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Structural Studies on $M_2X_4(PR_3)_4$ Compounds (M = Re, W; X = Cl, Br; R = Me, *n*-Pr, *n*-Bu). The First Examples of Simple Three-Way Disorder of Dimetal Units within Ordered Ligand Cages

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The following, previously known, multiply bonded dirhenium and ditungsten compounds have been characterized by X-ray crystallography: $Re_2Cl_4(PMe_3)_4$ (**1**), $[Re_2Cl_4(PMe_3)_4]ReO_4$ (**2**), $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (**3**), $Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (**4**), and $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4{\cdot}C_7H_8$ (**5**). Pertinent crystal data are as follows: for **1**, monoclinic space group *C*2/*c*, a = 18.058 (3) Å, b = 9.247 (1) Å, c = 18.725 (2) Å, β = 124.64 (1)°, V = 2572 (1) Å^3, Z = 4; for **2**, orthorhombic space group *Pmcn*, a = 14.166 (2) Å, b = 9.799 (2) Å, c = 20.836 (4) Å, V = 2892 (1) Å^3, Z = 4; for **3**, monoclinic space group *I*2/*a*, a = 18.564 (6) Å, b = 14.766 (6) Å, c = 19.283 (5) Å, β = 106.21 (2)°, V = 5076 (3) Å^3, Z = 4; for **4**, monoclinic space group *C*2/*c*, a = 18.513 (5) Å, b = 14.767 (4) Å, c = 19.381 (6) Å, β = 104.57 (2)°, V = 5128 (2) Å^3, Z = 4; for **5**, triclinic space group $P\bar{1}$, a = 13.947 (1) Å, b = 20.743 (7) Å, c = 13.612 (6) Å, α = 96.28 (3)°, β = 117.78 (2)°, γ = 74.73 (2)°, V = 3361 (2) Å^3, Z = 2. Complexes **3**–**5** exhibit an unprecedented form of crystallographic disorder for this type of compound in which the dimetal unit adopts three orientations within a quasi-cube of halide and phosphine ligands. These complexes have the dimetal unit in three orientations with occupancies of 43%, 29%, 28% for **3**, 50%, 32%, 18% for **4**, and 88%, 8.5%, 3.5% for **5**. Compounds **1** and **2** are not disordered in any way. The role played by the size and shape of the phosphine in promoting this type of disorder is discussed.

Introduction

The tendency of the M_2 units to be disordered within the quasi-cube cages formed by the eight ligand atoms in $M_2X_8^{2-}$ species, as well as in their substituted derivatives, has been recognized for some years.[1] There are, of course, a number of cases in which no disorder is detected, while at the other extreme there are cases where the M_2 units are found equally in all three principal directions within the cube. This occurs in those cases, namely, in $(n\text{-}NBu_4)_2Re_2I_8$[2] and $Re_2Cl_6(PEt_3)_2$ in one[3] but not the other[4] of its two crystalline forms, when the quasi-cube lies in the crystal with one of its body diagonals along a crystallographic 3-fold axis. The most extreme disorder of all has been found in $Re_2Cl_4(PEt_3)_4$[5] and $Mo_2Cl_4(PEt_3)_4$,[6] where the M_2 units occupy equally all three principal orientations and in addition the PEt_3 and Cl ligands are disordered so that there appears to be half of each at each vertex of the cube. In these two cases the crystallographic site symmetry is O_h.

We have been interested in trying to understand what factors determine the type and extent of disorder that occurs. We have recently observed the first examples of 3-fold *but unequal* disorder in some $Re_2X_8^{2-}$ systems, and we have discussed the behavior of their ionic systems in terms of the role of Coulombic forces.[7] In this report we turn our attention to the behavior of $M_2X_4L_4$ systems. Prior to this work, 14 such compounds have been studied (see Results and Discussion for details) but only in the two $M_2Cl_4(PEt_3)_4$ compounds mentioned above has any disorder been found, and in these cases it was of the most extreme type, as just noted. We wondered if the ligands could not be so chosen as to produce an intermediate type of disorder, and we formulated a hypothesis as to what sort of ligands would give this result. In this paper we describe our experimental results, which reveal the first examples of $M_2X_4(PR_3)_4$ compounds to show an ordered set of ligands within which there are disordered M_2 units.

Experimental Section

Compounds **1**, **3**, and **4** were prepared by the method of Walton et al.[8] The block-shaped crystals, all of which were dark blue-green, grew on a pine boiling stick that was placed in the reaction flask. Compound **2** was prepared serendipitously by placing a small quantity (≈0.2 g) of **1** dissolved in 10 mL of dichloromethane in a Schlenk tube and then layering with 20 mL of isomeric hexanes. The tube was inadvertently exposed to air. After a period of 1 week, platelike orange crystals of **2** appeared on the walls of the tube; yield ≈60%. We have found this method of making **2** to be entirely reproducible. Compound **5** was prepared by the method of Schrock et al.[9] Suitable crystals were obtained by layering a toluene solution of $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ with methanol at −10 °C. After a few days block-shaped, blue-green crystals of **5** had formed.

X-ray Crystallography. The structures of all five complexes were determined by general methods which have been fully described elsewhere.[10] Data reductions and refinements were carried out by standard methods using well-established computational procedures.[11] The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II–VI list the positional and thermal parameters for structures **1**–**5**, respectively. Selected bond distances and bond angles are found in Tables VII and VIII, respectively. An ORTEP diagram of **1** is shown in Figure 1. The Re, halogen, and P atoms of **3** and **4** are numbered in a similar way. ORTEP diagrams of **2** and **5** are shown in Figures 2 and 3, respectively. Complete tables of crystal parameters, data collection, structure refinement, bond distances, and bond angles as well as structure factors are available as supplementary material.

$Re_2Cl_4(PMe_3)_4$ (1). The Patterson peak search and the direct-methods program in SHELXS-86[12] led to the location of the two Re atoms and also the immediate coordination sphere of eight atoms. At this stage no distinction could be made between chlorine and phosphorus atoms, and so all were tentatively treated as chlorine atoms. After a sequence of successive least-squares cycles and difference Fourier maps, using the SHELX-76[13] package, it became apparent which were the phosphorus atoms, since all carbon atoms were located with P–C bond lengths of ≃1.8 Å. All hydrogen atoms belonging to the methyl groups were also located and refined isotropically. Subsequent anisotropic refinement on the rest of the molecule was successfully completed to give residuals of R =

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Table I. Crystal Data for Compounds **1–5**

compd	$Re_2Cl_4(PMe_3)_4$	$[Re_2Cl_4(PMe_3)_4]ReO_4$	$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$	$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$	$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4{\cdot}C_7H_8$
formula	$Re_2Cl_4P_4C_{12}H_{36}$	$Re_3O_3Cl_4P_4C_{12}H_{36}$	$Re_2Cl_4P_4C_{36}H_{84}$	$Re_2Br_4P_4C_{36}H_{84}$	$W_2Cl_4P_4C_{55}H_{116}$
fw	818.53	1068.74	1155.18	1332.98	1410.95
space group	*C*2/*c* (No. 15)	*Pmcn* (No. 62)	*Ia*/2 (No. 15)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	18.058 (3)	14.166 (2)	18.564 (6)	18.513 (5)	13.947 (1)
b, Å	9.247 (1)	9.799 (2)	14.766 (6)	14.767 (4)	20.743 (7)
c, Å	18.725 (2)	20.836 (4)	19.283 (5)	19.381 (6)	13.612 (6)
α, deg	90.000	90.000	90.000	90.000	96.28 (3)
β, deg	124.64 (1)	90.000	106.21 (2)	104.57 (2)	117.78 (2)
γ, deg	90.000	90.000	90.000	90.000	74.73 (2)
V, Å^3	2572 (1)	2892 (1)	5076 (3)	5128 (2)	3361 (2)
Z	4	4	4	4	2
d_{calc}, g/cm^3	2.113	2.456	1.512	1.726	1.394
μ(Mo Kα), cm^{-1}	101.96	133.20	51.898	80.153	37.79
radiation monochromated in incident beam: $\lambda_{Mo\,K\alpha}$, Å	0.71073	0.71073	0.71073	0.71073	0.71073
temp, °C	22 ± 2	22 ± 2	22 ± 2	20 ± 2	−80 ± 2
transm factors: max, min	99.73, 83.95	99.99, 53.76	99.99, 69.21	99.51, 53.35	99.99, 81.61
R[a]	0.0275	0.0537	0.0564	0.0776	0.0418
R_w[b]	0.0355	0.0624	0.0769	0.0967	0.0570

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $W = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $Re_2Cl_4(PMe_3)_4$ (**1**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Re(1)	0.000	0.15672 (5)	0.750	1.844 (9)
Re(2)	0.000	−0.08624 (5)	0.750	1.877 (9)
Cl(1)	−0.1458 (1)	0.2569 (3)	0.6878 (1)	3.36 (5)
Cl(2)	−0.0238 (1)	−0.1876 (3)	0.6216 (1)	3.38 (5)
P(1)	−0.0243 (1)	0.2078 (3)	0.6116 (1)	2.69 (5)
P(2)	−0.1575 (1)	−0.1366 (3)	0.6841 (1)	2.96 (5)
C(1)	−0.1298 (6)	0.156 (1)	0.5104 (6)	4.2 (3)
C(2)	0.0612 (6)	0.156 (1)	0.5939 (5)	4.2 (3)
C(3)	−0.0268 (8)	0.399 (1)	0.6005 (6)	5.3 (3)
C(4)	−0.1709 (7)	−0.330 (1)	0.6779 (7)	4.7 (3)
C(5)	−0.2409 (6)	−0.083 (1)	0.5724 (7)	4.4 (3)
C(6)	−0.2098 (6)	−0.082 (1)	0.7390 (6)	4.7 (3)

[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. Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $[Re_2Cl_4(PMe_3)_4]ReO_4$ (**2**)

atom	*x*	*y*	*z*	*B*,[a] Å^2
Re(1)	0.250	0.3465 (1)	0.289	2.16 (2)
Re(2)	0.250	0.2597 (1)	0.38715 (6)	1.86 (2)
Re(3)	0.250	0.6999 (2)	0.04119 (6)	2.95 (3)
Cl(1)	0.4048 (4)	0.3784 (6)	0.2529 (3)	3.5 (1)
Cl(2)	0.250	0.4330 (8)	0.4637 (4)	2.8 (2)
Cl(3)	0.250	0.0231 (8)	0.3827 (5)	3.4 (2)
P(1)	0.250	0.1454 (9)	0.2190 (4)	2.8 (2)
P(2)	0.250	0.5926 (9)	0.3090 (4)	3.0 (2)
P(3)	0.4180 (4)	0.2374 (6)	0.4146 (3)	2.8 (1)
O(1)	0.250	0.550 (3)	0.077 (1)	5.6 (7)
O(2)	0.348 (1)	0.711 (2)	−0.0044 (8)	5.2 (5)
O(3)	0.250	0.827 (3)	0.096 (1)	4.4 (6)
C(11)	0.145 (2)	0.031 (2)	0.222 (1)	4.2 (6)
C(12)	0.250	0.220 (4)	0.138 (2)	6 (1)
C(21)	0.352 (2)	0.670 (3)	0.349 (1)	4.2 (6)
C(22)	0.250	0.661 (4)	0.228 (2)	6 (1)
C(31)	0.490 (1)	0.115 (2)	0.369 (1)	3.3 (5)
C(32)	0.417 (2)	0.169 (3)	0.497 (1)	4.9 (6)
C(33)	0.488 (2)	0.394 (2)	0.418 (1)	3.8 (6)

[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 IV. Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (**3**)

atom[a]	*x*	*y*	*z*	*B*,[b] Å^2
Re(1)[i]	0.250	0.0631 (1)	0.000	4.51 (6)
Re(2)[i]	0.250	0.2156 (1)	0.000	4.60 (6)
Re(3)[ii]	0.2958 (1)	0.1394 (1)	−0.0274 (1)	4.66 (6)
Re(4)[iii]	0.2071 (1)	0.1374 (1)	−0.0540 (1)	4.62 (6)
Cl(1)	0.3814 (2)	0.0184 (3)	0.0388 (2)	7.5 (1)
Cl(2)	0.2519 (3)	0.2588 (3)	−0.1229 (3)	9.0 (2)
P(1)	0.2529 (3)	0.0266 (3)	−0.1235 (2)	5.8 (1)
P(2)	0.3840 (2)	0.2520 (3)	0.0374 (3)	6.1 (1)
C(1)	0.337 (1)	0.047 (1)	−0.150 (1)	11.4 (9)
C(2)	0.343 (2)	0.016 (2)	−0.214 (2)	19 (2)
C(3)	0.435 (2)	0.045 (2)	−0.217 (1)	15 (1)
C(4)	0.173 (1)	0.057 (1)	−0.196 (1)	10.3 (8)
C(5)	0.157 (2)	0.020 (2)	−0.265 (2)	15 (1)
C(6)	0.085 (2)	0.051 (2)	−0.321 (1)	15 (1)
C(7)	0.247 (2)	−0.097 (1)	−0.107 (2)	14 (1)
C(8)	0.271 (2)	−0.156 (2)	−0.129 (3)	21 (2)
C(9)	0.265 (1)	−0.261 (1)	−0.116 (1)	10.3 (8)
C(10)	0.438 (1)	0.226 (1)	−0.025 (1)	10.8 (8)
C(11)	0.507 (2)	0.249 (2)	−0.017 (2)	17 (1)
C(12)	0.552 (1)	0.222 (1)	−0.072 (1)	10.6 (8)
C(13)	0.360 (2)	0.370 (1)	0.024 (2)	15 (1)
C(14)	0.383 (3)	0.434 (2)	0.050 (2)	25 (2)
C(15)	0.358 (1)	0.541 (1)	0.037 (1)	14 (1)
C(16)	0.440 (1)	0.231 (1)	0.129 (1)	9.1 (7)
C(17)	0.512 (2)	0.255 (3)	0.156 (2)	19 (1)
C(18)	0.556 (1)	0.231 (2)	0.234 (1)	12.7 (9)

[a] i–iii represent sites modeled as 0.215 Re, 0.29 Re, and 0.28 Re, respectively. [b] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

0.0275 and R_w = 0.0355. The success of this refinement supported the choice of space group *C*2/*c* rather than *Cc*.

$[Re_2Cl_4(PMe_3)_4]ReO_4$ (2). Systematic absences were consistent with the orthorhombic space groups *Pmcn* (nonstandard setting of *Pnma*) and $P2_1cn$ (nonstandard setting of $Pna2_1$). Successful solution and refinement of the structure was achieved in the centric group. Anisotropic refinement on all non-hydrogen atoms gave *R* = 0.0537 and R_w = 0.0624.

$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (3). All ten atoms of the $Re_2Cl_4P_4$ moiety and some of the carbon atoms were located by using the direct-methods program in SHELXS-86.[12] From subsequent difference Fourier maps, another two pairs of Re atoms were also found, centered about the same point as the principal pair, indicating a possible disorder of the Re_2 unit in three orientations. In the initial stages of refinement, the site occupancy factors (sof's) of Re(1) and Re(2) (the principal pair) were allowed to vary against the sum of Re(3) (and Re(3)′) and Re(4) (and Re(4)′) (sof's of Re(3) and Re(4) were constrained to be equal to one another), giving values of 0.44, 0.28, and 0.28 for Re(1)/Re(2), Re(3), and Re(4), respectively. The sof of Re(1)/Re(2) was then fixed at 0.44, and the sof's of Re(3) and Re(4) were allowed to refine freely against each other, giving values of 0.29 for Re(3) and 0.28 for Re(4). These latter two sof's were then fixed so that the sof for Re(1)/Re(2) refined freely to a final value of 0.43. The final stages of refinement gave sof values of 0.43, 0.29, and 0.28 for the three orientations, to give a sum of 1.00. The rest of

Table V. Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (**4**)

atom[a]	x	y	z	B,[b] Å^2
Re(1)^{i}	0.000	0.0372 (2)	0.250	4.36 (8)
Re(2)^{i}	0.000	0.1898 (2)	0.250	3.52 (7)
Re(3)^{ii}	0.0471 (2)	0.1156 (3)	0.2996 (2)	4.59 (8)
Re(4)^{iii}	−0.0420 (4)	0.1133 (5)	0.2832 (3)	4.7 (1)
Br(1)	0.0113 (2)	−0.0112 (3)	0.3802 (2)	8.6 (1)
Br(2)	0.1378 (2)	0.2398 (2)	0.2791 (2)	7.2 (1)
P(1)	0.1336 (5)	−0.0002 (6)	0.2746 (5)	6.5 (2)
P(2)	0.0077 (5)	0.2292 (6)	0.3754 (4)	5.7 (2)
C(11)	0.183 (2)	0.028 (2)	0.203 (2)	8 (1)
C(12)	0.258 (2)	−0.004 (4)	0.215 (2)	15 (2)
C(13)	0.293 (2)	0.018 (3)	0.153 (2)	15 (2)
C(14)	0.198 (2)	0.021 (3)	0.363 (2)	12 (1)
C(15)	0.260 (3)	−0.021 (4)	0.391 (2)	17 (2)
C(16)	0.313 (2)	0.000 (3)	0.458 (2)	12 (1)
C(17)	0.114 (3)	−0.122 (3)	0.268 (2)	14 (1)*
C(18a)^{iv}	0.118 (7)	−0.172 (8)	0.316 (6)	10.0*
C(18b)^{iv}	0.162 (7)	−0.184 (8)	0.268 (5)	10.0*
C(18c)^{iv}	0.101 (7)	−0.172 (8)	0.221 (6)	10.0*
C(19a)^{v}	0.120 (4)	−0.285 (4)	0.223 (3)	8 (2)*
C(19b)^{v}	0.111 (4)	−0.288 (5)	0.273 (3)	9 (2)*
C(21)	0.008 (2)	0.357 (2)	0.360 (2)	12 (1)
C(22)	−0.010 (3)	0.425 (3)	0.377 (3)	21 (2)
C(23a)^{v}	−0.017 (3)	0.522 (4)	0.348 (3)	6 (1)*
C(23b)^{v}	0.005 (4)	0.516 (4)	0.387 (3)	7 (2)*
C(24)	−0.076 (2)	0.205 (2)	0.413 (1)	7 (1)
C(25)	−0.081 (2)	0.241 (4)	0.477 (2)	14 (2)
C(26)	−0.156 (2)	0.213 (3)	0.494 (2)	15 (2)
C(27)	0.092 (2)	0.206 (3)	0.444 (1)	10 (1)
C(28)	0.113 (3)	0.226 (4)	0.513 (2)	17 (2)
C(29)	0.186 (2)	0.204 (3)	0.561 (2)	14 (1)

[a] i–iii represent sites modeled as 0.25 Re, 0.32 Re, and 0.18 Re, respectively. iv and v represent sites modeled as $^1/_3$ C and $^1/_2$ C, respectively. [b] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

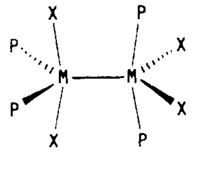
the structure was developed by an alternating sequence of least-squares calculations and difference Fourier maps to give $R = 0.0564$ and $R_w = 0.0769$.

$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (4). The refinement of the sof's of the Re atoms in this structure was carried out in a manner similar to that first described for compound **3**, giving values of 0.50, 0.32, and 0.18 for the three orientations. In addition, there was found to be a disorder involving the carbon chains of the P-*n*-Pr$_3$ ligands. Carbon atoms C(18a), C(18b), and C(18c) were each assigned a sof of $^1/_3$, while C(19a) and C(19b) were each assigned a sof of $^1/_2$. Because of the low data to parameter ratio of 6.8, residuals of $R = 0.0777$ and $R_w = 0.0967$ could not be improved upon.

$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4{\cdot}C_7H_8$ (5). Solution and refinement of this structure were also carried out in a manner similar to that for **3**. Values of the sof's for the three pairs of W atoms were found to be 0.88, 0.085, and 0.035. The crystallographic asymmetric unit was found to contain one formula unit of $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ and one molecule of solvent toluene. No disorder involving the P-*n*-Bu$_3$ ligands was found. All atoms were refined anisotropically, giving residuals of $R = 0.0418$ and $R_w = 0.0570$.

Results and Discussion

Molecular Structures. The molecular structures of all five complexes are qualitatively the same, namely with the $M_2X_4P_4$ arrangement



for which the point symmetry is D_{2d}.

The compounds themselves and their molecular structures do not entail any surprises. Compounds **1**, **3**, and **4** were all previously

Table VI. Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4{\cdot}C_7H_8$ (**5**)

atom[a]	x	y	z	B,[b] Å^2
W(1)^{i}	0.15318 (2)	0.20531 (2)	0.26956 (3)	2.132 (8)
W(2)^{i}	0.10000 (2)	0.27767 (2)	0.38248 (3)	2.114 (7)
W(3)^{ii}	0.0581 (4)	0.2753 (3)	0.2415 (4)	4.0 (1)
W(4)^{ii}	0.1888 (3)	0.2064 (2)	0.3875 (3)	3.3 (1)
W(5)^{iii}	0.0769 (6)	0.2063 (5)	0.3145 (7)	2.5 (2)
W(6)^{iii}	0.2001 (6)	0.2659 (5)	0.3350 (7)	2.8 (2)
Cl(1)	−0.0104 (2)	0.1865 (1)	0.1083 (2)	3.51 (5)
Cl(2)	0.3543 (2)	0.1739 (1)	0.3535 (2)	3.42 (5)
Cl(3)	0.0795 (2)	0.3899 (1)	0.3324 (2)	3.59 (5)
Cl(4)	0.0849 (2)	0.2142 (1)	0.5092 (2)	3.46 (5)
P(1)	0.1796 (2)	0.0919 (1)	0.3437 (2)	3.00 (5)
P(2)	0.1575 (2)	0.2831 (1)	0.1411 (2)	3.03 (5)
P(3)	0.2813 (2)	0.2938 (1)	0.5419 (2)	2.75 (5)
P(4)	−0.1094 (2)	0.2977 (1)	0.2798 (2)	2.87 (5)
C(1)	0.0528 (6)	0.0699 (4)	0.3268 (7)	3.4 (2)
C(2)	0.0646 (7)	−0.0035 (5)	0.3506 (8)	4.3 (2)
C(3)	−0.0498 (7)	−0.0112 (5)	0.3376 (7)	4.4 (2)
C(4)	−0.0405 (8)	−0.0852 (5)	0.3571 (9)	6.1 (3)
C(5)	0.2844 (7)	0.0769 (5)	0.4938 (7)	4.0 (2)
C(6)	0.3529 (8)	0.0040 (5)	0.5276 (8)	5.2 (3)
C(7)	0.4392 (8)	−0.0013 (6)	0.6544 (8)	5.7 (3)
C(8)	0.373 (1)	0.0135 (8)	0.722 (1)	8.3 (5)
C(9)	0.2435 (7)	0.0274 (5)	0.2743 (7)	4.4 (3)
C(10)	0.1694 (7)	0.0242 (5)	0.1491 (7)	4.4 (3)
C(11)	0.2402 (8)	−0.0247 (6)	0.0968 (7)	5.3 (3)
C(12)	0.164 (1)	−0.0299 (8)	−0.0282 (9)	7.9 (4)
C(13)	0.2714 (6)	0.3276 (5)	0.2099 (7)	3.9 (2)
C(14)	0.3118 (7)	0.3528 (5)	0.1366 (8)	5.2 (3)
C(15)	0.4091 (7)	0.3861 (6)	0.2163 (9)	5.9 (3)
C(16)	0.4490 (9)	0.4162 (7)	0.148 (1)	9.5 (4)
C(17)	0.0249 (7)	0.3452 (5)	0.0622 (7)	3.8 (2)
C(18)	0.0174 (6)	0.3867 (5)	−0.0293 (7)	3.8 (2)
C(19)	−0.1041 (7)	0.4313 (5)	−0.0886 (7)	4.2 (2)
C(20)	−0.1150 (8)	0.4715 (5)	−0.1848 (7)	4.4 (3)
C(21)	0.1742 (8)	0.2343 (6)	0.0278 (7)	5.0 (3)
C(22)	0.2747 (9)	0.1748 (6)	0.0642 (8)	5.8 (3)
C(23)	0.276 (1)	0.1401 (7)	−0.0484 (9)	8.3 (4)
C(24)	0.380 (1)	0.082 (1)	−0.005 (1)	11.6 (6)
C(25)	0.3717 (6)	0.3248 (4)	0.5033 (6)	3.4 (2)
C(26)	0.4744 (6)	0.3443 (5)	0.6002 (7)	4.1 (2)
C(27)	0.5337 (7)	0.3777 (5)	0.5511 (8)	4.8 (3)
C(28)	0.6316 (8)	0.3999 (6)	0.649 (1)	7.0 (4)
C(29)	0.3693 (7)	0.2227 (4)	0.6406 (7)	3.3 (2)
C(30)	0.4462 (8)	0.2396 (5)	0.7612 (7)	4.4 (3)
C(31)	0.4964 (9)	0.1736 (5)	0.8317 (7)	5.1 (3)
C(32)	0.570 (1)	0.1933 (7)	0.9565 (9)	8.2 (4)
C(33)	0.2444 (7)	0.3632 (5)	0.6270 (7)	4.3 (2)
C(34)	0.1704 (7)	0.3513 (6)	0.6732 (8)	5.5 (3)
C(35)	0.1287 (9)	0.4180 (7)	0.7263 (9)	7.3 (4)
C(36)	0.209 (1)	0.4404 (8)	0.826 (1)	8.5 (4)
C(37)	−0.1673 (6)	0.2247 (4)	0.2631 (7)	3.7 (2)
C(38)	−0.2778 (7)	0.2339 (6)	0.2598 (8)	5.3 (3)
C(39)	−0.3020 (7)	0.1660 (5)	0.2688 (9)	5.5 (3)
C(40)	−0.4197 (8)	0.1804 (6)	0.2582 (9)	6.6 (3)
C(41)	−0.1779 (7)	0.3405 (5)	0.1445 (7)	4.1 (2)
C(42)	−0.3053 (7)	0.3635 (6)	0.0895 (8)	5.0 (3)
C(43)	−0.3463 (8)	0.3940 (6)	−0.0298 (9)	6.0 (3)
C(44)	−0.4726 (9)	0.4141 (6)	−0.0903 (9)	5.9 (3)
C(45)	−0.1684 (8)	0.3505 (5)	0.3679 (9)	5.9 (3)
C(46)	−0.1334 (9)	0.4150 (6)	0.4082 (9)	6.6 (4)
C(47)	−0.1798 (9)	0.4504 (6)	0.4903 (8)	5.8 (3)
C(48)	−0.302 (1)	0.4726 (7)	0.438 (1)	8.2 (4)
C(49)	0.1590 (9)	0.7655 (6)	0.3144 (9)	6.0 (3)
C(50)	0.241 (1)	0.7830 (7)	0.4150 (9)	7.3 (4)
C(51)	0.323 (1)	0.8190 (6)	0.417 (1)	7.0 (4)
C(52)	0.313 (1)	0.8339 (7)	0.319 (1)	7.4 (4)
C(53)	0.231 (1)	0.8158 (8)	0.215 (1)	7.5 (4)
C(54)	0.1573 (9)	0.7821 (7)	0.2163 (8)	6.3 (4)
C(55)	0.071 (1)	0.7315 (7)	0.308 (1)	7.9 (4)

[a] i–iii represent sites modeled as 0.880 W, 0.085 W, and 0.035 W, respectively. [b] All atoms were refined anisotropically, and they 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 VII. Selected Bond Distances (Å) for the Five Complexes[a]

$Re_2Cl_4(PMe_3)_4$ (**1**)		$[Re_2Cl_4(PMe_3)_4]ReO_4$ (**2**)		$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (**3**)		$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (**4**)		$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4{\cdot}C_7H_8$ (**5**)	
Re(1)–Re(2)	2.247 (1)	Re(1)–Re(2)	2.205 (1)	Re(1)–Re(2)	2.252 (2)	Re(1)–Re(2)	2.253 (4)	W(1)–W(2)	2.267 (1)
Re(1)–Cl(1)	2.379 (2)	Re(1)–Cl(1)	2.341 (6)	Re(3)–Re(3)′[b]	2.238 (3)	Re(3)–Re(3)′[b]	2.248 (4)	W(3)–W(4)[b]	2.279 (5)
Re(1)–P(1)	2.417 (2)	Re(1)–P(1)	2.457 (9)	Re(4)–Re(4)′[b]	2.241 (3)	Re(4)–Re(4)′[b]	2.254 (4)	W(5)–W(6)[b]	2.27 (2)
Re(2)–Cl(2)	2.381 (2)	Re(1)–P(2)	2.445 (9)	Re(1)–Cl(1)	2.435 (4)	Re(1)–Br(1)	2.581 (4)	W(1)–Cl(1)	2.407 (2)
Re(2)–P(2)	2.417 (2)	Re(2)–Cl(2).	2.329 (8)	Re(1)–P(1)	2.456 (5)	Re(1)–P(1)	2.462 (9)	W(1)–Cl(2)	2.411 (2)
		Re(2)–Cl(3)	2.321 (8)	Re(2)–Cl(2)	2.463 (5)	Re(2)–Br(2)	2.578 (4)	W(1)–P(1)	2.530 (2)
		Re(2)–P(3)	2.456 (6)	Re(2)–P(2)	2.449 (4)	Re(2)–P(2)	2.467 (8)	W(1)–P(2)	2.535 (3)
		Re(3)–O(1)	1.65 (3)					W(2)–Cl(3)	2.404 (2)
		Re(3)–O(2)	1.69 (2)					W(2)–Cl(4)	2.393 (3)
		Re(3)–O(3)	1.68 (2)					W(2)–P(3)	2.527 (2)
								W(2)–P(4)	2.518 (2)

[a] Numbers in parentheses are standard deivations in the least significant digits. [b] M–M bond distance for the minor orientations.

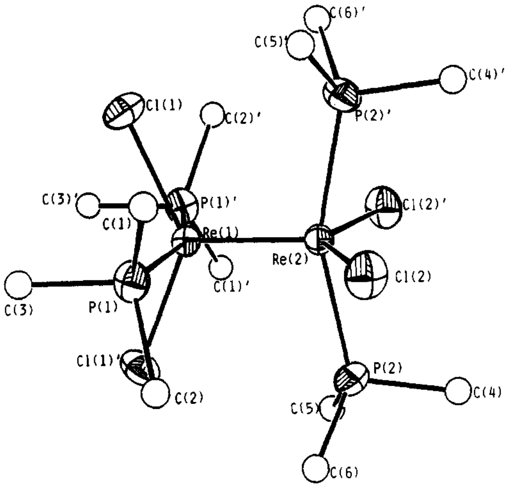


Figure 1. ORTEP diagram of $Re_2Cl_4(PMe_3)_4$ (**1**) showing 50% probability ellipsoids. Carbon atoms are shown as spheres of arbitrary radii. The Re, halogen, and P atoms of compounds **3** and **4** are labeled in a similar way.

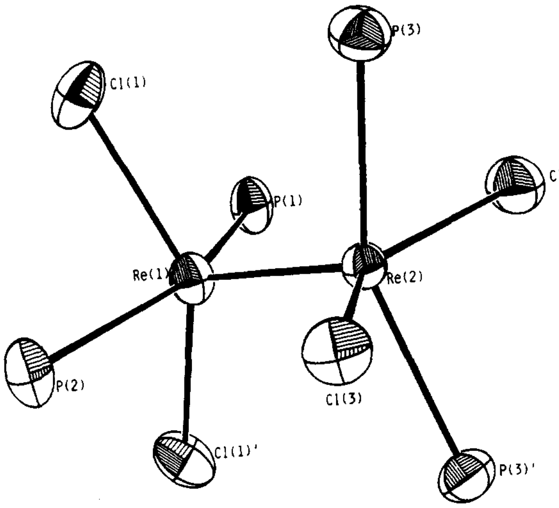


Figure 2. ORTEP diagram of the cation in **2**, $[Re_2Cl_4(PMe_3)_4]^+$, showing only the Re, Cl, and P atoms as 50% probability ellipsoids.

reported by Ebner and Walton.[8] Their Re–Re distances are well within the narrow range of 2.247–2.253 Å and are consistent with the previously established value (ca. 2.24 Å) for an electron-rich Re–Re triple bond, i.e., one based on a $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration.[14] Compound **2** is a new one, but its preparation does not involve any real novelty. It has already been shown by Walton that **1** can be oxidized by $NOPF_6$ to give $[Re_2Cl_4(PMe_3)]PF_6$.[15] In addition, Walton has previously observed the formation of the perrhenate ion when a benzene solution of $Re_2Cl_4(PEt_3)_4$ was exposed to O_2.[16]

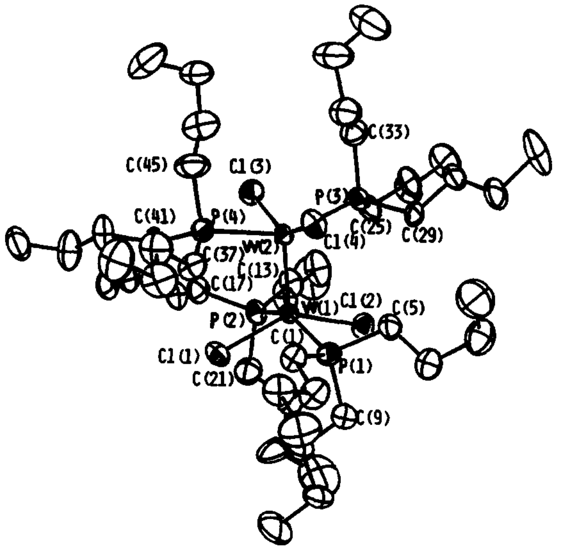


Figure 3. ORTEP diagram of $W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ (**5**) showing 50% probability ellipsoids. For the sake of clarity, only the major orientation is shown and only the α-carbon atom of each *n*-butyl group is labeled.

Compound **5** has been known for several years and is an important starting material in the preparation of other multiply bonded ditungsten compounds.[1b] The W–W bond length of 2.27 Å is within the established range, 2.26–2.31 Å, for W–W quadruple bonds in compounds of this general class.

Compound **2** is of additional interest in connection with the question of how the gain or loss of δ or δ* electrons affects the length of the metal–metal bond. This question has been the subject of a previous comprehensive discussion,[17] wherein the series $[Re_2Cl_4(PMe_2Ph)_4]^{0,+,2+}$ played a key role.[14] It was pointed out that while the loss of a δ* electron would favor a shortening of the Re–Re bond, the increase in oxidation state would favor a weakening of the Re–Re bond because of contraction (and thus poorer overlap) of the metal d orbitals. The net effect of these two opposing factors might thus be only a slight contraction of the bond distance, and in the series of PMe_2Ph compounds, the changes were indeed small, viz., 0.023 and ca. 0.003 Å. In the present case, the contraction caused by loss of one δ* electron is a little larger, namely, 0.042 Å. Since other factors could contribute to the net observed change (e.g., crystal-packing forces, internal repulsions), there is no simple explanation for why the

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(14) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Thomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

(15) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattleberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953.

(16) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

(17) Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

Table VIII. Selected Bond Angles (deg) for the Five Complexes[a]

$Re_2Cl_4(PMe_3)_4$ (**1**)		$[Re_2Cl_4(PMe_3)_4]ReO_4$ (**2**)		$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (**3**)		$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (**4**)		$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4 \cdot C_7H_8$ (**5**)	
Re(2)–Re(1)–Cl(1)	112.93 (6)	Re(2)–Re(1)–Cl(1)	110.6 (1)	Re(2)–Re(1)–Cl(1)	105.7 (1)	Re(2)–Re(1)–Br(1)	106.1 (1)	W(2)–W(1)–Cl(1)	109.18 (6)
Re(2)–Re(1)–P(1)	101.26 (6)	Re(2)–Re(1)–P(1)	104.0 (2)	Re(2)–Re(1)–P(1)	102.7 (1)	Re(2)–Re(1)–P(1)	103.0 (2)	W(2)–W(1)–Cl(2)	108.76 (5)
Cl(1)–Re(1)–P(1)	85.57 (8)	Re(2)–Re(1)–P(2)	103.2 (2)	Cl(1)–Re(1)–P(1)	87.0 (2)	Br(1)–Re(1)–P(1)	85.3 (2)	W(2)–W(1)–P(1)	103.44 (6)
Re(1)–Re(2)–Cl(2)	113.17 (6)	Cl(1)–Re(1)–P(1)	85.0 (2)	Re(1)–Re(2)–Cl(2)	105.0 (1)	Re(1)–Re(2)–Br(2)	106.7 (1)	W(2)–W(1)–P(2)	102.43 (5)
Re(1)–Re(2)–P(2)	101.10 (6)	Cl(1)–Re(1)–P(2)	85.5 (2)	Re(1)–Re(2)–P(2)	102.7 (1)	Re(1)–Re(2)–P(2)	103.6 (2)	Cl(1)–W(1)–P(1)	88.51 (7)
Cl(2)–Re(2)–P(2)	85.64 (9)	Re(1)–Re(2)–Cl(2)	110.5 (2)	Cl(2)–Re(2)–P(2)	86.6 (2)	Br(2)–Re(2)–P(2)	84.7 (2)	Cl(1)–W(1)–P(2)	84.14 (8)
		Re(1)–Re(2)–Cl(3)	110.4 (2)					Cl(2)–W(1)–P(1)	82.72 (8)
		Re(1)–Re(2)–P(3)	104.4 (1)					Cl(2)–W(1)–P(2)	87.92 (8)
		Cl(2)–Re(2)–Cl(3)	139.1 (3)					W(1)–W(2)–Cl(3)	109.06 (6)
		Cl(2)–Re(2)–P(3)	84.6 (2)					W(1)–W(2)–Cl(4)	108.19 (5)
		Cl(3)–Re(2)–P(3)	85.4 (2)					W(1)–W(2)–P(3)	104.40 (5)
		O(1)–Re(3)–O(2)	108.0 (8)					W(1)–W(2)–P(4)	101.89 (5)
								Cl(3)–W(2)–P(3)	83.77 (7)
								Cl(3)–W(2)–P(4)	87.98 (7)
								Cl(4)–W(2)–P(3)	87.02 (7)
								Cl(4)–W(2)–P(4)	84.55 (7)

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

Table IX. $M_2X_4L_4$ Compounds with Known Structures

entry	compd	notes[a]	ref
1	$[Re_2Cl_4(PMe_3)_4]ReO_4$ (**2**)	ND	this work
2	$Re_2Cl_4(PMe_2Ph)_4$	ND	14
3	$[Re_2Cl_4(PMe_2Ph)_4]PF_6$	ND	14
4	$[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$	ND	14
5	$Mo_2Cl_4(PMe_2Ph)_4$	ND	6
6	$Mo_2Cl_4(PHPh_2)_4$	ND	6
7	$Mo_2I_4(NCPh)_4$	ND	18
8	$Mo_2(NCO)_4(PMe_3)_4$	ND	19
9	$Mo_2(NCS)_4(PMe_3)_4$	ND	19
10	$Mo_2Cl_4(PMe_3)_4$	ND	20
11	$Mo_2Br_4(PMe_3)_4$	ND	21
12	$Mo_2I_4(PMe_3)_4$	ND	21, 22
13	$W_2Cl_4(PMe_3)_4$	ND	20
14	$Re_2Cl_4(PMe_3)_4$ (**1**)	ND	this work
15	$Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ (**3**)	metals disordered 3×	this work
16	$Re_2Br_4(P\text{-}n\text{-}Pr_3)_4$ (**4**)	metals disordered 3×	this work
17	$W_2Cl_4(P\text{-}n\text{-}Bu_3)_4$ (**5**)	metals disordered 3×	this work
18	$Re_2Cl_4(PEt_3)_4$	metal and ligand atoms disordered	5
19	$Mo_2Cl_4(PEt_3)_4$		6

[a] ND = no disorder.

change is 0.023 Å in one case and 0.042 Å in the other. Both are small, as expected.

Causes and Nature of Crystal Disorder. We turn now to the major part of this work, namely, the factors that account for the occurrence, or absence, of crystallographic disorder in these and related compounds. We report here the first three examples of the disordered packing of $M_2X_4L_4$ species that is limited to the metal atoms themselves. In the $M_2Cl_4(PEt_3)_4$ compounds, the ligands are disordered as well, whereas in all other cases there is no disorder at all.

To preface the discussion, it must be pointed out that although we commonly talk about "disordering of M_2 units within quasi-cube ligand cages", this is unlikely to be a correct description of what really occurs. It is true that we cannot see more than one set of eight ligand atoms, but most likely these are two or three sets which are so nearly superimposed (but *not exactly*) that it is impossible to resolve them. In other words, it is not just the M_2 units that take up two or three orientations but the entire molecules that do so. We cannot actually confirm the presence of the two or three ligand sets, but we do clearly see the two or three sets of metal atoms.

In the case of $M_2X_8^{2-}$ species, where all the ligands are small, identical, and nearly spherical, the M_2X_8 units would presumably be very highly disordered were it not for the presence of countercations placed unsymmetrically around them, as previously discussed.[7] For the neutral molecules, $M_2X_4L_4$, we must seek an explanation in terms of molecular shape and intermolecular forces. Counting the five compounds whose structures are reported here, we now have a total of 19 known structures, which are listed in Table IX. In 14 cases there is no disorder, and for some of these the reason is obvious. For the four compounds containing the PMe_2Ph ligand (entries 2–5), the large phenyl groups project outward parallel to the molecular axis, making the molecules very much longer than they are in cross section. It is thus impossible for any molecule to be oriented perpendicular to the direction adopted by the others. A somewhat similar situation occurs for the sixth compound in the table, while the next three (entries 7–9) are so wafer-shaped that again any orientation perpendicular to the main one is impossible.

The remaining compounds that display no disorder are all $M_2X_4(PMe_3)_4$ species (entries 1 and 8–14). For entry 1, ionic packing forces could be responsible, but this still leaves seven such compounds for which an explanation must be found in the molecular shape and the way in which the molecules are packed. All of them are either isomorphous or show very similar packing in their crystals, so if we can explain one, we can explain them all. At the same time, however, whatever feature of the PMe_3 compounds we focus on to explain why they are not disordered, we must be able to extract from this same feature an explanation for why the remaining compounds in Table IX (entries 15–19) are disordered.

There is one such feature that can explain much, if not all, of the observed behavior, and it is this: Consider, for simplicity, a cubic array of ligands within which we place an octahedron of metal atoms whose pairs of opposite vertices represent the three different potential orientations of M_2 units. It is easy to see in Figure 4 that the three lines that pass from the nearest three metal atoms to a given vertex intersect at that vertex and then their extensions diverge considerably as they extend out from the cube. In other words, the three M–L bonds to the same ligand from metal atoms at the three possible locations within the cube take quite distinct directions, such that any two make an angle of about 20°. If the ligand in question is a tertiary phosphine, then the directions of the 3-fold axes relating the three P–C bonds will also be different for each orientation of the metal atoms by the same amount. In short, the regions of space occupied by the sets of three carbon atoms bonded to the phosphorus atoms, the methyl carbon atoms in PMe_3, are different for each differently oriented $M_2X_4(PMe_3)_4$ molecule occupying the site, even if the positions of the P atoms themselves are *exactly* the same.

In the case of $M_2X_4(PMe_3)_4$ molecules, the intermolecular contacts are made directly between methyl groups on one molecule and methyl groups or X atoms of its neighbors. Thus, the displacements or mismatching of the methyl groups that would result

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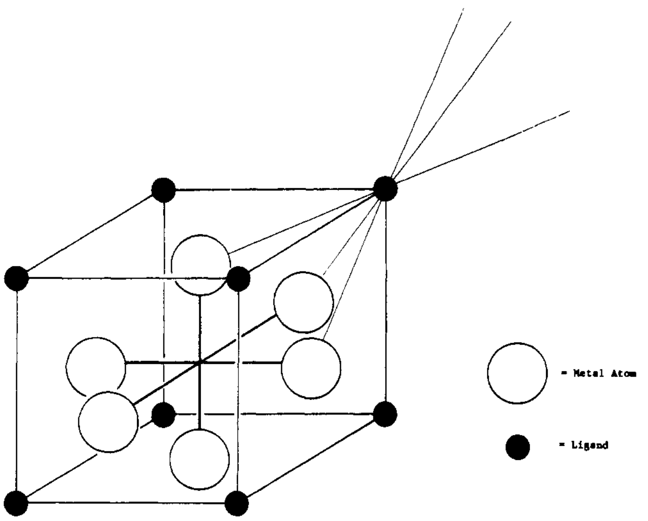

Figure 4. Diagram showing three different potential orientations of M_2 units within a cubic array of ligands. Note how the three M-L bonds diverge considerably as they extend out from the cube.

from having a molecule lying at 90° to the correct direction can be severe enough to make this kind of misorientation energetically impossible—at least to a detectable degree.

In the case of $M_2X_4(PR_3)_4$ molecules where the R groups are C_3H_7 or C_4H_9, there is enough flexibility ("slop") in the collection of three of these, that they can compensate for the misorientation of the 3-fold axes of the PR_3 units by deploying the outer two or three carbon atoms on each one in a somewhat disordered fashion. There are indeed always either observable disorder or very large displacement parameters observed in these cases. The fact that each of the three possible orthogonal directions for the molecules is observed to a different extent is simply due to the fact that each of these directions is distinct (nonequivalent) in the crystal, so that the extents to which "slop" in the phosphine ligands can compensate for the misorientation relative to the neighbors are, naturally, different for each one. We would, finally, draw the conclusion that, for all $M_2X_4(PR_3)_4$ molecules where R = C_3H_7 or any longer C_nH_{2n+1} chain, 2- or most likely 3-fold disorder is to be expected in these crystals.

We are left with now only one observation to explain: Namely, why do the $M_2X_4(PEt_3)_4$ compounds show not only 3-fold disorder of the M_2 units but statistical disordering of the X and PEt_3 groups over the eight vertices of the quasi-cube? One answer—which really is not an answer—is that the $M_2X_4(PEt_3)_4$ molecules lie on crystallographic sites of cubic symmetry and hence both of these disorders are demanded. However, this simply raises the question of why the molecules are capable of packing in this way. This is a question to which we have no concrete answer. Evidently, the $M_2X_4(PEt_3)_4$ molecules have lost the "knobbiness" of the $M_2X_4(PMe_3)_4$ molecules and become smoother without, however, having achieved the "sloppiness" of those with the larger R groups. They represent that kind of special case that is often extremely difficult to explain in chemistry.

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Supplementary Material Available: For compound **1**, a complete table of positional and thermal parameters and, for all five crystal structures, full tables of crystal parameters and details of data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters and ORTEP diagrams (44 pages); tables of observed and calculated structure factors (80 pages). Ordering information is given on any current masthead page.

Notes

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Model Studies Related to Hemerythrin. Synthesis and Characterization of a Bridged Tetranuclear Iron(III) Complex

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Oligomeric oxo-bridged iron complexes have been found to mediate a variety of functions in biology.[1] Of particular interest are the proteins known or presumed to contain an oxo-bridged diiron core in their active site: hemerythrin,[2-4] purple acid phosphatase,[5] ribonucleotide reductase,[6] and methane monooxygenase.[7,8] Of these proteins, the main structural features of the functional center in hemerythrin are those that are best understood. As such, it continues to be a focus of extensive chemical and physical studies, not only because it is of intrinsic interest but also because it is considered prototypical of diiron proteins about which much less is known.

One of the more interesting features to emerge from recent hemerythrin-directed model studies is an appreciation for the facility with which many of these form iron aggregates of a nuclearity higher than two.[9-12] In many cases, the factors that govern the formation of a particular iron oligomer are still poorly understood, and as such, the actual structure formed from a particular ligand system can be difficult to predict. For instance, in a recent report,[13] Wieghardt et al. proposed the stabilization of a (μ-oxo)bis(μ-acetato)diiron(III) core using Takamoto's[14] 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane ligand system (L_1) as the

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