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The Crystal and Molecular Structure of $[AsPh_4]^+[Re_2Cl_7PBu^n{}_2Ph]^-$

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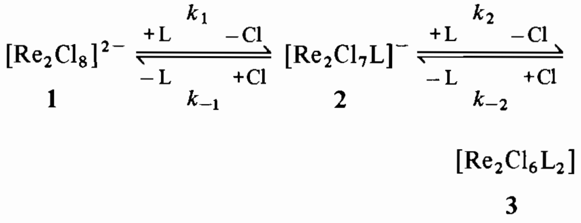
Abstract

The title compound crystallizes in the space group $P\bar{1}$ with unit cell dimensions of $a = 11.791(2)$, $b = 20.272(3)$, $c = 19.586(3)$ Å, $\alpha = 93.91(1)$, $\beta = 106.94(2)$, $\gamma = 105.34(1)°$, $V = 4265.20$ Å^3 and $Z = 4$. There is no crystallographically imposed symmetry and the structure is free from disorder. There are two formula units per asymmetric unit with Re–Re distances of 2.209(1) and 2.218(1) Å. Both adopt an essentially eclipsed geometry with average torsion angles of 8.68 and 1.72°, respectively. The structure provides evidence for a phosphine induced chloride labilizing effect across the quadruple bond.

Introduction

A kinetic study of the substitution of chloride by tertiary phosphine and arsine in $[Re_2Cl_8]^{2-}$ has provided the following reaction scheme [1].



$$\underset{\mathbf{1}}{[Re_2Cl_8]^{2-}} \underset{k_{-1}}{\overset{k_1}{\xrightleftharpoons[-L\quad +Cl]{+L\quad -Cl}}} \underset{\mathbf{2}}{[Re_2Cl_7L]^-} \underset{k_{-2}}{\overset{k_2}{\xrightleftharpoons[-L\quad +Cl]{+L\quad -Cl}}} \underset{\mathbf{3}}{[Re_2Cl_6L_2]}$$

An interesting feature of this work was that all four rate constants were measured and that the intermediate complexes **2** were isolated. The reactions were all associative and the rate constants were in the order $k_2 > k_1$ and $k_{-2} \gg k_{-1}$. This rate order suggested that phosphine was activating across the quadruple bond for loss of chloride. It was decided to undertake a crystallographic study of complexes **2** to confirm their structure and to see if bond length data could provide evidence for ground state activation.

Experimental

Attempts to obtain chemically significant crystallographic results for complex **2** with $L = P(Bu^n)_3$ were not successful. There were disorder problems involving both the Re_2 unit and the butyl groups [2]. The di-n-butylphenylphosphine derivative however proved satisfactory. Crystals of the title complex were grown as previously described [1]. All data were corrected for Lorentz and polarization effects and also for absorption by the method of Walker and Stuart [3]. The crystal data are given in Table 1. The structure was solved by Patterson methods, SHELX86 [4], and refined by block matrix least-squares using SHELX76 [5]. With full matrix least-squares the number of variable parameters with all atoms isotropic was 393. The maximum number of variable parameters, 400, was thus exceeded if more than one atom was refined anisotropically. For this reason blocked matrix refinement with two blocks was used. Each least-squares run was of fourteen cycles with the blocks using alternate even and odd numbered cycles. Hydrogen atoms were included in calculated positions on the butyl groups only with fixed thermal parameters.

The rhenium, chlorine, arsenic and phosphorus atoms were refined anisotropically. The thermal parameters were terms U_{ij} of $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$.

The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [6–8]. All calculations were performed on a VAX 8700 computer. The ORTEP program was used to obtain the drawings [9].

Discussion

The asymmetric unit of the crystal contained two units of $[AsPh_4]^+[Re_2Cl_7PBu^n{}_2Ph]^-$. Some positional parameters, bond lengths and bond angles for the anions, A and B, are given in Tables 2 and 3. An ORTEP drawing of A is given in Fig. 1 and views

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TABLE 1. Crystal data for $[AsPh_4]^+[Re_2Cl_7PBu^n_2Ph]^-$

Formula	$Re_2Cl_7PC_{14}H_{23} \cdot AsC_{24}H_{20}$
Space group	$P\bar{1}$
a (Å)	11.791(2)
b (Å)	20.272(3)
c (Å)	19.586(3)
α (°)	106.94(2)
β (°)	93.91(1)
γ (°)	105.34(1)
U (Å^3)	4265.20
μ (cm^{-1})	66.6
F(000)	2352
Z	4
Crystal size (mm)	0.20 × 0.25 × 0.08
Radiation Mo Kα graphite monochromator (Å)	$\lambda = 0.70930$
Diffractometer	Enraf-Nonius CAD4F
Orienting reflections, range (°)	25, $13 < \theta < 20$
Temperature (°C)	22
Scan method	$\omega - 2\theta$
Data collection range	$4 < 2\theta < 56°$
No. unique data	5922
Total $I > 3\sigma I$	5907
No. parameters fitted	249/255
Transmission factors, max./min.	0.967/0.583
R [a] (%)	4.13
R_w [b] (%)	3.66
Quality-of-fit indicator[c]	1.17
Largest shift/e.s.d., final cycle	<0.001
Largest positive peak (e/Å^3)	1.5
Largest negative peak (e/Å^3)	0.66

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

down the Re_2-Re_1 and Re_4-Re_3 bonds of A and B are given in Figs. 2 and 3. These structures clearly confirm the identity of complex 2.

Metal–Metal Bond Lengths

It is clear that while the broad features of A and B are similar there are small but important differences in bond lengths and angles. The geometry of B is close to being fully eclipsed with an average absolute dihedral angle, torsion angle, down the M–M axis of only 1.72° while A has a torsion angle of 8.68°, Table 4. Most surprising are the different M–M bond lengths measured for A and B, Table 5. This difference, 0.009 Å is more than three times the standard deviation in the bond lengths. It is also independent of the method of structure refinement. Identical results are observed with full matrix least-squares with all atoms isotropic.

Some of the factors which contribute to the bond length of quadruply bonded M–M systems (all other factors being equal) are: (i) deviation from eclipsed geometry (torsion angle), (ii) non-bonded repulsions, (iii) the use of ligands which are s-(p-) filters.

TABLE 2. Fractional atomic coordinates for $[Re_2Cl_7PBu_2Ph]^-$

Re1	0.50007(7)	0.76168(4)	0.60599(4)
Re2	0.34502(7)	0.66372(4)	0.57451(4)
Re3	−0.01428(7)	0.27123(4)	0.87904(4)
Re4	0.12536(7)	0.25552(4)	0.94912(4)
As1	−0.03135(17)	0.84374(10)	0.46807(9)
As2	0.30189(17)	0.92125(10)	0.88693(10)
Cl1	0.6563(4)	0.7139(3)	0.6137(2)
Cl2	0.5229(5)	0.7973(3)	0.7295(2)
Cl3	0.4109(5)	0.8529(3)	0.6134(2)
Cl4	0.5661(4)	0.7862(2)	0.5041(2)
Cl5	0.4196(5)	0.5699(3)	0.5762(2)
Cl6	0.2725(4)	0.6572(3)	0.6807(2)
Cl7	0.1876(4)	0.7021(2)	0.5442(2)
Cl8	−0.1831(4)	0.2297(3)	0.9258(3)
Cl9	−0.0778(5)	0.1634(3)	0.7858(3)
Cl10	0.0960(5)	0.3211(3)	0.8034(2)
Cl11	−0.0400(4)	0.3852(3)	0.9251(2)
Cl12	0.0268(5)	0.2073(3)	1.0285(3)
Cl13	0.1394(6)	0.1401(3)	0.8896(3)
Cl14	0.3037(4)	0.3022(3)	0.9155(3)
P1	0.3537(4)	0.6173(3)	0.4427(2)
P2	0.1784(5)	0.3734(3)	1.0464(2)
C1	0.2384(15)	0.5301(9)	0.4109(8)
C2	0.1201(18)	0.5289(10)	0.4231(10)
C3	0.0291(18)	0.4621(11)	0.3997(10)
C4	0.0560(18)	0.3995(11)	0.3640(10)
C5	0.1701(19)	0.4011(11)	0.3510(10)
C6	0.2643(17)	0.4678(11)	0.3748(10)
C7	0.4889(14)	0.5964(9)	0.4239(8)
C8	0.5210(17)	0.5774(10)	0.3459(9)
C9	0.5852(19)	0.6376(11)	0.3230(10)
C10	0.6041(19)	0.6170(11)	0.2448(10)
C11	0.3072(16)	0.6695(9)	0.3893(9)
C12	0.2660(18)	0.6316(10)	0.3104(9)
C13	0.2283(19)	0.6795(11)	0.2696(11)
C14	0.3261(19)	0.7429(11)	0.2709(11)
C15	0.2986(16)	0.3745(9)	1.1139(9)
C16	0.4152(18)	0.4128(10)	1.1148(10)
C17	0.5030(19)	0.4118(11)	1.1666(11)
C18	0.4686(18)	0.3733(11)	1.2126(10)
C19	0.3591(20)	0.3325(11)	1.2131(11)
C20	0.2725(20)	0.3357(11)	1.1614(10)
C21	0.2388(18)	0.4507(9)	1.0145(10)
C22	0.2819(19)	0.5228(10)	1.0694(10)
C23	0.3581(23)	0.5793(12)	1.0312(13)
C24	0.3870(25)	0.6514(14)	1.0795(14)
C25	0.0538(17)	0.3896(10)	1.0938(10)
C26	0.0848(19)	0.4493(11)	1.1666(11)
C27	−0.0323(24)	0.4470(15)	1.2042(14)
C28	−0.1201(24)	0.4583(14)	1.1701(14)

It has been clearly shown for quadruply bonded molybdenum complexes that the torsion angle is directly related to M–M distances. Cotton *et al.* have measured M–M distances for a series of $Mo_2X_4L_2$ complexes with torsion angles in the range 20 to 45° [10]. It is clearly the case that delta bond overlap will decrease with increasing torsion angle and that for

TABLE 3. Important bond distances and angles in $[Re_2Cl_7PBu_2Ph]^-$

Distances (Å)			
Re1–Re2	2.209(1)	Re1–Cl1	2.312(6)
Re1–Cl2	2.288(5)	Re1–Cl3	2.331(6)
Re1–Cl4	2.328(5)	Re2–Cl5	2.303(6)
Re2–Cl6	2.327(5)	Re2–Cl7	2.299(6)
Re2–P1	2.496(5)	Re3–Re4	2.218(1)
Re3–Cl8	2.307(5)	Re3–Cl9	2.301(5)
Re3–Cl10	2.312(6)	Re3–Cl11	2.331(5)
Re4–Cl12	2.292(6)	Re4–Cl13	2.346(6)
Re4–Cl14	2.291(5)	Re4–P2	2.474(4)
As1–C53	1.973(18)	As1–C59	1.904(17)
As1–C65	1.914(15)	As1–C71	1.887(17)
As2–C29	1.899(15)	As2–C35	1.875(20)
As2–C41	1.890(19)	As2–C47	1.906(15)
P1–C1	1.826(15)	P1–C7	1.789(19)
P1–C11	1.841(22)	P2–C15	1.862(20)
P2–C21	1.842(21)	P2–C25	1.842(21)
Angles (°)			
Cl1–Re1–Re2	101.6(1)	Cl2–Re1–Re2	102.4(1)
Cl2–Re1–Cl1	87.5(2)	Cl3–Re1–Re2	102.4(1)
Cl3–Re1–Cl1	155.9(2)	Cl3–Re1–Cl2	86.7(2)
Cl4–Re1–Re2	110.6(1)	Cl4–Re1–Cl1	87.2(2)
Cl4–Re1–Cl2	146.9(2)	Cl4–Re1–Cl3	85.0(2)
Cl5–Re2–Re1	106.1(1)	Cl6–Re2–Re1	106.2(1)
Cl6–Re2–Cl5	87.9(2)	Cl7–Re2–Re1	104.4(1)
Cl7–Re2–Cl5	149.0(2)	Cl7–Re2–Cl6	89.0(2)
P1–Re2–Re1	99.3(1)	P1–Re2–Cl5	82.0(2)
P1–Re2–Cl6	154.3(2)	P1–Re2–Cl7	87.7(2)
Cl8–Re3–Re4	101.8(2)	Cl9–Re3–Re4	103.3(2)
Cl9–Re3–Cl8	87.0(2)	Cl10–Re3–Re4	101.7(1)
Cl10–Re3–Cl8	156.5(2)	Cl10–Re3–Cl9	88.3(2)
Cl11–Re3–Re4	112.1(1)	Cl11–Re3–Cl8	86.0(2)
Cl11–Re3–Cl9	144.6(2)	Cl11–Re3–Cl10	84.6(2)
Cl12–Re4–Re3	105.2(2)	Cl13–Re4–Re3	105.5(2)
Cl13–Re4–Cl12	87.6(2)	Cl14–Re4–Re3	106.7(2)
Cl14–Re4–Cl12	147.9(2)	Cl14–Re4–Cl13	87.8(2)
P2–Re4–Re3	98.8(1)	P2–Re4–Cl12	86.6(2)
P2–Re4–Cl13	155.6(2)	P2–Re4–Cl14	84.7(2)
C1–P1–Re2	104.0(6)	C7–P1–Re2	113.5(5)
C11–P1–Re2	114.5(6)	C25–P2–Re4	113.7(5)
C15–P2–Re4	107.5(6)	C21–P2–Re4	113.1(6)

torsion angles close to 45° the delta bond's contribution to bond order and bond length reduction will be very small. Cotton *et al.* have estimated the delta bonds overall contribution to bond length reduction to be 0.019 Å. In the present case, however, the complex with the greater torsion angle has the shorter M–M bond. It therefore appears that for small torsion angles < 20° the relief of non-bonded repulsions is greater than the loss of delta overlap. The importance of intraionic (intramolecular) non-bonded repulsions in eclipsed geometry M_2L_8 systems is well known. The strongest interaction in both A and B is between the phosphine and the chloride opposite on the other rhenium. Thus the Re_2–Re_1–Cl_4 and the Re_4–Re_3–Cl_{11} angles are at 110.6 and 112.1° about 10° larger than all other Re–Re–Cl angles and are similar to those reported for $Re_2Cl_6L_2$ complexes [11, 12]. The M–M bonds in A and B are also shorter than that of $[Re_2Cl_8]^{2-}$ but longer than that of $[Re_2Me_8]^{2-}$, Table 5. These differences could be due

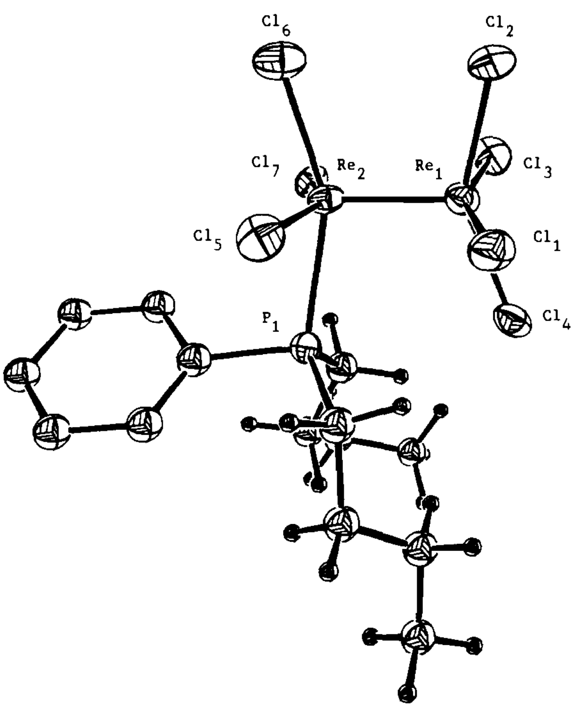

Fig. 1. An ORTEP drawing of $[Re_2Cl_7P^nBu_2Ph]^-$, A.

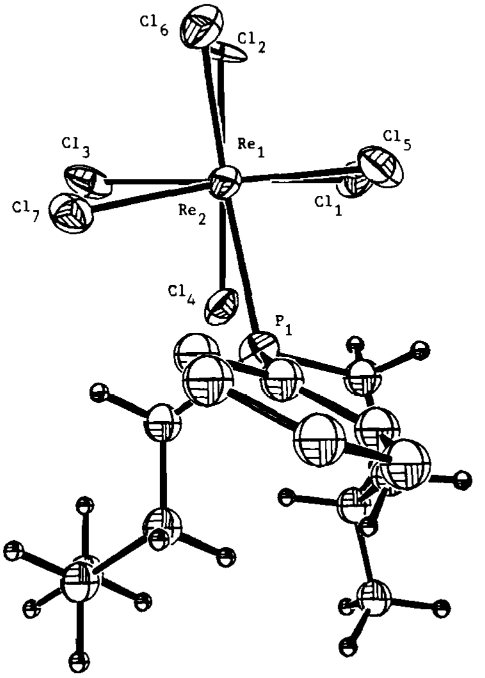

Fig. 2. View down the Re_2–Re_1 bond of A.

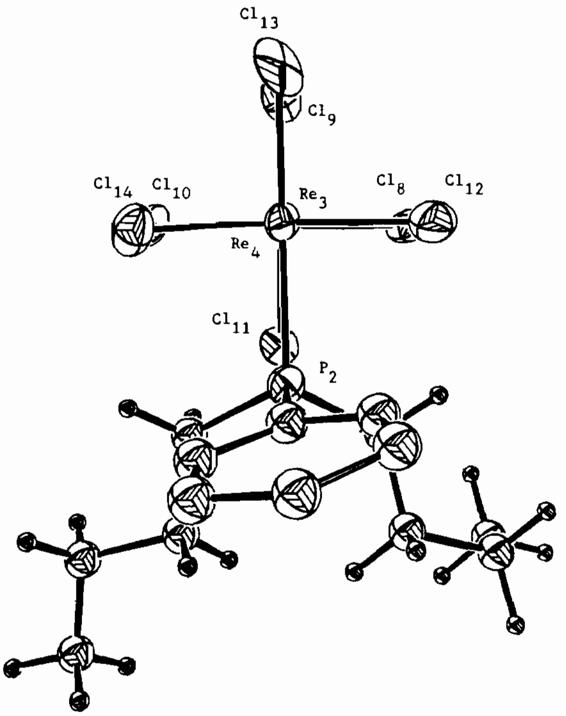

Fig. 3. View down the Re_4–Re_3 bond of B.

TABLE 4. Torsion angles (°)

	Angle (°)	Average (°)
Cl_1–Re_1–Re_2–Cl_5	4.88	
Cl_2–Re_1–Re_2–Cl_6	6.88	
Cl_3–Re_1–Re_2–Cl_7	11.03	
P_1–Re_2–Re_1–Cl_4	11.93	8.68
Cl_8–Re_3–Re_4–Cl_{12}	0.16	
Cl_9–Re_3–Re_4–Cl_{13}	2.03	
Cl_{10}–Re_3–Re_4–Cl_{14}	3.16	
P_2–Re_3–Re_4–Cl_{11}	1.54	1.72

TABLE 5. M–M distances (Å)

		Distance (Å)	Reference
$[Re_2Cl_7PBu_2Ph]^-$	A	2.209(1)	
	B	2.218(1)	
$Re_2Cl_6(PMePh_2)_2$		2.227(1)	12
$[Re_2Cl_8]^{2-}$		2.224(1)	14
$[Re_2Me_8]^{2-}$		2.178(1)	15

to in the former to a higher charge on $[Re_2Cl_8]^{2-}$ and to the leakage of s-(p-) electron density from Re in the latter [13].

The different torsion angles observed for A and B may be due to crystal packing forces however no strong contacts were found. All contacts within 4 Å of the chlorine and phosphorus atoms were examined. The closest contact 3.39 Å involved Cl_{12} of B. The closest contact involving A was Cl_1...C_5 of 3.66 Å.

Rhenium–Chlorine Bond Lengths

The Re–Cl distances for Re_2 and Re_4 show a *trans* influence by the phosphine ligands. The Re_2–Cl_6 and Re_4–Cl_{13} distances (*trans* to P) are about 0.025 Å longer than the Re–Cl distances on Re_2 and Re_4 which are *cis* to P. These *trans* influence effects are similar to those observed for $Re_2Cl_6L_2$, L = PEt_3 and PPh_2Me [11, 12]. However it is the Re–Cl distances on Re_1 and Re_3 which are of most importance from the mechanistic point of view and which permit, for the first time, the investigation of ligand effects across the quadruple bond.

The B structure which closely approaches C_s symmetry has (within experimental error) symmetrical Re–Cl bond lengths. The Re_3–Cl_{11} bond, *cis* to P on Re_4, is 0.02 Å longer than the other three Re_3–Cl distances and is most likely to be the weakest Re–Cl bond. In the less symmetrical A structure two of the Re_1–Cl bonds show increased length, Re_1–Cl_3 and Re_1–Cl_4, the latter is *cis* to P on Re_2.

The kinetic and crystallographic results would suggest that associative substitution on 2 would lead to $Re_2Cl_6L_2$ which would not have *trans* geometry. However it is possible that the kinetic product could rotate into the more sterically stable *trans* form.

References

1 J. Ferry, P. McArdle and M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, (1989) 767.
2 J. Ferry, *Ph.D. Thesis*, National University of Ireland, 1987.
3 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
4 G. M. Sheldrick, *SHELX86*, a computer program for crystal structure determination, University of Göttingen, F.R.G., 1986.
5 G. M. Sheldrick, *SHELX76*, a computer program for crystal structure determination, University of Cambridge, U.K., 1976.
6 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A, 24* (1968) 321.
7 R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys., 42* (1965) 3175.
8 D. T. Cromer and D. J. Liberman, *J. Chem. Phys., 53* (1970) 1891.
9 C. K. Johnson, *ORTEP, Rep. ORNL (US) 1965-3794*, Oak Ridge National Laboratory, Oak Ridge, TN, revised 1971.
10 F. L. Campbell, F. A. Cotton and G. L. Powell, *Inorg. Chem., 24* (1985) 4384.
11 F. A. Cotton and B. M. Foxman, *Inorg. Chem., 7* (1968) 213.
12 F. A. Cotton, M. P. Diebold and W. J. Roth, *Inorg. Chim. Acta, 144* (1988) 17.
13 R. G. Woolley, *Inorg. Chem., 18* (1979) 2945.
14 F. A. Cotton, B. A. Frenz, B. R. Stults and T. R. Webb, *J. Am. Chem. Soc., 98* (1976) 2768.
15 F. A. Cotton, L. D. Gage, K. Mertis, L. W. Shive and G. Wilkinson, *J. Am. Chem. Soc., 98* (1976) 6922.