Complex Halides of the Transition Metals. Part XVII.[1,2] Crystal and Molecular Structure of Di-μ-chloro-bis{[bis(diphenylphosphino)ethane]-dichlororhenium}–Bis(Acetonitrile)

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Crystals of the title compound are triclinic, space group $P\bar{1}$, $a = 10{\cdot}299(1)$, $b = 11{\cdot}566(1)$, $c = 12{\cdot}991(1)$ Å, $\alpha = 104{\cdot}45(1)$, $\beta = 105{\cdot}52(1)$, $\gamma = 98{\cdot}54(1)°$, and $Z = 1$. The intensities of 3250 reflections above background were collected and the structure refined by least-squares techniques to R 0·066. The molecule exists as a centrosymmetric chlorine-bridged dimer with a pseudo-octahedral environment about the rhenium atoms. The Re–Re distance [3·809(1) Å] is inconsistent with the presence of metal–metal interaction and the structure is therefore reminiscent of that of Re_2Cl_{10}.

THE octahalogenodirhenate(III) anions $[Re_2X_8]^{2-}$ react with unidentate tertiary phosphines under *mild* reaction conditions to afford dinuclear metal–metal bonded substitution products of the type $[ReX_3(PR_3)]_2$.[3-5] The reaction of these same dianions with the bidentate sulphur donor 2,5-dithiahexane (dth) yields the complexes $[ReX_3(dth)]_2$, whose electronic spectra[6] and reactivity patterns[1] so closely resemble those of the phosphine complexes $[ReX_3(PR_3)]_2$ that they must possess a closely related structure.[7] In contrast to these observations we have found[1,6] that the related product from the reaction of the salt $[Bu_4N]_2[Re_2Cl_8]$ with 1,2-bis(diphenylphosphino)ethane (dppe), $[ReCl_3(dppe)]_n$,[3] has properties consistent with the presence of magnetically dilute rhenium(III) centres. In view of this surprising result we have carried out a single-crystal *X*-ray structure analysis on this complex, the crystals of which were found to be those of the acetonitrile solvate of $[ReCl_3(dppe)]_2$. Full structural details are now reported.[2]

EXPERIMENTAL

The preparative procedure described in ref. 3 did not afford crystals of sufficient quality for a crystal-structure analysis, and the following procedure was found to be necessary. A solution of $[Bu_4N]_2[Re_2Cl_8]$ (0·6 g) in acetonitrile (10 ml) was added to 1,2-bis(diphenylphosphino)-ethane (1·0 g) which had been pressed into a pellet at the bottom of a test tube. After 3 days a green supernatant solution was removed, and further $[Bu_4N]_2[Re_2Cl_8]$ (0·6 g) in acetonitrile (10 ml) was added. After a further 3 days, a mixture of yellow-red crystals, green crystals, and excess of dppe was separated from the solution. The yellow-red crystals of $[ReCl_3(dppe)]_2{,}2MeCN$ were mechanically separated from the green crystals and washed with diethyl ether.

Crystal Data.—$C_{56}H_{54}Cl_6N_2P_4Re_2$, $M = 1464{\cdot}0$, Triclinic, $a = 10{\cdot}299(1)$, $b = 11{\cdot}556(1)$, $c = 12{\cdot}991(1)$ Å, $\alpha = 104{\cdot}45(1)$, $\beta = 104{\cdot}52(1)$, $\gamma = 98{\cdot}54(1)°$, $U = 1414{\cdot}15$ Å^3, $D_m = 1{\cdot}729(5)$, $Z = 1$, $D_c = 1{\cdot}722$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, $\mu(\text{Mo-}K_\alpha) = 49{\cdot}8$ cm^{-1}. Space group $P\bar{1}$ from diffraction symmetry, lack of systematic absences, and equality of Friedel pairs.

Data Collection.—A crystal with dimensions 0·058 × 0·131 × 0·126 mm was mounted along a nonprincipal crystallographic direction on an Enraf-Nonius CAD 4 *X*-ray diffractometer. Unit-cell parameters were determined from least-squares refinement of the 2θ values of 73 reflections measured at positive and negative 2θ by use of graphite-monochromated Mo-K_α radiation. All reflections from a hemisphere of reciprocal space with $2\theta < 80°$ were collected. The θ—2θ scanning technique with a variable scanning speed was used with a 2θ range of $1{\cdot}6 + \tan\theta$ centred about the average peak position. The aperture was set at 3 × 4 mm. Each reflection was first scanned (20·1° min^{-1}) to determine its approximate intensity, and then twice at a slower rate necessary to accumulate a minimum net count of 100 counts above background. The maximum rate for the slower scan was set at 6·7° min^{-1} with the majority of reflections counted at this rate. Those reflections for which the minimum net count could not be obtained in 180 s were considered weak. This limit corresponded closely to $I < 3\sigma(I)$. For no observed reflections were the results of the two slow scans statistically different. Background counts were made for 1/4 of the scan time at each end of both scans. Three control reflections, monitored alternately after each 20 reflections, decreased in intensity by *ca.* 15% during the course of measuring the 4807 data points. Following correction for background, Lorentz and polarization effects, and absorption, the data set was divided into 4 groups within which the intensity of the control reflections did not differ by >4%, and these groups were scaled to a common scale using the control

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reflections and a group of *ca.* 800 reflections consisting of Friedel pairs from *ca.* 400 reflections which were collected separately for intergroup scaling. The final data set consisted of 3250 observed reflections.

Structure Analysis.—The positions of the rhenium, chlorine, and phosphorous atoms were determined from a Patterson function. The remaining nonhydrogen atoms were located from a difference synthesis. The structure was refined by minimization of $\Sigma w(F_o - F_c)^2$ by a modified block-diagonal technique owing to storage limitations of the computer. Least-squares refinement of the scale factor and positional and thermal parameters of the rhenium, chlorine, and acetonitrile, together with alternate halves of the dppe ligand, reduced R to 0·060 and the weighted factor, R', to 0·066. The weights were taken as $w = 1/\sigma(F)^2$ where $\sigma(F)$ was based on counting statistics. Atomic scattering factors from ref. 8 were used with real and imaginary anomalous scattering corrections for rhenium, chlorine, and phosphorus. The final estimated standard deviation of an observation of unit weight was 0·99. Final positional and thermal parameters are listed in Tables 1 and 2, and molecular dimensions in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21228 (3 pp., 1 microfiche).*

TABLE 1

Atomic positional parameters ($\times 10^4$; for Re $\times 10^5$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Re	37181(5)	48855(5)	36172(5)
Cl(1)	2093(4)	5358(3)	4496(3)
Cl(2)	5325(4)	4448(3)	2689(3)
Cl(3)	5602(4)	6432(3)	5168(3)
P(1)	3052(4)	6179(3)	2520(3)
P(2)	2053(4)	3339(3)	2112(3)
C(1)	1515(15)	5321(12)	1308(11)
C(2)	1657(15)	3937(12)	0894(12)
C(3)	1253(25)	3574(23)	6303(18)
C(4)	1518(20)	3964(17)	7547(20)
N	1743(22)	4310(17)	8514(16)
C(5)	2487(15)	7560(13)	3128(12)
C(6)	3178(19)	8188(13)	4271(12)
C(7)	2802(23)	9283(15)	4761(15)
C(8)	1870(25)	9744(16)	4134(19)
C(9)	1245(22)	9150(17)	3048(21)
C(10)	1578(20)	8033(16)	2485(17)
C(11)	4345(14)	6823(12)	1950(11)
C(12)	4214(17)	6441(15)	0802(13)
C(13)	5257(19)	7024(18)	0459(16)
C(14)	6345(22)	7913(18)	1195(22)
C(15)	6483(20)	8293(16)	2333(16)
C(16)	5482(16)	7748(15)	2725(16)
C(17)	0449(15)	2868(13)	2383(12)
C(18)	−0773(16)	3120(14)	1828(16)
C(19)	−2011(20)	2778(16)	2118(17)
C(20)	−1981(21)	2169(17)	2955(17)
C(21)	−0735(22)	1896(19)	3464(16)
C(22)	0450(19)	2246(16)	3175(16)
C(23)	2480(15)	1865(13)	1532(13)
C(24)	3601(22)	1518(17)	2111(18)
C(25)	3939(23)	0398(18)	1649(23)
C(26)	3078(23)	−0367(17)	607(18)
C(27)	1979(24)	−0012(16)	070(19)
C(28)	1608(17)	1089(15)	506(14)

DISCUSSION

As shown in Figures 1 and 2, the structure consists of centrosymmetric $[ReCl_3(dppe)]_2$ units with nonbonded acetonitrile molecules in holes in the lattice. The $[ReCl_3(dppe)]_2$ unit results from two symmetrical Re–Cl–Re bridges, so the overall structure of this unit is that of two pseudo-octahedra sharing an edge. The octahedral geometry about each rhenium is distorted by the bridging chlorine atoms and by the presence of the dppe molecule which is *trans* to them.

TABLE 2

Anisotropic thermal parameters * ($\times 10^4$; for Re $\times 10^5$), with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	808(6)	334(4)	406(4)	96(4)	54(4)	62(3)
Cl(1)	114(5)	55(3)	59(3)	12(3)	21(3)	7(2)
Cl(2)	100(4)	72(3)	62(3)	26(3)	23(3)	15(3)
Cl(3)	113(4)	38(3)	56(3)	0(3)	−7(3)	11(2)
P(1)	103(4)	35(3)	47(3)	16(3)	16(3)	11(2)
P(2)	86(4)	32(3)	48(3)	13(3)	5(3)	3(2)
C(1)	134(21)	40(13)	36(11)	0(13)	−22(12)	−4(9)
C(2)	128(20)	38(12)	57(12)	25(13)	4(13)	13(10)
C(3)	226(40)	188(34)	72(20)	44(29)	34(24)	23(21)
C(4)	112(25)	74(19)	127(24)	14(17)	20(22)	44(18)
N	298(39)	115(21)	83(17)	79(23)	−17(22)	14(16)
C(5)	116(20)	57(14)	62(13)	12(13)	24(13)	24(11)
C(6)	211(28)	50(14)	46(13)	33(16)	31(16)	−8(10)
C(7)	297(39)	67(17)	83(17)	69(22)	48(22)	12(14)
C(8)	301(43)	63(19)	115(22)	64(23)	40(26)	6(17)
C(9)	215(35)	80(20)	190(30)	86(22)	40(27)	47(21)
C(10)	198(30)	80(18)	139(22)	73(20)	17(21)	43(17)
C(11)	105(19)	51(13)	54(12)	34(13)	29(13)	21(10)
C(12)	141(23)	116(19)	57(14)	57(17)	35(15)	41(13)
C(13)	142(26)	130(23)	107(19)	77(20)	43(19)	51(18)
C(14)	187(33)	92(21)	210(33)	58(22)	108(28)	85(22)
C(15)	195(30)	91(18)	109(19)	45(19)	94(21)	39(15)
C(16)	100(21)	83(17)	127(20)	2(15)	30(17)	31(15)
C(17)	87(20)	45(14)	42(13)	11(13)	−8(13)	−24(11)
C(18)	74(20)	50(15)	108(19)	11(14)	8(16)	−9(13)
C(19)	146(28)	60(17)	89(19)	81(17)	16(19)	−7(14)
C(20)	145(29)	79(19)	87(19)	−5(19)	49(20)	−21(15)
C(21)	161(31)	128(25)	59(17)	−6(22)	26(19)	4(16)
C(22)	128(25)	80(19)	91(19)	−9(17)	29(18)	32(15)
C(23)	81(19)	43(14)	54(13)	17(13)	13(13)	−2(11)
C(24)	186(32)	63(18)	125(23)	44(30)	31(23)	3(16)
C(25)	180(34)	61(20)	210(34)	52(21)	30(28)	−17(21)
C(26)	206(35)	56(18)	96(20)	42(21)	35(22)	−12(15)
C(27)	214(36)	45(17)	135(25)	29(20)	62(25)	−8(16)
C(28)	112(23)	66(17)	67(16)	−3(16)	23(16)	−3(13)

* The form of the approximation is: $f = f_0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Of greatest interest in this dimer is the Re–Re distance [3·809(1) Å] which is inconsistent with the presence of a strong Re–Re bond as observed in other rhenium(III) compounds. The Re–Re distance is much longer than those in the $[Re_2Cl_8]^{2-}$ dianion (2·24 Å),[9] in the trimer Re_3Cl_9 (2·48 Å),[10] in the dimer $Re_2(O_2CPh)_4Cl_2$ (2·235 Å),[11] and even in metallic rhenium (2·74 Å).[8] Thus the molecule is probably best viewed as containing essentially isolated rhenium(III) centres in octahedral environments.

With the exception of the absence of a short Re–Re distance as observed in most other dimeric rhenium(III) species, the geometry of the $[ReCl_3(dppe)]_2$ unit is quite comparable to that of other rhenium(III) derivatives. The terminal Re–Cl bond lengths [2·307(4), 2·322(4) Å] are in good agreement with similar reported Re–Cl

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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distances.[7,12-14] The chlorine atoms of the bridging bonds are slightly further [2·496(3), 2·502(3) Å] from the rhenium atoms than are the terminal chlorines by *ca.* 0·2 Å, as in Re_2Cl_{10}.[15] The Re–P bond lengths [2·370(3) and 2·371(3) Å] agree well with reported values.[12,16]

TABLE 3
Molecular dimensions

(*a*) Bond distances (Å)

Re–Re′	3·809(1)	C(12)–C(13)	1·407(25)
Re–Cl(3)	2·496(3)	C(13)–C(14)	1·362(29)
Re–Cl(3′)	2·502(3)	C(14)–C(15)	1·396(33)
Re–Cl(1)	2·307(4)	C(15)–C(16)	1·396(25)
Re–Cl(2)	2·322(4)	C(16)–C(11)	1·423(21)
Re–P(1)	2·370(3)	C(17)–C(18)	1·395(22)
Re–P(2)	2·371(3)	C(18)–C(19)	1·445(25)
P(1)–C(1)	1·863(14)	C(19)–C(20)	1·432(28)
P(2)–C(2)	1·857(14)	C(20)–C(21)	1·408(29)
C(1)–C(2)	1·596(18)	C(21)–C(22)	1·397(28)
P(1)–C(5)	1·839(14)	C(22)–C(17)	1·394(24)
P(1)–C(11)	1·831(14)	C(23)–C(24)	1·383(26)
P(2)–C(17)	1·808(15)	C(24)–C(25)	1·418(28)
P(2)–C(23)	1·848(15)	C(25)–C(26)	1·403(33)
C(5)–C(6)	1·421(21)	C(26)–C(27)	1·349(31)
C(6)–C(7)	1·422(23)	C(27)–C(28)	1·407(25)
C(7)–C(8)	1·358(30)	C(28)–C(23)	1·396(22)
C(8)–C(9)	1·344(33)	C(3)–C(4)	1·506(33)
C(9)–C(10)	1·451(27)	C(4)–N	1·170(31)
C(10)–C(5)	1·364(24)	Cl(1)–Cl(2′)	3·877(10)
C(11)–C(12)	1·410(20)	Cl(3)–Cl(3′)	3·236(10)

(*b*) Bond angles (°)

Re–Cl(3)–Re′	99·48(13)	C(5)–C(6)–C(7)	117·9(15)
Cl(1)–Re–Cl(2)	177·97(12)	C(6)–C(7)–C(8)	120·6(19)
Cl(1)–Re–Cl(3)	91·77(12)	C(7)–C(8)–C(9)	120·7(20)
Cl(1)–Re–Cl(3′)	89·56(12)	C(8)–C(9)–C(10)	122·0(20)
Cl(1)–Re–P(1)	88·63(12)	C(9)–C(10)–C(5)	116·8(18)
Cl(1)–Re–P(2)	92·06(11)	C(10)–C(5)–C(6)	121·7(14)
Cl(2)–Re–Cl(3)	88·75(11)	P(1)–C(11)–C(12)	121·9(11)
Cl(2)–Re–Cl(3′)	92·46(11)	P(1)–C(11)–C(16)	116·4(10)
Cl(2)–Re–P(1)	89·35(12)	C(11)–C(12)–C(13)	116·7(15)
Cl(2)–Re–P(2)	87·48(12)	C(12)–C(13)–C(14)	122·0(19)
Cl(3)–Re–Cl(3′)	80·71(14)	C(13)–C(14)–C(15)	121·6(19)
Cl(3)–Re–P(1)	98·31(12)	C(14)–C(15)–C(16)	119·2(16)
Cl(3)–Re–P(2)	175·80(11)	C(15)–C(16)–C(11)	118·9(14)
Cl(3′)–Re–P(1)	177·91(15)	C(16)–C(11)–C(12)	121·7(13)
Cl(3′)–Re–P(2)	97·61(12)	P(2)–C(17)–C(18)	121·7(12)
P(1)–Re–P(2)	83·50(11)	P(2)–C(17)–C(22)	118·6(12)
Re–P(1)–C(1)	109·8(5)	C(17)–C(18)–C(19)	119·4(16)
Re–P(2)–C(2)	108·2(5)	C(18)–C(19)–C(20)	119·9(16)
P(1)–C(1)–C(2)	108·2(9)	C(19)–C(20)–C(21)	118·6(18)
P(2)–C(2)–C(1)	108·9(10)	C(20)–C(21)–C(22)	120·3(18)
Re–P(1)–C(5)	119·5(5)	C(21)–C(22)–C(17)	122·0(17)
Re–P(1)–C(11)	116·3(5)	C(22)–C(17)–C(18)	119·8(14)
Re–P(2)–C(17)	114·4(5)	P(2)–C(23)–C(24)	121·1(13)
Re–P(2)–C(23)	119·7(5)	P(2)–C(23)–C(28)	118·0(11)
C(1)–P(1)–C(5)	102·0(6)	C(23)–C(24)–C(25)	120·8(19)
C(1)–P(1)–C(11)	106·5(6)	C(24)–C(25)–C(26)	118·2(21)
C(2)–P(2)–C(17)	107·6(6)	C(25)–C(26)–C(27)	119·7(19)
C(2)–P(2)–C(23)	102·7(6)	C(26)–C(27)–C(28)	123·7(20)
P(1)–C(5)–C(6)	116·2(10)	C(27)–C(28)–C(23)	116·7(16)
P(1)–C(5)–C(10)	121·6(13)	C(28)–C(23)–C(24)	120·9(15)
		C(3)–C(4)–N	177·5(21)

Deviations from regular octahedral geometry about the rhenium atoms result primarily from steric restraints due to the dppe and $ReCl_2Re$ rings. The P–Re–P angle [83·50(11)°] reflects the restraining effect of the C_2H_4 bridge in dppe, a structural feature common to other dppe complexes of rhenium[16-18] and of iridium and rhodium.[19] The acute Cl(3)–Re–Cl(3′) angle [80·71(14)°] is very close to the corresponding angle (81·35°) in the Re_2Cl_{10} structure, which is likewise composed of two octahedra sharing an edge. The phosphorus and ethane carbon atoms are not coplanar with the least-squares plane through the rhenium and bridging chlorine atoms; P(1) and C(1) lie 0·076 and 0·234 Å below and P(2) and C(2) 0·159 and 0·620 Å above this plane.

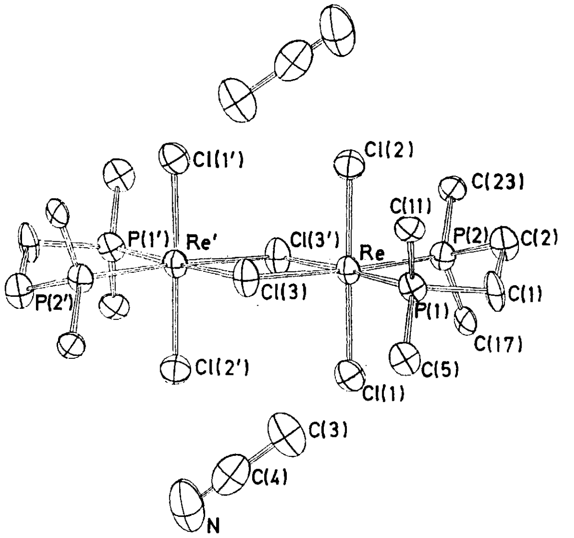

FIGURE 1 The molecular structure showing 50% probability ellipsoids. Primed or unlabelled atoms are related to unprimed atoms by a centre of symmetry

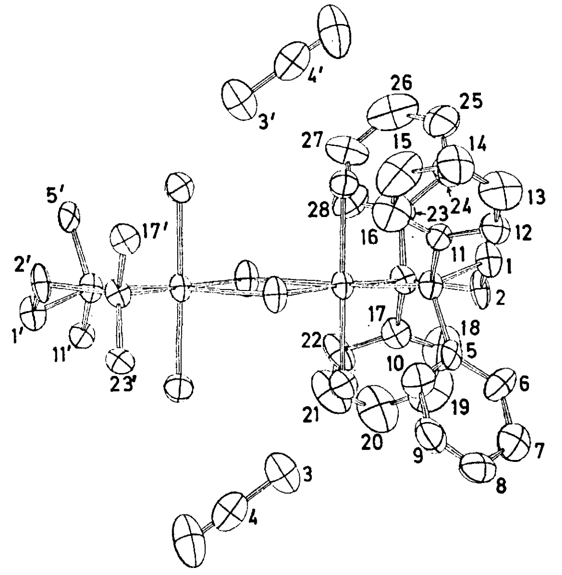

FIGURE 2 Partial molecular structure showing the numbering scheme used for the carbon atoms

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The internal dimensions and angles of the dppe ligand are as expected. The ethane bridge is similarly normal.[19] Mean P–C bond lengths are 1·860 Å, while the mean P–C(phenyl bridge-head) distance is 1·835 Å. The acetonitrile molecules are unexceptional.[13]

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