C_2 symmetry axis that is coincident with the Os(3)–Os(4) vector.

Curiously, the observation of only one *N*-methyl resonance of intensity 12 in the ^{1}H NMR spectrum is inconsistent with the solid-state structure. This anomally was resolved by a variable-temperature ^{1}H NMR study, which revealed the presence of a dynamical exchange process. At -80 °C the ^{1}H NMR spectrum showed two closely space *N*-methyl resonances at 3.78 and 3.84 ppm of intensity 6. As the temperature was raised, the resonances broadened, merged (-36 °C), and re-formed as the sharp singlet that is observed at 25 °C. Two dynamical processes that could explain this observation are as follows: The first is rotations about the C–N bonds that are slowed at low temperature. This could be expected on the basis of the structural evidence for partial C–N multiple bonding. The second is a polytopal rearrangement at Os(4) in which the semibridging carbonyl ligands shift rapidly between the Os(1)–Os(4) and Os(4)–Os(6) bonds, and the Os(2)–Os(4) and Os(4)–Os(5) bonds. As a consequence the *N*-methyl groups on the carbyne ligands would interchange their environments. With the available data these mechanisms cannot be distinguished.

In addition to its novel structure, compound **3** also possesses an unusual electronic configuration. In all previously reported examples the triply bridging alkanethiolato ligand was regarded as a five-electron donor.[14,15] If these ligands are five-electron donors in **3**, then assuming that the carbyne ligands serve as three-electron donors, the cluster would contain a total of 90 valence electrons. However, the edge-fused bitetrahedron should contain only 86 electrons.[16] An alternative possibility is that the thiolato ligands serve only as three-electron donors and the total valence electron count is the expected number 86. If the thiolato ligands are three-electron donors, then the sulfur atoms should contain an uncoordinated pair of electrons. Consideration of the geometry of the sulfur atoms (vide supra) suggests that this is not unreasonable. For both sulfur atoms, a plane is defined by two of the metal atoms, the sulfur atom, and the carbon atom (e.g., Os(1), Os(5), S(1), C(1)). The only other atom bonded to the sulfur atom is the third metal atom. As a result, a full hemisphere of space around the sulfur atom is vacant. Indeed, a lone pair of electrons could easily occupy part of this space.

When viewed in terms of two-center–two-electron, (2c–2e) bonding, it is found that atom Os(4) is electron deficient and atom Os(3) is electron rich unless the Os(3)–Os(4) bond is regarded as a donor–acceptor bond donating from Os(3) to Os(4). The requirement for use of such formalisms is becoming increasingly necessary when 2c–2e theory is applied to large clusters.[17] Cotton has pointed out that these situations often lead to the formation of semibridging carbonyl ligands.[18] In accord with this it was found that the two carbonyl ligand bonded to Os(4) have adopted semibridging bonding modes.

The fact that **3** contains only two hydride ligands indicates that 1 equiv of H_2 was eliminated at some stage in the condensation. Such eliminations have been observed previously in the high-temperature condensation of hydride-containing clusters.[4] No attempt was made to measure the small amounts of H_2 that could have been formed in the reaction. Overall the formation of **3** requires the loss of 4 mol of CO and 1 equiv of H_2 from 2 mol of **2**. Mechanistically, the condensation must be complex. A schematic representation of the condensation is shown in Figure 3. It is believed that the lone pairs of electrons on the thiolato ligands in **2** assist in the reaction through the formation of transient donor–acceptor bonds that join the clusters. Details of the condensation cannot be accurately predicted at this time. Figure 3 shows only the locations where key bonds must be formed and broken in order to produce **3**.

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Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares planes for compound **3** (3 pages); a table of structure factor amplitudes for compound **3** (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

New Mode of Bonding of Bis((diphenylphosphino)methyl)phenylphosphine, dpmp: Synthesis and Structure of a Sterically Crowded, Triply Bonded Dirhenium Complex, $[Re_2Cl_3(dpmp)_2]X$ (X = Cl, PF_6)

F. Albert Cotton* and Marek Matusz

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The reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with dpmp leads to reduction of the quadruple bond and results in the formation of a triply bridged complex, $[Re_2Cl_3(dpmp)_2]X$. The title compound has been isolated as the chloride and hexafluorophosphate salts. $[Re_2Cl_3(dpmp)_2]Cl$ crystallizes in the monoclinic space group *Cc* with the following unit cell dimensions: a = 13.130 (3) Å, b = 22.162 (4) Å, c = 23.634 (3) Å, β = 104.94 (1)°, V = 6645 (2) Å^3, and Z = 4. The hexafluorophosphate salt, $[Re_2Cl_3(dpmp)_2]PF_6$, was obtained by metathesis and crystallized in the monoclinic space group $P2_1/c$ with a = 24.835 (4) Å, b = 12.048 (3) Å, c = 24.047 (5) Å, β = 114.25 (2)°, V = 6560 (5) Å^3, and Z = 4. A new mode of bonding has been observed in which the triphosphine has doubly bridged the dimetal unit, with the middle phosphorus atom coordinated to one rhenium atom and both terminal phosphorus atoms coordinated to the other rhenium atom.

Introduction

Bifunctional phosphines have been used extensively to stabilize multiple bonds between metal atoms.[1,2] They have been shown to coordinate in two different ways, namely as bridges spanning a dimetallic core and as chelating ligands. A natural extension of the bifunctional phosphines are polyfunctional phosphines. As always with polyfunctional ligands, the problem of forming

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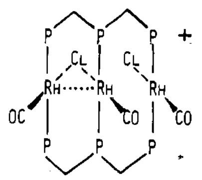
Table I. Crystal Data for **1** and **2**

formula	$[Re_2Cl_3(dpmp)_2]Cl\cdot 2CH_2Cl_2$	$[Re_2Cl_3(dpmp)_2]PF_6\cdot CH_2Cl_2$
fw	1697.10	1721.68
space group	*Cc*	$P2_1/c$
systematic absences	hkl, $h + k \neq 2n$; $00l$, $l \neq 2n$	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
a, Å	13.130 (3)	24.835 (4)
b, Å	22.162 (4)	12.048 (3)
c, Å	23.634 (3)	24.047 (5)
α, deg	90.0	90.0
β, deg	104.94 (1)	114.25 (2)
γ, deg	90.0	90.0
V, ^{3}	6645 (2)	6560 (5)
Z	4	4
d_{calcd}, g/cm^3	1.696	1.743
cryst size, mm	0.2 × 0.4 × 0.6	0.2 × 0.4 × 0.08
μ(Mo Kα), cm^{-1}	41.966	41.676
data collecn instrument	$P\bar{1}$	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientation reflecns: no.; range (2θ), deg	15; $20 < 2\theta < 25$	25; $20 < 2\theta < 25$
temp, °C	4	23
scan method	ω	
data collecn range, 2θ, deg	4–45	
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4504, 4372	7434, 5791
no. of params refined	387	396
transmission factors: max, min	0.998, 0.641	0.998, 0.686
R^a	0.0344	0.0548
$R_w{}^b$	0.0488	0.0706
quality-of-fit indicator^c	1.204	1.759
largest shift/esd, final cycle	0.04	2.13
largest peak, e/Å^3	1.27	1.52

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

polymeric materials is encountered and careful design of ligands and reaction conditions is necessary. Recently some attention has been focused on bis((diphenylphosphino)methyl)phenylphosphine (dpmp), a small-bite triphosphine that has been shown to form a diversified group of complexes with transition metals.[3-10] Of special interest to us is a group of compounds with a near-linear array of three metal atoms, a typical example being the trirhodium cation



Recent efforts in our laboratory have been focused on extending bonding between metal atoms from dimeric to multinuclear linear units. dpmp has been shown to coordinate in a linear fashion so as to stabilize almost linear triatomic arrangements of metal atoms, so we chose it as our initial ligand.

Experimental Section

Reagents. Tetrabutylammonium octachlorodirhenate, $(n\text{-}Bu_4N)_2Re_2Cl_8$, was prepared by a standard procedure.[12] Bis((diphenylphosphino)methyl)phenylphosphine, dpmp, was synthesized after the method of Appel.[13] Methanol was freshly distilled from magnesium methoxide.

Preparation of $[Re_2Cl_3(dpmp)_2]Cl$. A round-bottom flask was charged with 0.11 g (0.1 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$, 0.20 g (0.4 mmol) of dpmp, and 10 mL of methanol. The contents of the flask were refluxed for 36 h under argon. The reaction mixture was cooled and filtered. The filtrate was concentrated by passing a stream of nitrogen over the solution. Crystalline material was deposited, and the solution was placed in a freezer to ensure complete crystallization. The product was separated by filtration, washed with small amounts of cold methanol and then ether, and finally vacuum-dried. The yield was 70 mg (45% based on Re) of brownish crystals. Single crystals were grown by layering ether onto a dichloromethane solution of **1**.

Preparation of $[Re_2Cl_3(dpmp)_2]PF_6$. A sample of $[Re_2Cl_3(dpmp)_2]Cl$ was suspended in reagent grade acetone and treated with excess NH_4PF_6. The reaction mixture was stirred for 0.5 h and evaporated to dryness. The solid residue was extracted with dichloromethane to give a brown solution. The solution was filtered and layered with ether. Brown crystals of the product separated in a few days.

X-ray Crystallographic Procedures. Single crystals of **1** and **2** were grown as described in the preparative procedures. Crystals of **1** and **2** had severe twinning problems. This could be explained on the basis that the $[Re_2Cl_3(dpmp)_2]^+$ cation is optically active and the reaction mixture is a racemic mixture of two enantiomorphs. In the case of **1** spontaneous resolution of enantiomorphs occurred and we were able to pick out a crystal that diffracted well and that contained molecules of one enantiomer only. In the case of **2** all the crystals examined were of the same quality and were a racemic mixture of the title compound.

Geometric and intensity data collection followed standard procedures.[14] Both crystals were found to be monoclinic, and the presence of mirror planes as well as axial lengths was confirmed by oscillation photographs. Centering of the monoclinic cell for **1** was confirmed by photographing the *ab* diagonal and systematically absent data were not collected. The ω-scan technique was used to collect the data points in the range $4 \leq 2\theta \leq 45°$. Monitoring of three check reflections showed no decay in intensity. The data were corrected for Lorentz and polarization effects. An empirical absorption correction[15] was applied on the basis of azimuthal scans of selected reflections with an χ angle near 90°.

Systematic absences for $[Re_2Cl_3(dpmp)_2]Cl$ (**1**) indicated space group $C2/c$ or Cc. Positions of rhenium atoms were found by the direct-methods program MULTAN, but the structure would not develop properly in the centrosymmetric space group $C2/c$. The very high percentage of

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Table II. Positional and Isotropic-Equivalent Displacement Parameters for $[Re_2Cl_3(dpmp)_2]Cl$ (**1**) and $[Re_2Cl_3(dpmp)_2]PF_6$ (**2**)[a]

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
				Complex **1**					
Re(1)	0.000	0.59683 (2)	0.000	2.125 (8)	C(43)	0.455 (2)	0.516 (1)	0.108 (1)	7.5 (5)*
Re(2)	−0.08879 (5)	0.50613 (2)	−0.01756 (2)	2.175 (9)	C(44)	0.424 (2)	0.4758 (9)	0.0600 (9)	6.2 (4)*
Cl(1)	−0.0654 (3)	0.6845 (2)	0.0362 (1)	3.67 (7)	C(45)	0.328 (1)	0.4926 (7)	0.0154 (7)	4.4 (3)*
Cl(2)	−0.2532 (2)	0.5308 (2)	−0.0867 (1)	3.28 (7)	C(50)	0.212 (1)	0.6376 (6)	−0.0536 (6)	2.9 (2)*
Cl(3)	−0.1568 (3)	0.4004 (1)	−0.0462 (2)	3.66 (8)	C(51)	0.209 (1)	0.6951 (6)	−0.0267 (6)	3.4 (3)*
Cl(4)	1.1547 (4)	0.5545 (2)	0.7743 (2)	5.6 (1)	C(52)	0.259 (1)	0.7448 (7)	−0.0413 (7)	4.1 (3)*
Cl(5)	1.4413 (5)	0.4794 (3)	0.8846 (3)	8.5 (1)*	C(53)	0.321 (1)	0.7372 (7)	−0.0810 (7)	4.4 (3)*
Cl(6)	1.5175 (8)	0.4881 (4)	0.7811 (5)	12.0 (2)*	C(54)	0.330 (1)	0.6816 (7)	−0.1063 (7)	4.2 (3)*
Cl(7)	1.380 (1)	0.6409 (7)	0.7142 (6)	17.9 (4)*	C(55)	0.275 (1)	0.6325 (6)	−0.0926 (6)	3.2 (2)*
Cl(8)	1.225 (1)	0.7327 (6)	0.6889 (6)	16.8 (4)*	C(60)	−0.277 (1)	0.5788 (6)	0.0522 (6)	3.3 (2)*
P(1)	−0.0767 (3)	0.6370 (1)	−0.1000 (1)	2.60 (6)	C(61)	−0.372 (1)	0.5604 (6)	0.0134 (6)	3.5 (3)*
P(2)	−0.0205 (3)	0.5067 (1)	−0.1054 (2)	2.59 (7)	C(62)	−0.461 (1)	0.5987 (7)	0.0014 (7)	4.3 (3)*
P(3)	0.1557 (3)	0.5716 (2)	−0.0280 (1)	2.57 (6)	C(63)	−0.456 (1)	0.6522 (8)	0.0241 (8)	5.4 (4)*
P(4)	−0.1691 (2)	0.5246 (2)	0.0661 (1)	2.65 (7)	C(64)	−0.363 (1)	0.6748 (8)	0.0628 (7)	4.8 (3)*
P(5)	0.0583 (2)	0.5645 (1)	0.1007 (1)	2.41 (6)	C(65)	−0.272 (1)	0.6353 (8)	0.0775 (7)	4.8 (3)*
P(6)	0.0376 (3)	0.4417 (1)	0.0499 (1)	2.63 (6)	C(70)	−0.229 (1)	0.4647 (6)	0.1023 (6)	3.2 (2)*
C(1)	−0.070 (1)	0.5746 (6)	−0.1502 (6)	2.9 (2)*	C(71)	−0.240 (1)	0.4750 (8)	0.1560 (7)	4.4 (3)*
C(2)	0.122 (1)	0.5164 (6)	−0.0892 (6)	2.9 (2)*	C(72)	−0.294 (1)	0.4332 (9)	0.1843 (8)	5.5 (4)*
C(3)	−0.0623 (9)	0.5544 (6)	0.1268 (6)	2.8 (2)*	C(73)	−0.340 (1)	0.3826 (8)	0.1512 (8)	5.3 (4)*
C(4)	0.120 (1)	0.4901 (6)	0.1083 (6)	2.9 (2)*	C(74)	−0.331 (1)	0.3725 (9)	0.0948 (8)	5.8 (4)*
C(10)	−0.214 (1)	0.6648 (6)	−0.1243 (6)	3.0 (2)*	C(75)	−0.274 (1)	0.4144 (7)	0.0688 (7)	4.2 (3)*
C(11)	−0.255 (1)	0.6788 (6)	−0.1834 (6)	3.2 (2)*	C(80)	0.1432 (9)	0.6101 (6)	0.1575 (5)	2.4 (2)*
C(12)	−0.359 (1)	0.6979 (8)	−0.2038 (8)	5.1 (3)*	C(81)	0.156 (1)	0.6715 (6)	0.1512 (6)	3.2 (2)*
C(13)	−0.420 (1)	0.7096 (8)	−0.1652 (7)	4.9 (3)*	C(82)	0.224 (1)	0.7073 (8)	0.1914 (7)	4.7 (3)*
C(14)	−0.375 (1)	0.6959 (6)	−0.1066 (6)	3.7 (3)*	C(83)	0.281 (1)	0.6795 (8)	0.2437 (7)	4.7 (3)*
C(15)	−0.276 (1)	0.6727 (7)	−0.0857 (6)	3.6 (3)*	C(84)	0.273 (1)	0.6187 (9)	0.2542 (8)	5.3 (4)*
C(20)	−0.0132 (9)	0.7044 (5)	−0.1245 (5)	2.5 (2)*	C(85)	0.203 (1)	0.5822 (7)	0.2089 (6)	3.6 (3)*
C(21)	−0.028 (1)	0.7581 (7)	−0.0995 (6)	3.9 (3)*	C(90)	−0.012 (1)	0.3831 (6)	0.0913 (6)	3.1 (2)*
C(22)	0.013 (1)	0.8119 (8)	−0.1122 (8)	5.1 (3)*	C(91)	−0.033 (1)	0.3270 (7)	0.0688 (7)	4.1 (3)*
C(23)	0.064 (1)	0.8113 (9)	−0.1559 (8)	5.6 (4)*	C(92)	−0.062 (1)	0.2789 (8)	0.1002 (7)	4.8 (3)*
C(24)	0.083 (1)	0.7562 (8)	−0.1828 (7)	4.9 (3)*	C(93)	−0.068 (1)	0.2928 (8)	0.1596 (7)	4.9 (3)*
C(25)	0.042 (1)	0.7012 (7)	−0.1668 (6)	3.8 (3)*	C(94)	−0.049 (1)	0.3484 (7)	0.1811 (7)	4.1 (3)*
C(30)	−0.0518 (9)	0.4467 (6)	−0.1609 (5)	2.8 (2)*	C(95)	−0.020 (1)	0.3948 (6)	0.1484 (6)	3.1 (2)*
C(31)	−0.159 (1)	0.4288 (7)	−0.1831 (7)	4.4 (3)*	C(100)	0.134 (1)	0.3965 (6)	0.0238 (6)	2.8 (2)*
C(32)	−0.187 (2)	0.3841 (9)	−0.2255 (9)	6.0 (4)*	C(101)	0.223 (1)	0.3769 (7)	0.0652 (7)	4.5 (3)*
C(33)	−0.107 (1)	0.3558 (9)	−0.2453 (8)	5.6 (4)*	C(102)	0.295 (1)	0.3369 (8)	0.0475 (8)	5.1 (4)*
C(34)	0.002 (1)	0.3703 (8)	−0.2216 (8)	5.3 (4)*	C(103)	0.275 (2)	0.3183 (9)	−0.0101 (9)	6.5 (4)*
C(35)	0.027 (1)	0.4196 (7)	−0.1819 (6)	3.6 (3)*	C(104)	0.175 (1)	0.3384 (8)	−0.0535 (8)	5.0 (3)*
C(40)	0.275 (1)	0.5454 (6)	0.0253 (6)	3.0 (2)*	C(105)	0.113 (1)	0.3763 (6)	−0.0327 (6)	3.5 (3)*
C(41)	0.314 (1)	0.5820 (7)	0.0753 (6)	3.7 (3)*	C(110)	1.464 (2)	0.528 (1)	0.830 (1)	8.5 (6)*
C(42)	0.403 (1)	0.5650 (8)	0.1170 (8)	5.4 (4)*	C(111)	1.262 (3)	0.672 (2)	0.730 (2)	14 (1)*
				Complex **2**					
Re(1)	0.68738 (2)	0.06759 (5)	0.41698 (2)	2.54 (1)	C(22)	0.5151 (8)	−0.253 (2)	0.3677 (8)	5.9 (5)*
Re(2)	0.75265 (2)	−0.04307 (5)	0.39675 (3)	2.66 (1)	C(23)	0.5360 (8)	−0.359 (2)	0.3643 (8)	6.4 (5)*
Cl(1)	0.6300 (2)	0.2283 (3)	0.4358 (2)	3.71 (9)	C(24)	0.5949 (7)	−0.391 (2)	0.3907 (8)	5.3 (4)*
Cl(2)	0.5921 (2)	0.0375 (3)	0.3349 (2)	3.49 (9)	C(25)	0.6364 (7)	−0.303 (2)	0.4238 (7)	4.9 (4)*
Cl(3)	0.7423 (2)	−0.2362 (3)	0.3835 (2)	4.2 (1)	C(30)	0.8608 (7)	−0.174 (1)	0.5405 (7)	4.5 (4)*
Cl(10)	0.4567 (4)	0.6210 (8)	0.4681 (4)	12.2 (2)*	C(31)	0.8846 (8)	−0.179 (2)	0.6022 (8)	5.6 (4)*
Cl(11)	0.3579 (3)	0.4784 (8)	0.4497 (4)	12.1 (2)*	C(32)	0.9398 (9)	−0.253 (2)	0.6282 (9)	7.5 (6)*
P(1)	0.6661 (2)	−0.0857 (4)	0.4733 (2)	3.24 (9)	C(33)	0.959 (1)	−0.304 (2)	0.591 (1)	8.3 (6)*
P(2)	0.7963 (2)	−0.0833 (4)	0.5033 (2)	3.4 (1)	C(34)	0.9347 (9)	−0.300 (2)	0.5318 (9)	7.1 (5)*
P(3)	0.7540 (2)	0.1401 (4)	0.5159 (2)	3.2 (1)	C(35)	0.8835 (7)	−0.232 (2)	0.5048 (8)	5.5 (4)*
P(4)	0.8215 (2)	0.0944 (3)	0.3953 (2)	3.09 (9)	C(40)	0.7867 (6)	0.276 (1)	0.5239 (6)	3.4 (3)*
P(5)	0.7026 (2)	0.1917 (3)	0.3443 (2)	2.71 (9)	C(41)	0.7615 (7)	0.357 (1)	0.4809 (7)	4.7 (4)*
P(6)	0.6997 (2)	−0.0287 (3)	0.2851 (2)	2.98 (9)	C(42)	0.7867 (7)	0.466 (2)	0.4882 (8)	5.3 (4)*
P(7)	0.8795 (6)	0.536 (1)	0.3468 (6)	17.9 (5)*	C(43)	0.8381 (8)	0.489 (2)	0.5405 (9)	6.5 (5)*
F(1)	0.878 (1)	0.659 (3)	0.372 (1)	28 (1)*	C(44)	0.8622 (8)	0.410 (2)	0.5821 (8)	5.8 (5)*
F(2)	0.897 (1)	0.554 (3)	0.278 (2)	28 (1)*	C(45)	0.8379 (7)	0.296 (2)	0.5765 (7)	4.8 (4)*
F(3)	0.942 (2)	0.545 (4)	0.359 (2)	35 (2)*	C(50)	0.7283 (6)	0.149 (1)	0.5764 (7)	4.2 (4)*
F(4)	0.876 (2)	0.405 (3)	0.317 (2)	29 (2)*	C(51)	0.7421 (7)	0.065 (2)	0.6218 (8)	5.0 (4)*
F(5)	0.841 (1)	0.485 (3)	0.383 (1)	24 (1)*	C(52)	0.7206 (7)	0.072 (2)	0.6685 (8)	5.5 (4)*
F(6)	0.816 (1)	0.561 (3)	0.291 (1)	27 (1)*	C(53)	0.6865 (8)	0.158 (2)	0.6671 (8)	5.7 (4)*
C(1)	0.7384 (6)	−0.152 (1)	0.5201 (6)	3.6 (3)*	C(54)	0.6754 (7)	0.249 (2)	0.6260 (8)	5.3 (4)*
C(2)	0.8187 (6)	0.044 (1)	0.5496 (6)	3.7 (3)*	C(55)	0.6962 (7)	0.243 (1)	0.5805 (7)	4.4 (4)*
C(3)	0.7816 (6)	0.225 (1)	0.3627 (6)	3.2 (3)*	C(60)	0.8583 (6)	0.050 (1)	0.3469 (7)	3.9 (3)*
C(4)	0.6795 (6)	0.120 (1)	0.2717 (6)	3.4 (3)*	C(61)	0.8662 (7)	−0.062 (1)	0.3403 (7)	4.3 (4)*
C(10)	0.6308 (6)	−0.064 (1)	0.5270 (6)	3.2 (3)*	C(62)	0.8977 (7)	−0.093 (2)	0.3056 (8)	5.2 (4)*
C(11)	0.6368 (7)	−0.150 (2)	0.5677 (7)	4.8 (4)*	C(63)	0.9212 (9)	−0.015 (2)	0.2796 (9)	7.0 (5)*
C(12)	0.6055 (8)	−0.138 (2)	0.6048 (8)	6.2 (5)*	C(64)	0.9140 (9)	0.095 (2)	0.2882 (9)	7.4 (6)*
C(13)	0.5694 (8)	−0.047 (2)	0.5982 (8)	5.6 (4)*	C(65)	0.8830 (8)	0.135 (2)	0.3231 (8)	6.0 (5)*
C(14)	0.5642 (7)	0.033 (2)	0.5574 (7)	4.8 (4)*	C(70)	0.8864 (6)	0.140 (1)	0.4612 (6)	3.4 (3)*
C(15)	0.5951 (6)	0.027 (1)	0.5202 (7)	3.9 (3)*	C(71)	0.9246 (7)	0.058 (2)	0.4959 (7)	5.0 (4)*
C(20)	0.6177 (6)	−0.199 (1)	0.4292 (6)	3.6 (3)*	C(72)	0.9757 (7)	0.084 (2)	0.5472 (8)	5.1 (4)*
C(21)	0.5586 (6)	−0.173 (1)	0.4013 (7)	4.1 (3)*	C(73)	0.9887 (7)	0.199 (2)	0.5615 (8)	5.4 (4)*

Table II (Continued)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C(74)	0.9547 (8)	0.281 (2)	0.5241 (8)	5.9 (5)*	C(93)	0.7881 (8)	−0.138 (2)	0.1600 (8)	5.9 (5)*
C(75)	0.8999 (7)	0.251 (2)	0.4751 (7)	4.9 (4)*	C(94)	0.7719 (7)	−0.214 (2)	0.1929 (8)	5.4 (4)*
C(80)	0.6657 (6)	0.324 (1)	0.3166 (6)	2.8 (3)*	C(95)	0.7463 (7)	−0.182 (1)	0.2318 (7)	4.6 (4)*
C(81)	0.6988 (6)	0.420 (1)	0.3181 (7)	3.8 (3)*	C(100)	0.6299 (6)	−0.102 (1)	0.2425 (6)	3.4 (3)*
C(82)	0.6689 (7)	0.517 (2)	0.2894 (8)	5.0 (4)*	C(101)	0.6045 (6)	−0.177 (1)	0.2675 (7)	3.8 (3)*
C(83)	0.6078 (7)	0.515 (2)	0.2625 (8)	5.4 (4)*	C(102)	0.5494 (6)	−0.223 (1)	0.2305 (7)	3.7 (3)*
C(84)	0.5740 (7)	0.421 (1)	0.2607 (7)	4.4 (4)*	C(103)	0.5208 (7)	−0.193 (1)	0.1682 (7)	4.7 (4)*
C(85)	0.6071 (6)	0.323 (1)	0.2917 (6)	3.6 (3)*	C(104)	0.5468 (7)	−0.120 (2)	0.1436 (8)	5.3 (4)*
C(90)	0.7374 (6)	−0.064 (1)	0.2378 (6)	3.0 (3)*	C(105)	0.6020 (6)	−0.069 (1)	0.1792 (6)	3.7 (3)*
C(91)	0.7539 (7)	0.011 (1)	0.2044 (7)	4.2 (4)*	C(110)	0.421 (1)	0.541 (2)	0.505 (1)	9.1 (7)*
C(92)	0.7800 (7)	−0.029 (2)	0.1651 (8)	5.3 (4)*					

[a] Starred values are refined isotropically. Anisotropically refined atoms are given in the form of the isotropic-equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

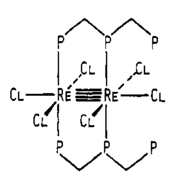
Table III. Selected Bond Distances (Å) and Their Estimated Standard Deviations for $[Re_2Cl_3(dpmp)_2]Cl$ (**1**) and $[Re_2Cl_3(dpmp)_2]PF_6$ (**2**)

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
				Complex **1**				
Re(1)	Re(2)	2.307 (1)	Re(2)	Cl(3)	2.537 (3)	P(2)	C(2)	1.830 (13)
Re(1)	Cl(1)	2.371 (3)	Re(2)	P(2)	2.464 (3)	P(3)	C(2)	1.860 (13)
Re(1)	P(1)	2.484 (3)	Re(2)	P(4)	2.504 (3)	P(4)	C(3)	1.848 (12)
Re(1)	P(3)	2.372 (3)	Re(2)	P(6)	2.443 (3)	P(5)	C(3)	1.855 (12)
Re(1)	P(5)	2.413 (3)	P(1)	C(1)	1.837 (13)	P(5)	C(4)	1.825 (12)
Re(2)	Cl(2)	2.410 (3)	P(2)	C(1)	1.859 (13)	P(6)	C(4)	1.860 (13)
				Complex **2**				
Re(1)	Re(2)	2.300 (1)	Re(2)	Cl(3)	2.348 (3)	P(2)	C(2)	1.839 (12)
Re(1)	Cl(1)	2.553 (3)	Re(2)	P(2)	2.386 (3)	P(3)	C(2)	1.874 (12)
Re(1)	Cl(2)	2.407 (3)	Re(2)	P(4)	2.391 (3)	P(4)	C(3)	1.854 (12)
Re(1)	P(1)	2.472 (3)	Re(2)	P(6)	2.464 (3)	P(5)	C(3)	1.868 (11)
Re(1)	P(3)	2.435 (3)	P(1)	C(1)	1.863 (12)	P(5)	C(4)	1.818 (12)
Re(1)	P(5)	2.445 (3)	P(2)	C(1)	1.841 (12)	P(6)	C(4)	1.850 (12)

the data observed (over 3σ) and the fact that symmetry-equivalent reflections could not be successfully averaged suggested the noncentrosymmetric space group *Cc*. Refinement was therefore continued in *Cc*, and the choice of space group was confirmed by successful refinement. At the final stage enantiomorphs were changed and the enantiomorph giving a lower *R* factor (3.4 vs. 4.2%) was chosen as the correct solution. Rhenium atoms in **2** were found by the direct-methods program. The remaining atoms in both structures were found by alternating least-squares and difference Fourier programs. The final difference Fourier map in **1** showed no peaks of chemical significance. In the structure of **2** there was remaining electron density around the PF_6 anion, indicating slight disorder. No attempts were made to model it. The details of data collection and structure refinement are given in Table I.

Results and Discussion

The work reported here was begun in the naive hope that by reaction of 2 mol of dpmp with $Re_2Cl_8^{2-}$ we might obtain some sort of useful intermediate, e.g. I or II, from which further reactions might be used to obtain tri- or tetranuclear species. The reaction did not proceed in this way for two reasons. First, the dpmp exercised its potential as a reducing agent and converted the Re_2^{6+} center to an Re_2^{4+} center. Second, the dpmp ligand manifested a mode of coordination not previously observed, in which it doubly bridges the dimetal unit as shown in III. Two salts, chloride and hexafluorophosphate, of the $[Re_2Cl_3(dpmp)_2]^+$ cation have been isolated and structurally characterized.



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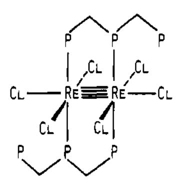

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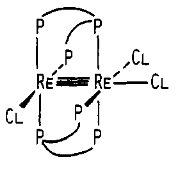

III

In the case of compound **1** we were able to select a crystal that diffracts well and that has been shown to be a pure enantiomorph. The molecule crystallized in the noncentrosymmetric space group *Cc*. Compound **2**, although inherently optically active, formed racemic crystals with a pair of molecules, being opposite enantiomers related by an inversion center. The space group $P2_1/c$ for **2** has been uniquely determined from systematic absences.

The cationic parts of **1** and **2** are virtually identical; the difference lies in different counterions and the amount of lattice solvent. The different packing forces dictate slight geometric differences in the cations in **1** and **2**. The bonding mode for dpmp was unprecedented when this paper was written. We have now learned[11] of a similar bonding mode found in a $[Rh_2(dmmm)_2(CO)_2]^{2+}$ cation (dmmm is the all-methyl analogue of dpmp). The $[Re_2Cl_3(dpmp)_2]^+$ cation consists of a triply bonded dirhenium core, with one Re atom being pentacoordinate and the other being hexacoordinate. The backbone of the phosphine and one rhenium atom form a six-membered ring in a boat conformation. The middle phosphorus atom in the triphosphine ligand is coordinated to one rhenium atom, and the two terminal phosphorus atoms are coordinated to the other rhenium. The phosphine acts as both chelating and bridging ligand. The second phosphine is coordinated in a similar fashion in a head-to-tail arrangement. With two bulky phosphines the molecule is severely crowded and distorted from any ideal geometry. To a very crude approximation one rhenium atom has four ligands as in a typical M_2X_8 molecule and the second rhenium atom has an additional axial chloride. A similar situation has been observed for $Re_2X_5(dppm)_2$ (X = Cl, Br) compounds.[16,17]

The ORTEP diagram, together with a labeling scheme (for fully labeled ORTEP diagrams of **1** and **2** see the supplementary material), is presented in Figure 1. Table II contains positional and isotropic-equivalent displacement parameters for **1** and **2**. Selected

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(16) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.
(17) Cotton, F. A.; Shive, L. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2239.

Table IV. Selected Bond Angles (deg) and Their Estimated Standard Deviations for $[Re_2Cl_3(dpmp)_2]Cl$ (**1**) and $[Re_2Cl_3(dpmp)_2]PF_6$ (**2**)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
					Complex **1**						
Re(2)	Re(1)	Cl(1)	124.45 (9)	Re(1)	Re(2)	P(4)	90.64 (8)	Re(2)	P(2)	C(1)	109.5 (4)
Re(2)	Re(1)	P(1)	94.54 (8)	Re(1)	Re(2)	P(6)	99.51 (8)	Re(2)	P(2)	C(2)	113.6 (4)
Re(2)	Re(1)	P(3)	100.18 (8)	Cl(2)	Re(2)	Cl(3)	80.6 (1)	C(1)	P(2)	C(2)	102.4 (6)
Re(2)	Re(1)	P(5)	86.32 (7)	Cl(2)	Re(2)	P(2)	83.4 (1)	Re(1)	P(3)	C(2)	109.0 (4)
Cl(1)	Re(1)	P(1)	87.3 (1)	Cl(2)	Re(2)	P(4)	90.7 (1)	Re(2)	P(4)	C(3)	106.3 (4)
Cl(1)	Re(1)	P(3)	135.4 (1)	Cl(2)	Re(2)	P(6)	156.0 (1)	Re(1)	P(5)	C(3)	106.4 (4)
Cl(1)	Re(1)	P(5)	86.6 (1)	Cl(3)	Re(2)	P(2)	87.7 (1)	Re(1)	P(5)	C(4)	112.6 (4)
P(1)	Re(1)	P(3)	89.2 (1)	Cl(3)	Re(2)	P(4)	99.8 (1)	C(3)	P(5)	C(4)	104.7 (6)
P(1)	Re(1)	P(5)	173.1 (1)	Cl(3)	Re(2)	P(6)	76.5 (1)	Re(2)	P(6)	C(4)	108.3 (4)
P(3)	Re(1)	P(5)	97.4 (1)	P(2)	Re(2)	P(4)	169.6 (1)	P(1)	C(1)	P(2)	108.1 (6)
Re(1)	Re(2)	Cl(2)	104.31 (8)	P(2)	Re(2)	P(6)	102.7 (1)	P(2)	C(2)	P(3)	105.2 (7)
Re(1)	Re(2)	Cl(3)	168.43 (9)	P(4)	Re(2)	P(6)	86.2 (1)	P(4)	C(3)	P(5)	109.1 (6)
Re(1)	Re(2)	P(2)	82.56 (7)	Re(1)	P(1)	C(1)	105.6 (4)	P(5)	C(4)	P(6)	106.8 (6)
					Complex **2**						
Re(2)	Re(1)	Cl(1)	166.09 (7)	P(1)	Re(1)	P(5)	168.2 (1)	Re(2)	P(2)	C(1)	106.0 (4)
Re(2)	Re(1)	Cl(2)	106.27 (7)	P(3)	Re(1)	P(5)	103.7 (1)	Re(2)	P(2)	C(2)	111.8 (4)
Re(2)	Re(1)	P(1)	90.61 (8)	Re(1)	Re(2)	Cl(3)	123.73 (8)	C(1)	P(2)	C(2)	108.0 (5)
Re(2)	Re(1)	P(3)	99.17 (8)	Re(1)	Re(2)	P(2)	86.51 (8)	Re(1)	P(3)	C(2)	108.5 (4)
Re(2)	Re(1)	P(5)	82.73 (7)	Re(1)	Re(2)	P(4)	99.88 (8)	Re(2)	P(4)	C(3)	109.5 (4)
Cl(1)	Re(1)	Cl(2)	80.0 (1)	Re(1)	Re(2)	P(6)	94.77 (7)	Re(1)	P(5)	C(3)	114.7 (4)
Cl(1)	Re(1)	P(1)	102.1 (1)	Cl(3)	Re(2)	P(2)	85.4 (1)	Re(1)	P(5)	C(4)	108.3 (4)
Cl(1)	Re(1)	P(3)	76.1 (1)	Cl(3)	Re(2)	P(4)	136.4 (1)	C(3)	P(5)	C(4)	102.5 (5)
Cl(1)	Re(1)	P(5)	85.7 (1)	Cl(3)	Re(2)	P(6)	86.7 (1)	Re(2)	P(6)	C(4)	104.1 (4)
Cl(2)	Re(1)	P(1)	88.7 (1)	P(2)	Re(2)	P(4)	98.3 (1)	P(1)	C(1)	P(2)	108.8 (6)
Cl(2)	Re(1)	P(3)	154.2 (1)	P(2)	Re(2)	P(6)	171.3 (1)	P(2)	C(2)	P(3)	105.2 (6)
Cl(2)	Re(1)	P(5)	83.9 (1)	P(4)	Re(2)	P(6)	90.0 (1)	P(4)	C(3)	P(5)	104.1 (6)
P(1)	Re(1)	P(3)	86.9 (1)	Re(1)	P(1)	C(1)	106.3 (4)	P(5)	C(4)	P(6)	109.7 (6)

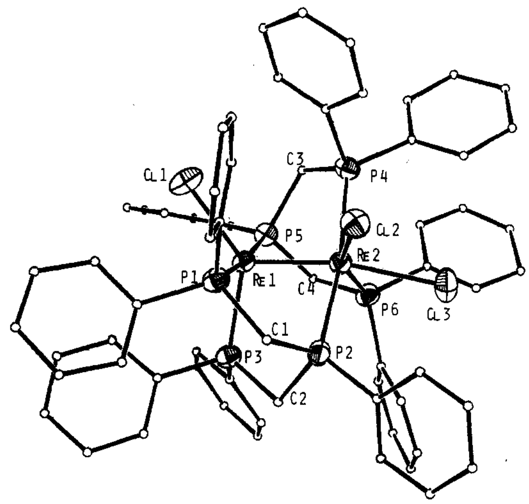

Figure 1. ORTEP drawing of the $[Re_2Cl_3(dpmp)_2]^+$ cation in **1** at the 50% probability level. Phenyl carbon atoms are represented as arbitrarily small circles for the sake of clarity. Only the immediate coordination sphere of the rhenium atoms has been labeled. For a completely labeled ORTEP drawing see the supplementary material.

bond distances can be found in Table III and selected bond angles in Table IV.

The Re-Re distance in **1** is 2.307 (1) Å and in **2** is 2.300 (1) Å. The difference is not statistically significant. The distance is slightly longer than that found in typical triply bonded, phosphine-bridged rhenium dimers[18] (2.234 (3) Å in $Re_2Cl_4(dppm)_2$) but compares favorably with 2.300 (1) Å in $[Re_2Cl_2(Ph_2Ppy)_4](PF_6)_2$.[19] Rhenium–phosphorus bonds in **1** vary from 2.372 (3) Å for Re(1)–P(3) to 2.504 (3) Å for Re(2)–P(4). These variations are partially due to the steric crowding, but the influence of the ligands on a particular rhenium atom should not be overlooked. Two chlorides, Cl(1) and Cl(2), are separated by 2.371 (3) and 2.410 (3) Å from rhenium atoms. The Re(2)–Cl(3) distance of 2.537 (3) Å is significantly longer and is typical for axial coordination. There are no close contacts between cations and anions in **1** or **2**.

We are currently exploring reactions of other tridentate ligands with multiply bonded dimers.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Labeled ORTEP diagrams, full listings of bond distances and angles, and listings of anisotropic displacement parameters for **1** and **2** (11 pages); tables of calculated and observed structure factors for **1** and **2** (51 pages). Ordering information is given on any current masthead page.

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(19) Barder, T. J.; Cotton, F. A.; Powell, G. L.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 1323.