	0.2936(5)	0.3784(5)	0.7735(7)	2.9(2)
C(38)	0.3032(6)	0.4506(5)	0.8475(8)	4.0(3)
C(39)	0.3160(7)	0.4631(6)	0.9787(9)	4.6(3)
C(40)	0.3221(6)	0.4010(6)	1.0364(9)	4.1(3)
C(41)	0.3127(6)	0.3292(6)	0.9662(9)	4.3(3)
C(42)	0.2995(6)	0.3166(5)	0.8346(8)	4.1(3)
C(43)	0.3898(5)	0.3774(4)	0.6075(7)	2.9(2)
C(44)	0.4057(6)	0.4020(5)	0.5053(9)	3.9(3)
C(45)	0.4848(7)	0.4069(6)	0.506(1)	4.6(3)
C(46)	0.5495(7)	0.3867(6)	0.601(1)	5.1(3)
C(47)	0.5326(6)	0.3627(6)	0.700(1)	4.5(3)
C(48)	0.4537(5)	0.3583(6)	0.7048(9)	3.9(2)
C(49)	0.2711(5)	0.0631(5)	0.4117(9)	3.5(2)
C(50)	0.2311(6)	0.0767(5)	0.2760(9)	3.8(2)
C(51)	0.1390(5)	0.4449(5)	0.5438(8)	3.4(2)
C(52)	0.2303(6)	0.4540(5)	0.5643(9)	4.1(3)
C(53)	0.4296(9)	0.1067(9)	1.049(1)	8.0(5)
C(54)	0.6347(7)	0.1107(7)	0.321(1)	5.8(4)
C(55)	0.0009(8)	0.2334(8)	−0.237(1)	6.8(4)
C(56)	−0.1230(8)	0.0025(8)	0.367(1)	7.1(4)
C(57)	0.1094(7)	0.5213(8)	−0.041(1)	6.8(4)
C(58)	−0.2377(7)	0.315(1)	0.345(2)	8.4(5)
C(59)	0.3404(8)	0.4135(7)	1.1810(9)	6.0(4)
C(60)	0.6350(7)	0.3897(7)	0.593(2)	7.6(5)
C(100)	0.548(1)	0.362(1)	0.073(2)	11.5(8)
Cl(4)	0.5466(4)	0.2845(3)	0.1528(7)	14.2(3)
Cl(5)	0.5528(4)	0.4419(3)	0.1890(8)	16.1(3)
C(200)	0.292(1)	0.803(1)	0.316(2)	14(1)
Cl(6)	0.3528(4)	0.8633(4)	0.2856(7)	14.8(3)
Cl(7)	0.2071(4)	0.8560(5)	0.3477(8)	18.1(3)
C(300)	0.239(2)	0.858(1)	−0.074(3)	18(1)
Cl(8)	0.3128(5)	0.9292(5)	0.003(1)	19.5(4)
Cl(9)	0.1538(5)	0.9092(6)	−0.0297(8)	20.5(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

TABLE III. Positional and Isotropic Equivalent Thermal Parameters for $[ReCl_2(depe)_2]_2[Re_2Cl_8]\cdot 4CH_2Cl_2$ [a]

Atom	x	y	z	B (Å^2)
Re(1)	0.20131(3)	0.29906(3)	0.57524(4)	4.29(2)
Cl(1)	0.2351(2)	0.2899(2)	0.7232(3)	6.3(1)
Cl(2)	0.1666(2)	0.3091(2)	0.4282(3)	6.1(1)
P(1)	0.2086(2)	0.1977(2)	0.5563(3)	5.9(1)
P(2)	0.3010(2)	0.2945(2)	0.5190(4)	6.5(1)
P(3)	0.1922(2)	0.3997(2)	0.5962(3)	6.4(1)
P(4)	0.1010(2)	0.3020(2)	0.6281(3)	5.7(1)
C(1)	0.2807(9)	0.181(1)	0.518(3)	14(1)
C(2)	0.322(1)	0.221(1)	0.520(3)	15(1)
C(3)	0.120(1)	0.413(1)	0.638(3)	20(2)
C(4)	0.080(1)	0.375(1)	0.636(2)	13(1)
C(5)	0.179(1)	0.1070(8)	0.441(1)	9.0(7)
C(6)	0.1637(9)	0.1669(8)	0.466(1)	7.2(6)
C(7)	0.177(2)	0.155(1)	0.666(2)	14(1)
C(8)	0.214(2)	0.124(2)	0.680(3)	20(2)
C(9)	0.3105(9)	0.3160(9)	0.401(1)	7.6(6)
C(10)	0.368(1)	0.299(1)	0.356(1)	9.9(8)
C(11)	0.360(1)	0.337(2)	0.578(2)	13(1)
C(12)	0.385(2)	0.317(2)	0.643(2)	18(2)
C(13)	0.239(1)	0.432(1)	0.682(1)	10.9(8)
C(14)	0.214(2)	0.487(1)	0.718(2)	19(2)
C(15)	0.190(2)	0.446(1)	0.500(2)	15(1)
C(16)	0.238(1)	0.461(2)	0.466(3)	17(2)
C(17)	0.0888(9)	0.273(1)	0.742(1)	11.8(9)
C(18)	0.031(1)	0.282(1)	0.783(2)	11.3(9)
C(19)	0.0479(9)	0.271(1)	0.551(2)	12(1)
C(20)	−0.007(1)	0.292(1)	0.542(2)	15(1)
Re(2)	0.02799(4)	0.53391(4)	0.02557(6)	4.61(2)
Re(2')	0.0396(1)	0.4758(1)	−0.0155(2)	4.69(8)
Cl(3)	0.1004(2)	0.5400(2)	−0.0833(3)	6.8(1)
Cl(4)	0.0952(2)	0.4884(2)	0.1149(3)	7.1(1)
Cl(5)	−0.0135(2)	0.6132(2)	−0.0382(4)	7.4(1)
Cl(6)	−0.0191(2)	0.5592(2)	0.1593(3)	7.0(1)
C(100)	−0.022(1)	0.414(1)	0.270(2)	12(1)
Cl(7)	0.0423(5)	0.3839(4)	0.3213(6)	16.0(4)
Cl(8)	−0.0800(5)	0.4033(5)	0.3406(6)	17.2(4)
C(200)	0.091(1)	0.543(1)	0.333(1)	12(1)
Cl(9)	0.0479(4)	0.5323(5)	0.4248(6)	16.5(4)
Cl(10)	0.1391(5)	0.5945(6)	0.3568(8)	21.3(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

TABLE IV. Selected Bond Distances (Å) for $[ReCl_2(dtpe)_2]Cl\cdot 3CH_2Cl_2$

Atom 1	Atom 2	Distance
Re	Cl(1)	2.310(3)
Re	Cl(2)	2.309(3)
Re	P(1)	2.482(2)
Re	P(2)	2.495(2)
Re	P(3)	2.496(2)
Re	P(4)	2.484(2)
P(1)	C(1)	1.819(9)
P(1)	C(7)	1.82(1)
P(1)	C(49)	1.843(9)
P(2)	C(13)	1.820(9)
P(2)	C(19)	1.83(1)
P(2)	C(50)	1.826(9)
P(3)	C(37)	1.812(8)
P(3)	C(43)	1.813(9)
P(3)	C(52)	1.836(9)
P(4)	C(25)	1.83(1)
P(4)	C(31)	1.84(1)
P(4)	C(51)	1.837(8)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE V. Selected Bond Angles (°) for $[ReCl_2(dtpe)_2]Cl \cdot 3CH_2Cl_2$

Atom 1	Atom 2	Atom 3	Angle
Cl(1)	Re	Cl(2)	178.16(8)
Cl(1)	Re	P(1)	89.49(8)
Cl(1)	Re	P(2)	92.59(8)
Cl(1)	Re	P(3)	89.84(8)
Cl(1)	Re	P(4)	89.82(8)
Cl(2)	Re	P(1)	89.19(8)
Cl(2)	Re	P(2)	85.93(8)
Cl(2)	Re	P(3)	91.64(8)
Cl(2)	Re	P(4)	91.49(8)
P(1)	Re	P(2)	81.08(7)
P(1)	Re	P(3)	99.22(7)
P(1)	Re	P(4)	179.30(9)
P(2)	Re	P(3)	177.55(9)
P(2)	Re	P(4)	98.80(7)
P(3)	Re	P(4)	80.92(7)
Re	P(1)	C(1)	118.7(3)
Re	P(1)	C(7)	119.4(3)
Re	P(1)	C(49)	105.6(3)
C(1)	P(1)	C(7)	104.0(4)
C(1)	P(1)	C(49)	103.7(4)
C(7)	P(1)	C(49)	103.4(4)
Re	P(2)	C(13)	119.4(3)
Re	P(2)	C(19)	120.6(3)
Re	P(2)	C(50)	104.3(3)
C(13)	P(2)	C(19)	102.5(4)
C(13)	P(2)	C(50)	105.1(4)
C(19)	P(2)	C(50)	102.8(4)
Re	P(3)	C(37)	121.8(3)
Re	P(3)	C(43)	119.6(2)
Re	P(3)	C(52)	105.6(3)
C(37)	P(3)	C(43)	101.1(4)
C(37)	P(3)	C(52)	102.9(4)
C(43)	P(3)	C(52)	103.2(4)
Re	P(4)	C(25)	118.0(3)
Re	P(4)	C(31)	119.2(3)
Re	P(4)	C(51)	105.2(3)
C(25)	P(4)	C(31)	104.9(4)
C(25)	P(4)	C(51)	103.5(4)
C(31)	P(4)	C(51)	104.0(4)

Numbers in parentheses are e.s.d.s in the least significant digits.

Compound 2

The $[ReCl_2(depe)_2]^+$ cation is shown in Fig. 2, and the distances and angles are listed in Tables VI and VII. Again there is no crystallographically imposed symmetry, but the $ReCl_2P_4$ core group of atoms has effectively D_{2h} symmetry. The Re–Cl distances are of equal length, 2.335(3) Å, and the Re–P distances have a mean value of 2.450(3) Å.

The $[Re_2Cl_8]^{2-}$ ion in compound 2 is structurally closely akin to those found previously in other compounds [7b], although the Re–Re bond length, 2.213(1) Å (Table VIII), is slightly shorter than those previously reported, which were all in the range 2.23 ± 0.01 Å. The mean Re–Cl distance, 2.329(6) Å, and the mean Re–Re–Cl angle, 103.0(3)° (Table IX) are in excellent accord with the typical previous values, *viz.* 2.32 ± 0.01 Å and 103 ± 1°, respectively. As in all other cases, the $[Re_2Cl_8]^{2-}$ ion here shows a minor as well as a major orientation of the Re_2 unit within the pseudocubic set of eight Cl atoms, the populations of which are 74% and 26%. The mean torsion angle is zero degrees because the ion resides on an inversion center.

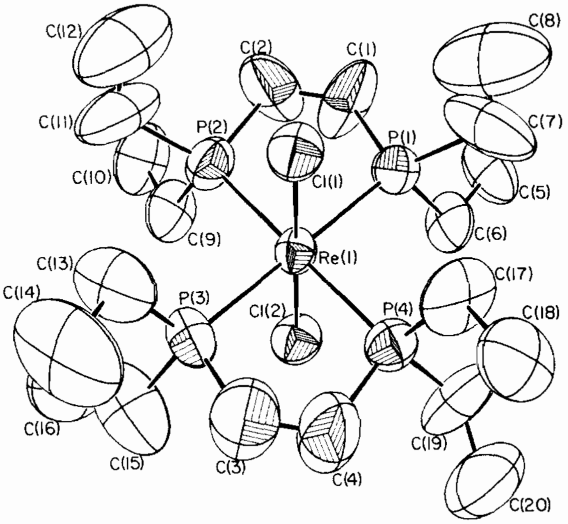

Fig. 2. An ORTEP drawing of the $[ReCl_2(depe)_2]^+$ ion in compound 2. All atoms are represented by their thermal displacement ellipsoids drawn at the 50% level.

TABLE VI. Selected Bond Distances (Å) for the $[ReCl_2(depe)_2]^+$ ion

Atom 1	Atom 2	Distance
Re(1)	Cl(1)	2.337(4)
Re(1)	Cl(2)	2.333(4)
Re(1)	P(1)	2.458(5)
Re(1)	P(2)	2.448(5)
Re(1)	P(3)	2.448(5)
Re(1)	P(4)	2.445(5)
P(1)	C(1)	1.81(2)
P(1)	C(6)	1.85(2)
P(1)	C(7)	2.06(4)
P(2)	C(2)	1.83(3)
P(2)	C(9)	1.83(2)
P(2)	C(11)	1.91(3)
P(3)	C(3)	1.79(3)
P(3)	C(13)	1.84(2)
P(3)	C(15)	1.82(3)
P(4)	C(4)	1.82(3)
P(4)	C(17)	1.85(2)
P(4)	C(19)	1.83(3)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE VII. Selected Bond Angles (°) for the [$ReCl_2(depe)_2$]$^+$ ion

Atom 1	Atom 2	Atom 3	Angle
Cl(1)	Re(1)	Cl(2)	179.2(2)
Cl(1)	Re(1)	P(1)	89.5(2)
Cl(1)	Re(1)	P(2)	90.1(2)
Cl(1)	Re(1)	P(3)	90.1(2)
Cl(1)	Re(1)	P(4)	91.1(2)
Cl(2)	Re(1)	P(1)	91.1(2)
Cl(2)	Re(1)	P(2)	90.5(2)
Cl(2)	Re(1)	P(3)	89.3(2)
Cl(2)	Re(1)	P(4)	88.4(2)
P(1)	Re(1)	P(2)	81.5(2)
P(1)	Re(1)	P(3)	178.8(2)
P(1)	Re(1)	P(4)	97.5(2)
P(2)	Re(1)	P(3)	99.6(2)
P(2)	Re(1)	P(4)	178.5(2)
P(3)	Re(1)	P(4)	81.4(2)
Re(1)	P(1)	C(1)	109.1(9)
Re(1)	P(1)	C(6)	116.2(7)
Re(1)	P(1)	C(7)	112.3(9)
C(1)	P(1)	C(6)	101.0(1)
C(1)	P(1)	C(7)	117.0(2)
C(6)	P(1)	C(7)	100.0(1)
Re(1)	P(2)	C(2)	106.6(9)
Re(1)	P(2)	C(9)	115.1(7)
Re(1)	P(2)	C(11)	119.5(9)
C(2)	P(2)	C(9)	104.0(1)
C(2)	P(2)	C(11)	109.0(1)
C(9)	P(2)	C(11)	101.0(1)
Re(1)	P(3)	C(3)	107.0(1)
Re(1)	P(3)	C(13)	116.8(8)
Re(1)	P(3)	C(15)	121.0(1)
C(3)	P(3)	C(13)	103.0(2)
C(3)	P(3)	C(15)	98.0(2)
C(13)	P(3)	C(15)	108.0(1)
Re(1)	P(4)	C(4)	107.6(9)
Re(1)	P(4)	C(17)	115.2(7)
Re(1)	P(4)	C(19)	114.8(8)
C(4)	P(4)	C(17)	105.0(1)
C(4)	P(4)	C(19)	104.0(1)
C(17)	P(4)	C(19)	108.0(1)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE VIII. Bond Distances (Å) for the [Re_2Cl_8]$^{2-}$ ion [a]

Atom 1	Atom 2	Distance
Re(2)	Re(2)	2.213(1)
Re(2)	Cl(3)	2.327(5)
Re(2)	Cl(4)	2.314(5)
Re(2)	Cl(5)	2.333(5)
Re(2)	Cl(6)	2.340(5)

[a] Distances are given only for the major orientation of the Re_2 unit. Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE IX. Bond Angles (°) for the [Re_2Cl_8]$^{2-}$ ion [a]

Atom 1	Atom 2	Atom 3	Angle
Re(2)	Re(2)	Cl(3)	103.2(1)
Re(2)	Re(2)	Cl(4)	103.8(1)
Re(2)	Re(2)	Cl(5)	102.9(1)
Re(2)	Re(2)	Cl(6)	102.2(1)
Cl(3)	Re(2)	Cl(4)	86.9(2)
Cl(3)	Re(2)	Cl(5)	87.8(2)
Cl(3)	Re(2)	Cl(6)	154.7(2)
Cl(4)	Re(2)	Cl(5)	153.3(2)
Cl(4)	Re(2)	Cl(6)	87.1(2)
Cl(5)	Re(2)	Cl(6)	86.6(2)

[a] Angles are given only for the major orientation of the Re_2 unit. Numbers in parentheses are e.s.d.s in the least significant digits.

Comparison of cations in 1 and 2

The dimensions of the [$ReCl_2(diphos)_2$]$^+$ ions in the two compounds differ in exactly the expected ways. The more basic phosphine, depe, gives Re–P distances that are shorter by 0.039(5) Å. As a result of better donation to Re^{3+} by the more basic phosphine, the Re–Cl distances in [$ReCl_2(depe)_2$]$^+$ are longer by 0.025(4) Å than those in [$ReCl_2(dtpe)_2$]$^+$.

Discussion

Previous studies [1, 8, 9] of the reaction of [Re_2Cl_8]$^{2-}$ with dppe had shown that if the reaction is carried out at room temperature the Re_2 unit remains intact ($Re_2Cl_6(dppe)_2$ is isolated) whereas in refluxing methanol [8] the compound [$ReCl_2(dppe)_2$]Cl is obtained. We therefore anticipated that the reactions described in 'Experimental' would lead to $Re_2Cl_6(diphos)_2$ products since conditions were mild. However, in both cases we have isolated only [$ReCl_2(diphos)_2$]$^+$ containing products.

In addition to the previously reported (but not structurally characterized) [$ReCl_2(dppe)_2$]Cl [8] Walton and coworkers have recently isolated [$ReCl_2(dppee)_2$]$Cl\cdot 4H_2O$ [10] (dppee = $Ph_2PCHCHPPh_2$), which they did not structurally characterize, and its reduction product, $ReCl_2(dppee)_2$, which was studied by X-ray crystallography. The latter has a *trans* structure with Re–Cl and Re–P distances of 2.422(2) and 2.405(2) Å, which are, respectively, longer and shorter than their counterparts in the [$ReCl_2(dtpe)_2$]$^+$ ion. These changes are quite in accord with the lowering of the oxidation state from Re^{III} to Re^{II}, whereby it would be expected that the Re–Cl bonds should become longer because of lower electrostatic attraction and the Re–P bonds should become shorter because of increased Re → P π-backbonding.

In addition to the $[ReCl_2(diphos)_2]^+$ cations mentioned above, the preparations of several others containing $Me_2PCH_2CH_2PMe_2$ (dmpe) [11] and $Ph_2PNHPPh_2$ [12] have also been reported, along with some physical properties. Only the $[ReCl_2(dmpe)_2]^+$ ion has previously been structurally characterized [11]. Its Re–Cl and Re–P distances, 2.337(1) and 2.438(3) Å respectively, are virtually the same as those we have found in $[ReCl_2(depe)_2]^+$, as would certainly have been expected.

Supplementary Material

Tables of structure factors, anisotropic thermal displacement tensor elements, and complete lists of bond distances and angles are available on request from author F.A.C.

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