Tetrachlorobis[1,2-bis(diphenylphosphino)ethane]dirhenium. A Rhenium–Rhenium Triple Bond in a Staggered Conformation

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The title compound has been obtained in crystalline form and its structure determined by X-ray crystallography. The bidentate dppe ligands are bridging and each rhenium atom is coordinated by a trans set of two Cl and two P atoms. The rotational conformation is staggered so that the idealized molecular symmetry is D_2, although the entire molecule constitutes the asymmetric unit. Each six-membered ring, Re–Re–P–C–C–P, has a chair conformation and the two are fused along the Re–Re bond in a manner similar to the *cis*-decalin structure. The Re–Re distance is 2.244 (1) Å. Other important molecular dimensions are Re–Cl(av) = 2.371 (16) Å, Re–P(av) = 2.438 (14) Å, Cl–Re–Cl(av) = 131.4 (10)°, and P–Re–P(av) = 164.6 (1)°. The structure provides the first example of a symmetrical Re–Re triple bond with a staggered conformation, and the Re–Re distance supports the view that the δ component of Re–Re quadruple bonds has very little effect on the length of the bond. The basic crystallographic data are as follows: space group $P2_1/n$; unit cell dimensions a = 22.976 (11) Å, b = 13.180 (4) Å, c = 16.693 (5) Å, β = 107.43 (6)°; Z = 4.

Introduction

The first triple bond between metal atoms,[2] discovered in 1966, was between rhenium atoms. It was found that reaction of excess $CH_3SCH_2CH_2SCH_3$, dithiahexane (DTH), with the $Re_2Cl_8{}^{2-}$ ion produced the compound $Re_2Cl_5(DTH)_2$ and that this consisted of the dinuclear units **1** linked into infinite chains


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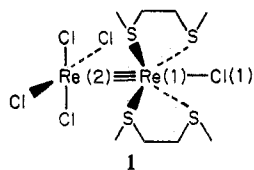
by loose interaction of Cl(1) on each molecule with Re(2) on another. The Re–Re distance in **1** is about 0.06 Å longer than those in the species then known and structurally characterized with Re–Re quadruple bonds, principally $Re_2Cl_8{}^{2-}$ and $Re_2Cl_6(PEt_3)_2$. This led to the tentative suggestion that the δ component of the quadruple bond might shorten the bond by about 0.06 Å. It was also evident from the structure of this molecule that loss of the δ component of the bond leads, as expected, to a staggered rotational conformation about the metal–metal bond.

Staggered conformations in molecules with metal–metal triple bonds have now been observed in numerous molecules[3] of the type $X_3M\equiv MX_3$ (M = Mo, W) and for $Mo_2(OSiMe_3)_6(NHMe_2)_2$,[4] in which each metal atom forms four bonds to ligand atoms. On the other hand, the molecule $Mo_2(O_2CCMe_3)_2(OCMe_3)_4$ nicely shows how the restraining effect of two bridging carboxylato groups can enforce an essentially eclipsed configuration even when there is no δ bond.[5]

It is interesting, however, that with dirhenium species further examples of the staggered configuration have not yet been documented. In each of two further Re–Re triple bonds there has been a steric reason for the maintenance of an eclipsed configuration. In the mixed oxide $La_4Re_2O_{10}$ each Re_2O_8 subunit has D_{4h} symmetry,[6] but this may be attributed to the demands of the tetragonally distorted fluorite structure of which it is a part. Similarly, in the $Re_2Cl_4(PEt_3)_4$ molecule an eclipsed configuration (D_{2d} symmetry) is found,[7] but it has been pointed out[7] that this could be due entirely to the steric requirements of the PEt_3 groups; when these very large groups are staggered with respect to one another, the entire set of eight ligands is eclipsed, as shown in **2**. Thus, the eclipsed configuration in this case argues neither for nor against the presence of a δ bond.

However, structure **2** appears now to have misled us regarding the presence of a δ bond for a different reason. The Re–Re distance, 2.232 (5) Å, is essentially the same as the

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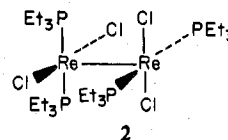
Re–Re distances, ~2.24 Å, in quadruply bonded species such as $Re_2Cl_8{}^{2-}$ $Re_2Cl_6(PEt_3)_2$, and this led us to suppose that the two additional electrons beyond the $\sigma^2\pi^4\delta^2$ configuration occupy an orbital which is nonbonding with respect to the Re–Re interaction, thus appearing to disallow their assignment to the δ^* orbital. However, an SCF–Xα–SW molecular orbital calculation[8] for $Re_2Cl_4(PH_3)_4$ has unequivocally produced a $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration.

In order to reconcile this computational result with all of the available experimental data, including the unambiguous observation that loss of one δ bonding electron from [Mo$_2$(SO$_4$)$_4$]$^{4-}$ causes an increase of 0.06 Å in the Mo–Mo distance, we tentatively adopted the following hypotheses. (1) Since many factors influence the lengths of M–M quadruple bonds, the change of 0.06 Å seen in $Re_2Cl_5(DTH)_2$ compared to $Re_2Cl_8{}^{2-}$ and $Re_2Cl_6(PEt_3)_2$ need not simply reflect the loss of the δ bond. It might, instead, be due to the unique character of the $Re_2Cl_5(DTH)_2$ molecule, for which we believe a true mixed-oxidation-state formulation, with Re(1) being formally Re^{2+} and Re(2) formally Re^{3+}, is appropriate. (2) The capacity of the relatively weak δ component to influence M–M distances might be much less in the third transition series than in the second. This notion received experimental support from the observation that while the lengths of Mo–Mo quadruple bonds, of which that in $Mo_2Me_8{}^{4-}$, 2.148 (2) Å,[9] is typical, are significantly less than those of Mo–Mo triple bonds[3] (which range from 2.16 to 2.22 Å), the comparable W–W quadruple bonds, in $W_2Me_8{}^{4-}$ (2.264 (3) Å[10a]) and [W$_2$Cl$_{8-x}$Me$_x$]$^{4-}$ (2.263 (2) Å[10b]), are very similar to those, 2.26–2.30 Å, in triply bonded W–W species.[3] In these comparisons we are comparing the same types of molecules for molybdenum and for tungsten, i.e., M_2X_6 types for the triple bonds. From a theoretical point of view such a difference in behavior can be understood by assuming that the presence of a filled inner 4f shell in the W and Re atoms makes them virtually incompressible (at the tremendously close internuclear distances concerned) compared to the Mo atom, so that once the σ and two π components have brought a pair of W or Re atoms to a distance such as 2.26 or 2.23 Å, the δ component, though it may add upward of 10 kcal/mol to the bond energy, cannot further shorten the bond very much.

To explore more fully this interesting and important question, it is obviously desirable to look at the structures of still other triply bonded dirhenium molecules, especially those

in which δ bonding is absent because the δ bond is canceled by the presence of a pair of electrons in the δ^* orbital. A prime candidate for such study is the $Re_2Cl_4(dppe)_2$ molecule, **3**, which can be obtained in good yield by reacting 1,2-bis(diphenylphosphino)ethane, dppe, with $Re_2Cl_4(PEt_3)_4$.[11] For this species it had already been anticipated from model building that a staggered structure with bridging dppe groups would be the most stable. Thus, **3** should present a truly representative example of a Re–Re triple bond in the context of a staggered but symmetrical set of eight ligand atoms.

Some crystals of **3** were first examined several years ago, even before the problem assumed its present interest, as just explained, but those showed evidence of extensive disorder and no effort was then made to solve the structure. When we encountered, more recently, a crystal showing no superficial evidence of disorder (though some was later found), a structure determination was promptly begun, the results of which are reported and discussed here.

Experimental Section

A crystalline sample of the compound was obtained by procedures already described.[11] The compound appears to be entirely stable in air and was handled without any form of protection.

X-ray Data Collection. Several crystals were ground to approximately spherical shape, and one with a radius of 0.104 mm was attached with epoxy cement to a glass fiber and mounted on a modified Syntex $P\bar{1}$ automated diffractometer. All data were collected at 3 ± 1 °C using Cu Kα radiation with a graphite-crystal monochromator in the incident beam. Details of the crystallographic procedures and the methods for solution and refinement of the structure have been previously described.[12] From axial photographs 15 reflections were computer centered and the resulting setting angles were used in the autoindexing program to select the best unit cell. The crystal was found to be monoclinic. The following cell constants were obtained by least-squares refinement using 15 reflections collected in a 2θ range of 50–70°: $a = 22.976$ (11) Å, $b = 13.180$ (4) Å, $c = 16.693$ (5) Å, $\beta = 107.43$ (3)°; $V = 4823$ (5) Å^3; $d_{calcd} = 1.81$ g/cm^3 for $Z = 4$ and a molecular weight of 1311.07.

A total of 7012 unique reflections were measured using the θ–2θ scan technique in the range 0° < 2θ < 122°. Variable scan rates from 4 to 24° min^{-1} were used with a symmetric scan range from 1.0° below the Cu Kα_1 peak to 1.0° above the Cu Kα_2 peak. Three standard reflections measured every 100 data points showed only small, random variations.

Solution and Refinement of the Structure. The structure was solved in the space group $P2_1/n$ (identified from systematic absences) using only those 5066 reflections with $F_o^2 > 3\sigma(F_o^2)$. The linear absorption coefficient for the compound is 129.12 cm^{-1} and a spherical absorption correction was performed ($\mu r = 1.3$). The positions of two rhenium atoms were determined from a three-dimensional Patterson map. These coordinates were improved by three cycles of least-squares refinement to give discrepancy indices

$$R_1 = \Sigma ||F_o| - |F_c||/|F_o| = 0.322$$

$$R_2 = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2} = 0.432$$

The function minimized during all least-square refinements was $\Sigma w(|F_o| - |F_c|)_2$, where the weighting factor, w, equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for the "ignorance" factor, ρ, in the calculation of σ.[12]

A difference Fourier map revealed the positions of the four chlorine and four phosphorus atoms. Subsequent least-squares refinements and difference Fourier maps located the remaining 52 carbon atoms. The positions of the nonhydrogen atoms were isotropically refined by four full-matrix least-squares cycles yielding $R_1 = 0.105$ and $R_2 = 0.147$. The two rhenium, four chlorine, and four phosphorus atoms were then refined anisotropically to convergence in three full-matrix least-squares cycles with $R_1 = 0.087$ and $R_2 = 0.123$.

At this point the difference Fourier map suggested the presence of another Re$_2$ unit located perpendicular to and midway between the established rhenium positions, but with a low occupancy. Disorder of this general type has previously been observed for Mo$_2$Cl$_8^{4-}$,[13] Re$_2$Cl$_8^{2-}$,[14] and most recently Re$_2$(CH$_3$)$_8^{2-}$.[15] Peak intensities from Fourier and difference Fourier maps indicated an occupancy of

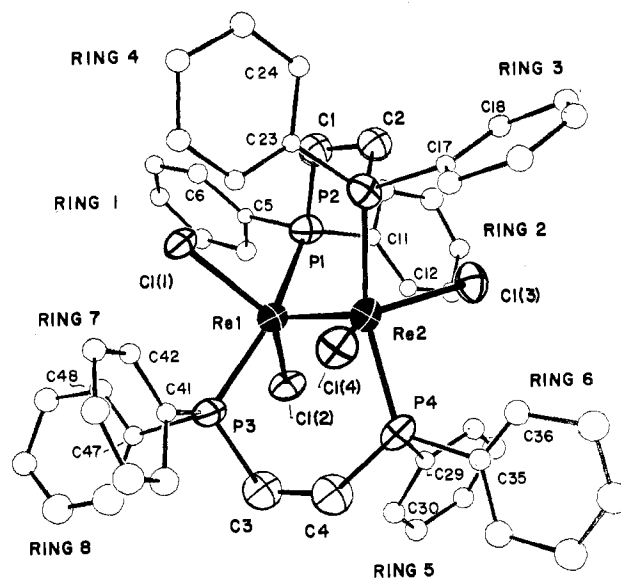**Figure 1.** ORTEP drawing of the entire Re$_2$Cl$_4$(dppe)$_2$ molecule, showing how the atoms are labeled. Numbers for unlabeled ring atoms follow from those given. Each atom is represented by its ellipsoid or sphere of thermal vibration scaled to enclose 35% of the electron density for the central atoms and 10% for the phenyl carbon atoms.
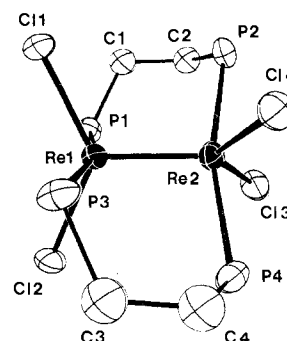

Figure 2. View of the central part of the Re$_2$Cl$_4$(dppe)$_2$ molecule emphasizing that the two C–C and the Re–Re bonds are practically parallel.

approximately 10%. Isotropic refinement of the disordered positions with a fixed multiplicity of 0.10 resulted in a significant drop in the residuals to $R_1 = 0.071$ and $R_2 = 0.104$, with the error in the observation of unit weight dropping from 2.66 to 2.16. Four full-matrix least-squares cycles using fixed isotropic B values equivalent to those of the majority rhenium atoms before they went anisotropic and variable multiplicities converged giving $R_1 = 0.0630$ and $R_2 = 0.0916$ with a final error in the observation of unit weight of 1.957. The occupancy of the minor rhenium atoms refined to 7% with the occupation of the principal rhenium atom sites kept fixed at 100%. No attempt was made to find additional sites for lighter atoms. The final difference Fourier map was featureless.

Results

The positional and thermal parameters for all atoms in the asymmetric unit, as well as the two partial rhenium atoms, are listed in Table I. The internuclear distances and bond angles that are pertinent to the metal–metal bond and the coordination chemistry are listed in Table II. Figure 1 shows an overall view of the molecule in which the numbering scheme is defined. Figures 2 and 3 show only the central portion of the molecule and emphasize the conformational features therein.

While the molecule has no crystallographic symmetry, it does have virtual D_2 symmetry, the recognition of which is helpful in describing and understanding it. The first of the three C_2 axes is, rather obviously, coincident with the Re–Re

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a, b]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	0.30867 (3)	0.29768 (5)	−0.01569 (4)	0.00151 (1)	0.00426 (3)	0.00394 (2)	−0.00009 (3)	0.00170 (3)	−0.00003 (5)
Re(2)	0.24903 (3)	0.19842 (5)	0.03587 (4)	0.00146 (1)	0.00490 (4)	0.00407 (3)	−0.00086 (4)	0.00101 (3)	0.00058 (5)
Re(3)	0.2360 (4)	0.2894 (6)	−0.0232 (5)	$B = 3.2500$ (0)					
Re(4)	0.3174 (5)	0.2256 (8)	0.0709 (6)	$B = 3.2500$ (0)					
Cl(1)	0.2640 (2)	0.4547 (2)	−0.0728 (2)	0.00228 (7)	0.0039 (2)	0.0049 (1)	0.0010 (2)	0.0021 (2)	0.0011 (3)
Cl(2)	0.4059 (1)	0.2268 (3)	0.0008 (2)	0.00148 (6)	0.0060 (2)	0.0065 (2)	0.0009 (2)	0.0025 (2)	−0.0001 (3)
Cl(3)	0.2841 (2)	0.1558 (3)	0.1816 (2)	0.00212 (7)	0.0090 (3)	0.0043 (1)	0.0005 (3)	0.0015 (2)	0.0032 (4)
Cl(4)	0.1577 (2)	0.1559 (3)	−0.0681 (2)	0.00172 (7)	0.0071 (2)	0.0050 (2)	−0.0013 (2)	−0.0003 (2)	−0.0002 (4)
P(1)	0.3507 (2)	0.3992 (3)	0.1092 (2)	0.00157 (6)	0.0049 (2)	0.0049 (2)	−0.0017 (2)	0.0020 (2)	−0.0016 (3)
P(2)	0.1971 (2)	0.3312 (3)	0.0899 (2)	0.00168 (7)	0.0066 (2)	0.0043 (1)	−0.0017 (2)	0.0022 (2)	−0.0010 (3)
P(3)	0.2832 (2)	0.2247 (3)	−0.1574 (2)	0.00299 (9)	0.0048 (2)	0.0040 (1)	0.0019 (2)	0.0015 (2)	−0.0005 (3)
P(4)	0.2880 (2)	0.0369 (3)	0.0032 (3)	0.00210 (8)	0.0044 (2)	0.0054 (2)	−0.0001 (2)	0.0006 (2)	0.0011 (3)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
C(1)	0.2926 (7)	0.472 (1)	0.1422 (9)	4.6 (3)	C(27)	0.0834 (8)	0.485 (1)	−0.1065 (11)	5.6 (4)
C(2)	0.2513 (7)	0.406 (1)	0.1734 (9)	4.6 (3)	C(28)	0.1257 (7)	0.418 (1)	−0.0612 (9)	4.5 (3)
C(3)	0.3036 (8)	0.089 (1)	−0.1541 (11)	6.0 (4)	C(29)	0.3670 (7)	−0.007 (1)	0.0550 (10)	4.9 (3)
C(4)	0.2731 (9)	0.018 (2)	−0.1091 (12)	6.4 (4)	C(30)	0.4019 (9)	−0.040 (2)	0.0053 (12)	6.6 (4)
C(5)	0.3984 (6)	0.498 (1)	0.0894 (8)	3.8 (3)	C(31)	0.4650 (9)	−0.075 (2)	0.0489 (13)	7.4 (5)
C(6)	0.3773 (8)	0.594 (1)	0.0631 (11)	6.2 (4)	C(32)	0.4835 (9)	−0.077 (2)	0.1340 (13)	6.9 (5)
C(7)	0.4166 (8)	0.670 (1)	0.0491 (11)	5.8 (4)	C(33)	0.4470 (10)	−0.045 (2)	0.1835 (13)	7.7 (5)
C(8)	0.4758 (8)	0.651 (2)	0.0612 (12)	6.4 (4)	C(34)	0.3886 (9)	−0.010 (2)	0.1408 (12)	6.6 (4)
C(9)	0.4988 (9)	0.557 (2)	0.0836 (13)	7.3 (5)	C(35)	0.2467 (8)	−0.071 (1)	0.0326 (11)	5.9 (4)
C(10)	0.4606 (9)	0.476 (2)	0.0984 (12)	6.7 (5)	C(36)	0.2045 (10)	−0.055 (2)	0.0708 (13)	7.3 (5)
C(11)	0.4036 (7)	0.347 (1)	0.2044 (9)	4.6 (3)	C(37)	0.1662 (12)	−0.135 (2)	0.0995 (16)	10.0 (7)
C(12)	0.4218 (7)	0.248 (1)	0.2111 (10)	4.8 (3)	C(38)	0.1878 (13)	−0.227 (2)	0.0821 (17)	10.9 (8)
C(13)	0.4643 (9)	0.212 (2)	0.2825 (13)	6.9 (5)	C(39)	0.2267 (13)	−0.254 (2)	0.0331 (18)	11.5 (8)
C(14)	0.4920 (9)	0.274 (2)	0.3483 (12)	6.9 (5)	C(40)	0.2615 (11)	−0.170 (2)	0.0061 (15)	8.7 (6)
C(15)	0.4762 (11)	0.369 (2)	0.3511 (15)	9.1 (6)	C(41)	0.2052 (7)	0.234 (1)	−0.2319 (9)	4.4 (3)
C(16)	0.4300 (10)	0.413 (2)	0.2736 (14)	7.9 (5)	C(42)	0.1744 (7)	0.322 (1)	−0.2384 (10)	5.1 (3)
C(17)	0.1464 (7)	0.275 (1)	0.1434 (9)	4.3 (3)	C(43)	0.1145 (8)	0.328 (1)	−0.2925 (11)	5.7 (4)
C(18)	0.1584 (8)	0.281 (1)	0.2285 (11)	5.6 (4)	C(44)	0.0892 (10)	0.249 (2)	−0.3396 (13)	7.7 (5)
C(19)	0.1146 (8)	0.239 (2)	0.2666 (11)	6.1 (4)	C(45)	0.1254 (12)	0.163 (2)	−0.3395 (16)	9.7 (7)
C(20)	0.0633 (9)	0.197 (1)	0.2172 (12)	6.4 (4)	C(46)	0.1866 (11)	0.151 (2)	−0.2865 (15)	9.0 (6)
C(21)	0.0518 (9)	0.188 (2)	0.1341 (13)	7.0 (5)	C(47)	0.3295 (7)	0.278 (1)	−0.2226 (10)	5.0 (3)
C(22)	0.0938 (8)	0.230 (1)	0.0940 (11)	6.0 (4)	C(48)	0.3486 (9)	0.374 (2)	−0.2129 (12)	6.9 (5)
C(23)	0.1428 (6)	0.425 (1)	0.0237 (8)	3.7 (3)	C(49)	0.3808 (11)	0.425 (2)	−0.2598 (15)	8.6 (6)
C(24)	0.1178 (7)	0.498 (1)	0.0666 (10)	4.9 (3)	C(50)	0.3903 (10)	0.364 (2)	−0.3239 (14)	8.3 (6)
C(25)	0.0746 (9)	0.566 (2)	0.0168 (12)	6.5 (4)	C(51)	0.3752 (14)	0.269 (3)	−0.3292 (20)	12.5 (9)
C(26)	0.0558 (8)	0.561 (1)	−0.0722 (11)	5.7 (4)	C(52)	0.3392 (15)	0.223 (3)	−0.2873 (21)	12.9 (10)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's in the least significant digits.
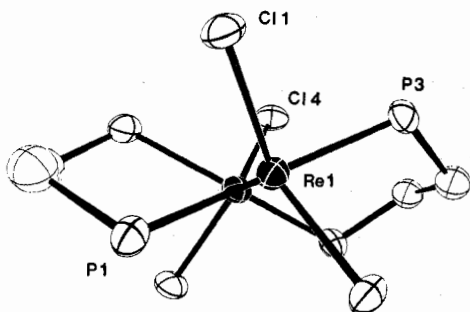

Figure 3. View of the central part of the Re₂Cl₄(dppe)₂ molecule emphasizing the eclipsed configuration and the *cis*-decalin-like fusion of the two chair-form rings.

bond. The second one bisects the two C–C bonds in the bridging PCCP chains; it is horizontal in Figure 3. The third one, also a perpendicular bisector of the Re–Re bond and, necessarily, perpendicular to the first two, bisects the two lines which can be drawn between the pairs of nongeminal chlorine atoms; it is approximately vertical in Figure 3.

Each of the six-membered rings formed by the rhenium atoms and the PCCP chains has a chair conformation. The two rhenium atoms and the two carbon atoms of the PCCP chain are virtually coplanar and the phosphorus atoms are on opposite sides of this plane. The two chairs share a common edge, the Re–Re bond; their conformations are related as in

cis-decalin, as may be clearly seen in Figure 3.

The rotational conformation about the Re–Re bond can be described as staggered, but the bonds on one end do not lie precisely halfway between those on the other end. Instead, four of the angles seen in projection down the Re–Re axis, namely, the Cl–Re₂–Cl and the P–Re₂–P angles, are 51° and the others are 39°. These deviations from 45° can doubtless be attributed to conformational demands of the six-membered rings.

A few words about the fractional (7%) disordering of the molecules are necessary. Because of the small fraction of molecules in the secondary orientation, we did not expect to be able to find any definite indication of a second set of positions for any of the lighter atoms and no attempt was made to do so. In fact, the disordering is such that those in the second sets could well be indistinguishable from those in the main set with this near superposition of all peripheral atoms being the feature that makes the disorder possible. It might seem at first thought that to tilt a molecule as complex and relatively unsymmetrical as this one by 90° and still have it fit into the main packing pattern would be impossible. It turns out that a remarkably good, though not by any means perfect, fit can be obtained when the second orientation of the Re–Re unit is along the third of the C_2 axes described earlier in this section. With respect to Re–Cl bonding, in fact, the two orientations are of almost exactly equal merit, because the geminal Cl···Cl distances and the shorter of the distances between Cl atoms on different rhenium atoms are almost

Table II. Interatomic Distances (Å) and Angles (deg) for Atoms Not Belonging to Phenyl Groups[a]

(A) Distances

Re(1)–Re(2)	2.244 (1)	P(1)–C(11)	1.82 (1)
Re(1)–Cl(1)	2.378 (2)	P(2)–C(2)	1.85 (1)
Re(1)–Cl(2)	2.359 (2)	P(2)–C(17)	1.83 (1)
Re(1)–P(1)	2.422 (3)	P(2)–C(23)	1.87 (1)
Re(1)–P(3)	2.457 (3)	P(3)–C(3)	1.84 (1)
Re(2)–Cl(3)	2.389 (3)	P(3)–C(41)	1.85 (1)
Re(2)–Cl(4)	2.356 (3)	P(3)–C(47)	1.87 (1)
Re(2)–P(2)	2.438 (3)	P(4)–C(4)	1.82 (1)
Re(2)–P(4)	2.434 (3)	P(4)–C(29)	1.85 (1)
P(1)–C(1)	1.85 (1)	P(4)–C(35)	1.86 (1)
P(1)–C(5)	1.80 (1)	C(1)–C(2)	1.49 (2)
		C(3)–C(4)	1.50 (2)

(B) Angles

Re(2)–Re(1)–Cl(1)	114.91 (7)	Re(1)–Re(2)–Cl(3)	118.00 (7)
Re(2)–Re(1)–Cl(2)	112.93 (7)	Re(1)–Re(2)–Cl(4)	111.55 (8)
Re(2)–Re(1)–P(1)	97.10 (7)	Re(1)–Re(2)–P(2)	98.41 (7)
Re(2)–Re(1)–P(3)	98.29 (8)	Re(1)–Re(2)–P(4)	96.65 (8)
Cl(1)–Re(1)–Cl(2)	132.13 (9)	Cl(3)–Re(2)–Cl(4)	130.4 (1)
P(1)–Re(1)–P(3)	164.6 (1)	P(2)–Re(2)–P(4)	164.7 (1)
Cl(1)–Re(1)–P(1)	82.9 (1)	Cl(3)–Re(2)–P(2)	81.1 (1)
Cl(1)–Re(1)–P(3)	90.28 (9)	Cl(3)–Re(2)–P(4)	89.3 (1)
Cl(2)–Re(1)–P(1)	89.9 (1)	Cl(4)–Re(2)–P(2)	91.0 (1)
Cl(2)–Re(1)–P(3)	84.4 (1)	Cl(4)–Re(2)–P(4)	86.2 (1)
Re(1)–P(1)–C(1)	113.8 (4)	Re(2)–P(2)–C(2)	111.6 (4)
Re(1)–P(1)–C(5)	110.5 (4)	Re(2)–P(2)–C(17)	110.1 (4)
Re(1)–P(1)–C(11)	122.2 (4)	Re(2)–P(2)–C(23)	124.9 (4)
C(1)–P(1)–C(5)	102.3 (5)	C(2)–P(2)–C(17)	103.5 (5)
C(1)–P(1)–C(11)	106.7 (5)	C(2)–P(2)–C(23)	105.7 (5)
C(5)–P(1)–C(11)	98.5 (5)	C(17)–P(2)–C(23)	98.5 (5)
Re(1)–P(3)–C(3)	111.4 (5)	Re(2)–P(4)–C(4)	112.5 (5)
Re(1)–P(3)–C(41)	121.5 (4)	Re(2)–P(4)–C(29)	123.0 (4)
Re(1)–P(3)–C(47)	113.6 (4)	Re(2)–P(4)–C(35)	111.1 (5)
C(3)–P(3)–C(41)	105.8 (6)	C(4)–P(4)–C(29)	107.1 (6)
C(3)–P(3)–C(47)	101.4 (6)	C(4)–P(4)–C(35)	102.3 (6)
C(41)–P(3)–C(47)	100.8 (5)	C(29)–P(4)–C(35)	98.2 (6)
P(1)–C(1)–C(2)	113.4 (8)	P(3)–C(3)–C(4)	118 (1)
P(2)–C(2)–C(1)	113.6 (8)	P(4)–C(4)–C(3)	117 (1)

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

exactly equal. With respect to the phosphorus atoms, however, there is a considerable mismatch, since in the second Re_2 orientation the two phosphorus atoms bound to the same rhenium atom are much (ca. 1.5 Å) too far apart if the dppe ligands retain exactly the positions appropriate to the main pair of rhenium atoms. Nonetheless, the observed placement of the subsidiary Re_2 unit is not too difficult to rationalize. It should be noted that no indication of Re atoms was seen along the third twofold axis, nor is this surprising since that would require an extremely unlikely form of chelation with phosphorus atoms roughly trans to each other and subtending a very small angle at the Re atom.

Discussion

The structure described here helps to clarify and confirm our understanding of M–M triple and quadruple bonds, although some interesting ambiguities remain, as will be pointed out later. We have here an unambiguous case in which a net triple bond results because two δ* electrons are present to cancel the effect of two δ electrons, and the configuration is staggered. The Re–Re distance, 2.244 (1) Å, is essentially the same as that in the eclipsed molecule $Re_2Cl_4(PEt_3)_4$, 2.232 (5) Å, and in the quadruply bonded species $Re_2Cl_6(PEt_3)_2$, 2.222 (3) Å,[16] and $Re_2Cl_8^{2-}$, also 2.222 (1) Å.[14] There may, in fact, be a small lengthening in $Re_2Cl_4(dppe)_2$ as compared to the two quadruply bonded species of 0.022 (4) Å, but

certainly the previously held belief that mere loss of δ bonding would necessarily cause a lengthening of ca. 0.06 Å is no longer tenable. Thus, it now appears quite possible that, as suggested in the Introduction, the quadruple bonds between metal atoms in the third transition series owe little if any of their shortness to the δ component of the bond, even though this component appears to have a distinct effect (≥ 0.06 Å) on the length of Mo–Mo quadruple bonds.

The staggered configuration is to be expected since the Re–Re triple bond imposes no rotational barrier, but it is not clear whether it is primarily nonbonded repulsions between ligated atoms or conformational preferences of the rings, or both in concert, that are responsible for the observed rotational conformation. The conformational preference of the rings certainly favors the observed structure, or something close to it, since an eclipsed structure would require the rings to have boat configurations. It could even be argued (from the point of view of the devil's advocate, but still with some force) that the present structure may not necessarily imply that rotation to a staggered conformation is a *consequence* of losing the δ bond since the forces favoring a staggered conformation could conceivably be sufficiently strong to overpower a modest (say ≤ 20 kcal mol^{-1}) δ bond. Indeed, the argument might run that loss of the δ bond is a consequence of the staggered conformation being imposed by the combined action of a variety of other forces. It is important to recognize, however, that even if this be the case, we are still dealing with a triple bond, since the δ bond cannot exist in the staggered configuration, regardless of what causes the configuration to be staggered.

The fact that the Re–Re bond length here is essentially equal to that in $Re_2Cl_4(PEt_3)_4$, the difference being equal to only twice the sum of the esd's, and, if different, slightly longer, is significant. It suggests that repulsive forces between ligand atoms on one metal atom and those on the other do not vary enough from one rotamer to another to affect the Re–Re distance.

Supplementary Material Available: A table of observed and calculated structure factors and a table of distances and angles in the phenyl groups (25 pages). Ordering information is given on any current masthead page.

References and Notes

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