Inorganica Chimica Acta, 144 (1988) 17–19

The Crystal and Molecular Structure of $Re_2Cl_6(PMePh_2)_2$

F. ALBERT COTTON*, MICHAEL P. DIEBOLD and WIESLAW J. ROTH

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, Tex. 77843, U.S.A.

(Received June 16, 1987)

Abstract

The title compound was obtained in crystalline form and the structure determined. It crystallizes in space group $P2_1/n$ with unit cell dimensions of $a = 10.221(3)$, $b = 11.747(4)$, $c = 15.189(6)$ Å, $\beta = 100.11(3)°$, $V = 1796(1)$ Å^3 and $Z = 2$. The molecule is rigorously centrosymmetric with the following principal dimensions: Re–Re, 2.227(1) Å; Re–P, 2.475(2) Å; Re–Cl(*trans* to P), 2.337(3) Å; Re–Cl (*cis* to P), 2.310(3) and 2.319(3) Å.

Introduction

Many complexes with stoichiometry $Re_2X_6(PR_3)_2$ (X = Cl, Br) have been reported [1]. These compounds can be made easily by the substitution of two anionic ligands with two neutral phosphine ligands under mild reaction conditions [2]. Like the parent octahalides, the $Re_2X_6(PR_3)_2$ complexes contain quadruple M–M bonds. These complexes have been characterized by electronic absorption spectroscopy [2, 3] and cyclic voltammetry [4] and their reduction by phosphines under forcing conditions has been studied in detail [3]. It is perhaps surprising that despite all of this work an X-ray crystal structure analysis has been carried out on only one of these molecules, namely $Re_2Cl_6(PEt_3)_2$ [5]. We now report the crystal and molecular structure of a second $Re_2X_6(PR_3)_2$ complex, $Re_2Cl_6(PPh_2Me)_2$ (**1**).

Experimental

Synthesis

All manipulations were carried out under an atmosphere of argon employing standard Schlenk line techniques. Solvents were freshly distilled from appropriate drying agents prior to use. A high yield synthesis for **1** has previously been reported [2b, 3]. The crystals that were crystallographically characterized were synthesized by the reduction of $ReCl_5$ (0.20 g) with $(\eta^6\text{-}C_6H_5PPhMe)Mo(PPh_2Me)_3$ [6] (0.50 g) in toluene (15 ml). The resulting solid was isolated and redissolved in CH_2Cl_2 (5 ml) and this solution was carefully layered with hexane. A number of crystals of **1** grew after 2 weeks.

X-ray Crystallography

A well formed crystal was mounted in a mineral oil filled glass capillary and placed on a Syntex P3 automated diffractometer. Data were collected and treated according to procedures routine to this laboratory and described in detail elsewhere [7]**. All data were corrected for Lorentz and polarization effects, and absorption corrections, based on 9 reflections with Eulerian angle χ near 90°, were applied.

The position of the metal atom was derived from a three dimensional Patterson function. The remaining non-hydrogen atoms were located in a series of least-squares refinements and differences Fourier syntheses. A molecule of CH_2Cl_2 was present in the lattice and located near a center of symmetry. This molecule was disordered over two positions which were related by this inversion center. This region was modelled by a CCl_2 unit at one of these positions and given half occupancy. In the final refinement all atoms were given anisotropic displacement parameters. Two relatively large residual peaks (>1.0 e/Å^3) were present in a final difference Fourier map. These peaks were located near the rhenium atom and were attributed to series termination error. No attempt was made to locate non-hydrogen atoms. See also 'Supplementary Material'.

Discussion

The first $Re_2X_6(PR_3)_2$ compound to be synthesized, $Re_2Cl_6(PPh_3)_2$, was too insoluble for single

---

*Author to whom correspondence should be addressed.

**Calculations were made on a departmental VAX 11-780 computer with SDP software.

0020-1693/88/$3.50

TABLE I. Crystal Data for $Re_2Cl_6(PPh_2Me)_2 \cdot CH_2Cl_2$ (1)

Formula	$Re_2Cl_8P_2C_{27}H_{28}$
Formula weight	1070.50
Space group	$P2_1/n$
Systematic absences	$0k0\ k = 2n + 1$
	$h0l\ h + l = 2n + 1$
a (Å)	10.221(3)
b (Å)	11.747(4)
c (Å)	15.189(6)
α (°)	90.0
β (°)	100.11(3)
γ (°)	90.0
V (Å^3)	1796(1)
Z	2
D_{calc} (g/cm^3)	1.980
Crystal size (mm)	0.3 × 0.2 × 0.5
μ(Mo Kα) (cm^{-1})	75.35
Data collection instrument	Syntex P3
Radiation (monochromated in incident beam	Mo Kα (λ_α = 0.71073 Å)
Orientation reflections, number, range (2θ)	25, 20° $\leq 2\theta \leq$ 31°
Temperature (°C)	23
Scan method	$\omega-2\theta$
Data collection range, 2θ (°)	$4.5 \leq 2\theta \leq 47.5$
No. unique data	2449
Total with $F_o^2 > 3\sigma(F_o^2)$	2157
No. parameters refined	190
Transmission factors, max./min.	0.9985/0.4310
R^a	0.0466
R_w^b	0.0655
Quality-of-fit indicator^c	1.562
Largest shift (e.s.d.), final cycle	0.28
Largest peak (e/Å^3)	1.215

[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 $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

TABLE II. Positional Parameters for $Re_2Cl_6(PPh_2Me)_2$ (1)[a]

Atom	x	y	z	B (Å^2)
Re	−0.04034(5)	−0.08433(4)	1.01533(3)	3.195(9)
Cl(1)	−0.2391(3)	−0.1286(3)	0.9200(2)	4.77(7)
Cl(1)	0.1632(3)	0.0409(3)	0.8745(2)	4.50(7)
Cl(3)	0.0604(4)	−0.2125(3)	0.9332(2)	4.69(7)
P	0.1284(3)	−0.1457(3)	1.1439(2)	3.50(6)
C(10)	−0.205(1)	−0.316(1)	1.1285(8)	4.0(3)
C(11)	−0.146(1)	−0.357(1)	1.057(1)	4.9(3)
C(12)	−0.018(1)	−0.333(1)	1.051(1)	5.4(3)
C(13)	0.059(1)	−0.265(1)	1.119(1)	5.4(3)
C(14)	0.005(2)	−0.223(1)	1.190(1)	5.3(3)
C(15)	−0.128(1)	−0.251(1)	1.1979(9)	4.7(3)
C(20)	0.053(1)	−0.276(1)	1.179(1)	5.1(3)
C(21)	0.072(2)	−0.379(1)	1.131(1)	6.0(4)
C(22)	0.009(2)	−0.480(1)	0.154(2)	10.2(6)
C(23)	−0.060(2)	−0.485(2)	1.223(2)	10.9(6)
C(24)	−0.077(2)	−0.385(2)	1.265(1)	10.5(5)
C(25)	−0.018(2)	−0.276(1)	1.248(1)	7.1(4)
C(30)	0.150(2)	−0.055(1)	1.2432(9)	4.9(3)
Cl(1A)	0.233(2)	−0.0740(9)	1.4874(7)	10.1(4)
Cl(2A)	−0.125(1)	−0.058(1)	1.394(1)	12.1(4)
C′	0.146(4)	0.034(4)	1.514(3)	9(1)

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

TABLE III. Important Bond Distances and Angles in $Re_2Cl_6(PPh_2Me)_2$ (1)[a]

Atom 1	Atom 2	Distance (Å)
Re	Re′	2.227(1)
	Cl(1)	2.337(3)
	Cl(2)	2.319(3)
	Cl(3)	2.310(3)
	P	2.475(2)

Atom 1	Atom 2	Atom 3	Angle (°)
Re′	Re	Cl(1)	112.47(8)
		Cl(2)	102.85(8)
		Cl(3)	104.52(8)
		P	101.08(6)
Cl(1)	Re	Cl(2)	88.5(1)
		Cl(3)	86.6(1)
		P	146.4(1)
Cl(2)	Re	Cl(3)	152.0(1)
		P	83.41(9)
Cl(3)	Re	P	85.47(9)

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

crystals suitable for X-ray studies to be grown [2]. Substitution of one phenyl group on the phosphine ligands with a methyl group increases the solubility of the molecule. While $Re_2Cl_6(PPh_2Me)_2$ has been known for some time [2b, 3] it has not, until now, been the subject of crystallographic analysis. Crystal data are given in Table I.

The positional and isotropic-equivalent displacement parameters for 1 are shown in Table II. Important bond distances and angles are presented in Table III. The crystal structure of 1 consists of discrete dimeric units (see Fig. 1). The dimensions of the central $Re_2Cl_6P_2$ portion of the molecule are quite similar to those of the previously characterized compound $Re_2Cl_6(PEt_3)_2$ [5]. Unlike $Re_2Cl_6(PEt_3)_2$, compound 1 shows no evidence of disorder in the organic constituents on the phoshine ligands. The $Re_2Cl_6(PPh_2Me)_2$ molecules reside on crystallographic centers of symmetry and thus the ligands are rigorously eclipsed. The M–M distance, 2.227(1)

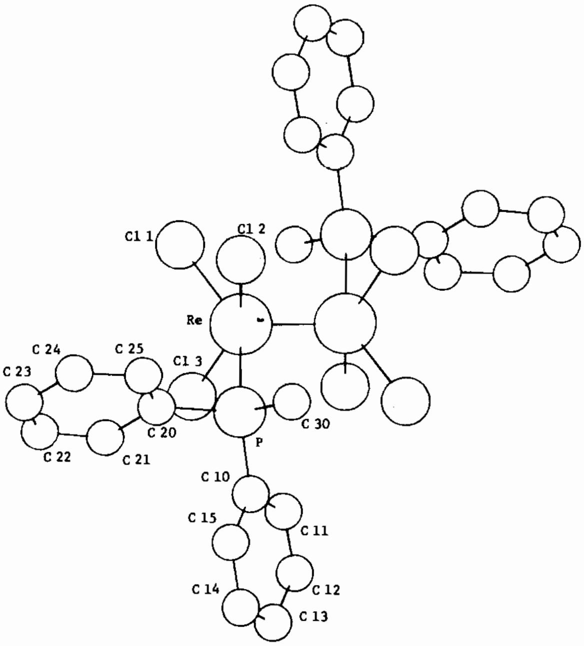

Fig. 1. A ball and stick drawing of the $Re_2Cl_6(PMePh_2)_2$ molecule showing the atomic numbering scheme.

Å, is completely normal for Re–Re quadruple bonds [1]. As in $Re_2Cl_6(PEt_3)_2$, the Re–Cl distances show a slight *trans* influence by the phosphine ligands. The two independent Re–Cl(*trans* to Cl) distances are nearly equal to one another and are about 0.02 Å shorter than the Re–Cl(*trans* to P) distance. Not only is the Cl(*trans* to P) atom farther from the Re atom than are the Cl(*trans* to Cl) atoms, the Re–Re–Cl(*trans* to P) angle is about 10° greater than the Re–Re–Cl(*trans* to Cl) angles. This sweeping back of the chlorine atoms *trans* to the phosphine groups is caused by steric interaction between this chlorine atom and the phoshine group attached to the opposite rhenium atom. It is interesting to note that, while this steric interaction causes the Re–Re–Cl(*trans* to P) angle to open up, the Re–Re–P angle (101.08°) is comparable to the Re–Re–Cl(*trans* to Cl) angles (average 103.68°). This phenomenon was also observed in $Re_2Cl_6(PEt_3)_2$.

Supplementary Material

For a listing of structure factors, complete tables of bond distances and angles, and a table of anisotropic thermal parameters contact author F.A.C.

Acknowledgement

We thank the National Science Foundation for support.

References

1 F. A. Cotton and R. A. Walton, 'Multiple Bonds between Metal Atoms', Wiley, 1982.
2 (a) F. A. Cotton, N. F. Curtis and W. R. Robinson, *Inorg. Chem., 4,* 1696 (1965); (b) J. San Filipo, Jr., *Inorg. Chem., 11,* 3140 (1972); (c) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc., 95,* 8177 (1973).
3 J. R. Ebner and R. A. Walton, *Inorg. Chem., 14,* 1987 (1975).
4 (a) D. J. Salmon and R. A. Walton, *J. Am. Chem. Soc., 100,* 991 (1978); (b) P. Brant, D. J. Salmon and R. A. Walton, *J. Am. Chem. Soc., 100,* 4424 (1978).
5 (a) M. J. Bennett, F. A. Cotton, B. M. Foxman and P. F. Stokely, *J. Am. Chem. Soc., 89,* 2759 (1967); (b) F. A. Cotton and B. M. Foxman, *Inorg. Chem., 7,* 213 (1968).
6 R. L. Luck, R. H. Morris and J. F. Sawyer, *Organometallics, 3,* 247 (1984).
7 A. Bino, F. A. Cotton and P. E Fanwick, *Inorg. Chem., 18,* 3558 (1978).