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A Triply Bonded $Re_2X_4L_4$ Compound with Cis Stereochemistry at Each Metal Atom

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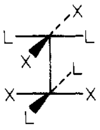
The reaction of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ with excess $Ph_2P(CH_2)_3PPh_2$ (dppp) in refluxing acetonitrile affords $Re_2Cl_4(dppp)_2$, a dark green crystalline solid. The dppp molecules are coordinated to give a $(dppp)Cl_2Re{\equiv}ReCl_2(dppp)$ molecule with virtual C_{2h} symmetry. Each six-membered Re(dppp) ring has a chair conformation. Principal molecular dimensions: Re–Re, 2.266 (1) Å; Re–Cl(av), 2.392 [8] Å; Re–P(av), 2.401 [1] Å. When compared with metal–ligand distances in $Re_2X_4(PR_3)_4$ species with trans stereochemistries, these results show the existence of a structural trans effect in $ReCl_2P_2$ units. The compound crystallizes in space group $P2_1/n$ with a = 13.019 (2) Å, b = 9.434 (4) Å, c = 20.900 (2) Å, β = 106.34 (1)°, V = 2463 (2) Å^3, and Z = 2. There is a crystallographic center of inversion at the midpoint of the Re–Re bond.

Introduction

Compounds of the general type $Re_2X_4L_4$ provided the first examples of the type of metal-to-metal triple bond that can be described as d^5–d^5 or, in terms of the occupied metal-based molecular orbitals, $\sigma^2\pi^4\delta^2\delta^{*2}$. Molecules of this sort also constitute the most extensively studied examples of such bonding, both experimentally[2-7] and theoretically.[8] In all previous cases, however, the stereochemistry has been of trans type, **1**, at each metal center. We report here the first description of such a compound with cis stereochemistry, **2**. This stereochemistry was achieved in a planned way, by choosing the ligand so that ring-closure probabilities (favoring the formation of six-membered rather than seven-membered rings) would be likely to give the desired stereochemistry.



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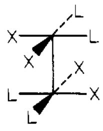

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Experimental Section

Starting Materials. $(n\text{-}Bu_4N)_2Re_2Cl_8$ was prepared as described elsewhere.[9] 1,3-Bis(diphenylphosphino)propane (dppp) was obtained from Strem Chemical Co. and used as received.

Reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ and dppp. $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.152 g, 0.133 mmol) and dppp (0.162 g, 0.393 mmol) were refluxed together in 25 mL of deoxygenated acetonitrile under a nitrogen atmosphere for 4 days. The dark, opaque suspension was cooled and filtered, and small, very dark green crystals were washed with absolute ethanol and diethyl ether and dried in vacuo; yield 0.031 g (17.6%). In addition, small crystals were recovered from a wooden boiling stick; these were found to be suitable for the structure determination. Infrared spectroscopy revealed that the latter consisted of the same material as that isolated in the bulk sample. Anal. Calcd for $ReCl_2P_2C_{27}H_{26}$: C, 48.4; H, 3.92; Cl, 10.59. Found (bulk sample): C, 47.6; H, 3.85; Cl, 10.4. Microanalysis were performed by Galbraith Laboratories, Knoxville, TN.

Physical Measurements. Infrared spectra were recorded as mineral oil mulls on a Pye-Unicam SP3-300 spectrophotometer. Electronic absorption spectra were also obtained in the solid state as mulls on a Perkin-Elmer 559 UV–visible spectrophotometer.

Table I. Summary of Crystal Data and Data Collection Parameters for $Re_2Cl_4(dppp)_2$

formula	Re_2Cl_4-$[(C_6H_5)_2PCH_2CH_2CH_2P(C_6H_5)_2]_2$
formula weight	1339.12
space group	$P2_1/n$
a, Å	13.019 (2)
b, Å	9.434 (4)
c, Å	20.900 (2)
β, deg	106.34 (1)
V, Å^3	2463 (2)
Z	2
d_{calcd}, g/cm^3	1.80
cryst size, mm	0.10 × 0.25 × 0.30
μ(Mo Kα), cm^{-1}	55.62
data collection instrument	Enraf-Nonius CAD-4
radiation	Mo Kα (graphite monochromated); $\lambda_{\bar{\alpha}}$ = 0.710 73 Å
scan method	2θ–ω
data collection range	$5° \leqslant 2\theta \leqslant 52°$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	3615
no. of parameters refined	393
R^a	0.0218
$R_w{}^b$	0.0280
quality-of-fit indicator^c	0.8520
largest shift/esd, final cycle	0.56

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

X-ray Data Collection and Reduction. A green, rectangular plate-shaped crystal of $Re_2Cl_4(dppp)_2$ having approximate dimensions 0.10 × 0.25 × 0.30 mm was coated with epoxy cement and mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite-crystal monochromator in the incident beam. The data were collected at a temperature of 26 ± 2 °C by using the 2θ–ω scan technique. The scan range in ω was calculated as $(0.70 + 0.35 \tan\theta)°$ with 25% extension on either end for background determination.

The data were processed by standard computer programs.[10] Lorentz and polarization corrections were applied. An empirical absorption correction was made, based on azimuthal ψ scans of eight reflections with χ near 90°.[11] The intensities of three standard reflections remained constant within experimental error throughout data collection; no decay correction was applied. A total of 4932 reflections were collected, of which 3977 were unique and not systematically absent. Intensities of equivalent reflections were averaged.

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*, Å^2
Re	−0.04260 (1)	0.06854 (2)	0.02901 (1)	1.877 (3)
Cl(1)	−0.23117 (9)	0.0882 (1)	−0.02509 (6)	3.38 (3)
Cl(2)	−0.0454 (1)	0.3102 (1)	−0.00414 (6)	3.19 (2)
P(1)	0.10659 (9)	0.1270 (1)	0.12283 (5)	2.31 (2)
P(2)	−0.09212 (9)	−0.1012 (1)	0.10044 (5)	2.37 (2)
C(1)	0.1744 (4)	−0.0255 (5)	0.1704 (2)	2.9 (1)
C(2)	0.1065 (4)	−0.1176 (6)	0.2022 (2)	3.0 (1)
C(3)	0.0176 (4)	−0.2030 (5)	0.1549 (2)	3.0 (1)
C(11)	0.2163 (4)	0.2438 (5)	0.1177 (2)	2.9 (1)
C(12)	0.3197 (4)	0.1938 (6)	0.1262 (2)	3.7 (1)
C(13)	0.4016 (4)	0.2869 (7)	0.1278 (3)	4.9 (1)
C(14)	0.3835 (4)	0.4300 (7)	0.1189 (3)	4.9 (1)
C(15)	0.2814 (4)	0.4790 (6)	0.1092 (3)	4.2 (1)
C(16)	0.1990 (4)	0.3870 (6)	0.1083 (2)	3.5 (1)
C(21)	0.0602 (4)	0.2296 (5)	0.1846 (2)	2.78 (9)
C(22)	0.1128 (4)	0.2159 (5)	0.2520 (2)	3.3 (1)
C(23)	0.0801 (4)	0.2955 (6)	0.2985 (2)	3.9 (1)
C(24)	−0.0020 (4)	0.3912 (6)	0.2785 (3)	4.2 (1)
C(25)	−0.0527 (5)	0.4068 (6)	0.2119 (3)	4.5 (1)
C(26)	−0.0213 (4)	0.3263 (6)	0.1659 (2)	3.7 (1)
C(31)	−0.1487 (3)	−0.0028 (5)	0.1587 (2)	2.74 (9)
C(32)	−0.2192 (4)	0.1082 (6)	0.1376 (3)	3.8 (1)
C(33)	−0.2655 (5)	0.1781 (6)	0.1812 (3)	4.9 (1)
C(34)	−0.2391 (4)	0.1406 (7)	0.2466 (3)	4.9 (1)
C(35)	−0.1696 (4)	0.0301 (7)	0.2686 (2)	4.4 (1)
C(36)	−0.1258 (4)	−0.0421 (6)	0.2253 (2)	3.6 (1)
C(41)	−0.1979 (4)	−0.2375 (5)	0.0739 (2)	2.85 (9)
C(42)	−0.1715 (4)	−0.3773 (6)	0.0653 (2)	3.4 (1)
C(43)	−0.2499 (4)	−0.4815 (6)	0.0530 (3)	4.0 (1)
C(44)	−0.3545 (4)	−0.4476 (6)	0.0490 (3)	4.1 (1)
C(45)	−0.3809 (4)	−0.3092 (7)	0.0553 (3)	4.8 (1)
C(46)	−0.3031 (4)	−0.2054 (6)	0.0673 (3)	4.3 (1)
H(1A)	0.233 (3)	0.016 (5)	0.205 (2)	3 (1)[a]
H(1B)	0.196 (4)	−0.063 (5)	0.137 (3)	5 (1)[a]
H(2A)	0.080 (3)	−0.054 (4)	0.231 (2)	3 (1)[a]
H(2B)	0.157 (3)	−0.175 (4)	0.231 (2)	2.4 (9)[a]
H(3A)	0.050 (3)	−0.256 (4)	0.129 (2)	2.0 (8)[a]
H(3B)	−0.009 (3)	−0.271 (4)	0.179 (2)	2.6 (9)[a]
H(12)	0.336 (3)	0.099 (4)	0.133 (2)	2.1 (9)[a]
H(13)	0.451 (6)	0.254 (9)	0.133 (4)	11 (3)[a]
H(14)	0.446 (4)	0.484 (5)	0.120 (2)	4 (1)[a]
H(15)	0.263 (4)	0.585 (5)	0.101 (2)	4 (1)[a]
H(16)	0.133 (4)	0.412 (6)	0.102 (3)	5 (1)[a]
H(22)	0.174 (3)	0.160 (4)	0.266 (2)	2.1 (9)[a]
H(23)	0.114 (4)	0.282 (5)	0.339 (2)	4 (1)[a]
H(24)	−0.027 (4)	0.450 (6)	0.307 (3)	6 (1)[a]
H(25)	−0.116 (4)	0.460 (6)	0.196 (3)	5 (1)[a]
H(26)	−0.058 (3)	0.347 (5)	0.121 (2)	3 (1)[a]
H(32)	−0.239 (4)	0.140 (6)	0.094 (2)	4 (1)[a]
H(33)	−0.316 (4)	0.277 (6)	0.162 (3)	6 (2)[a]
H(34)	−0.260 (4)	0.181 (5)	0.272 (2)	4 (1)[a]
H(35)	−0.140 (4)	0.012 (6)	0.316 (3)	5 (1)[a]
H(36)	−0.087 (3)	−0.113 (4)	0.241 (2)	1.9 (9)[a]
H(42)	−0.101 (4)	−0.409 (6)	0.067 (3)	5 (1)[a]
H(43)	−0.231 (4)	−0.573 (5)	0.051 (2)	3 (1)[a]
H(44)	−0.407 (4)	−0.519 (5)	0.043 (2)	4 (1)[a]
H(45)	−0.455 (5)	−0.296 (6)	0.053 (3)	6 (2)[a]
H(46)	−0.320 (3)	−0.123 (5)	0.073 (2)	2.2 (9)[a]

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

Table III. Important Interatomic Distances and Angles for $Re_2Cl_4(dppp)_2$

	Distances, Å		
Re–Re′	2.266 (1)	P(2)–C(3)	1.828 (5)
–Cl(1)	2.401 (1)	–C(31)	1.843 (5)
–Cl(2)	2.384 (1)	–C(41)	1.852 (5)
–P(1)	2.402 (1)	C(1)–C(2)	1.519 (8)
–P(2)	2.400 (1)	C(2)–C(3)	1.524 (8)
P(1)–C(1)	1.830 (6)		
–C(11)	1.832 (5)		
–C(21)	1.847 (5)		
	Angles, deg		
Re′–Re–Cl(1)	112.41 (4)	C(1)–P(1)–C(11)	104.0 (3)
–Cl(2)	111.23 (4)	–C(21)	103.7 (3)
–P(1)	99.42 (3)	C(11)–P(1)–C(21)	97.9 (2)
–P(2)	102.01 (3)	Re–P(2)–C(3)	116.1 (2)
Cl(1)–Re–Cl(2)	81.90 (5)	–C(31)	107.5 (2)
–P(1)	148.15 (5)	–C(41)	125.8 (2)
–P(2)	85.80 (5)	C(3)–P(2)–C(31)	103.9 (3)
Cl(2)–Re–P(1)	87.68 (5)	–C(41)	101.7 (3)
–P(2)	146.75 (5)	C(31)–P(2)–C(41)	98.5 (2)
P(1)–Re–P(2)	86.73 (4)	P(1)–C(1)–C(2)	116.0 (4)
Re–P(1)–C(1)	114.6 (2)	C(1)–C(2)–C(3)	116.7 (5)
–C(11)	123.7 (2)	P(2)–C(3)–C(2)	116.2 (4)
–C(21)	110.1 (2)		

Table IV. Spectral Properties of $Re_2Cl_4(Phos)_4$ Complexes[a]

complex	infrared spectra, cm^{-1}	electronic spectra, nm
$Re_2Cl_4(dppp)_2$	307 s, 292 sh (w), 270 m	820 m–s, 642 m, 568 w, 432 s, 364 s
$Re_2Cl_4(dppe)_2$[b]	333 vs, 303 ms	625 sh, 540 s, 500 s
$Re_2Cl_4(PEt_3)_4$[c]	325 s, 305 m	650 m, 492 sh, 365 s

[a] All spectra were recorded in the solid state (mulls). [b] Reference 4. [c] Reference 2.

The agreement factors for the averaging of 320 reflections were 1.7% on the basis of intensity and 1.2% on the basis of F_0. Only the 3615 data with $I \geq 3\sigma(I)$ were retained as observed and used in the refinement of the structure. Pertinent crystallographic data are summarized in Table I.

Structure Solution and Refinement. From the systematic absences of $0k0$, $k = 2n + 1$, and $h0l$, $h + l = 2n + 1$, the space group was determined to be $P2_1/n$. The Re atom position was determined from the top three peaks of a three-dimensional Patterson map. The remaining atoms were located by a sequence of alternate least-squares refinements and difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. All non-hydrogen atoms were anisotropically refined. Full-matrix least-squares refinement converged with unweighted and weighted agreement factors of $R = 0.0218$ and $R_w = 0.0280$. The parameter with the largest shift/esd (0.56) during the final least-squares cycle was the *x* coordinate of hydrogen atom H(13).

The final atomic positional and isotropic-equivalent thermal parameters are given in Table II. Important bond distances and angles within the molecule are listed in Table III.

Results and Discussion

Synthesis. The extended reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ and 1,3-bis(diphenylphosphino)propane (dppp) in acetonitrile yields dark green crystals, which the structure determination revealed to contain $Re_2Cl_4(dppp)_2$ molecules. This product, a Re^{II} complex containing a metal–metal triple bond (electron configuration $\sigma^2\pi^4\delta^2\delta^{*2}$), is the result of reduction of Re^{III} brought about by the phosphine ligand. This reaction is now well established for $Re_2Cl_8^{2-}$ and other Re^{III} species and tertiary phosphines and arsines.[2-5] Thus, a similar reaction of $Re_2Cl_8^{2-}$ with 1,2-bis(diphenylphosphino)ethane (dppe) in acetonitrile produces $Re_2Cl_4(dppe)_2$ although this species possesses a different molecular structure.[4,6]

Infrared and Electronic Spectra. Solid-state spectral results for $Re_2Cl_4(dppp)_2$ are presented in Table IV along with the corresponding data for $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(PEt_3)_4$, both of which exhibit trans $ReCl_2(Phos)_2$ moieties.[3,6] In the low-frequency infrared spectrum of $Re_2Cl_4(dppp)_2$, two bands of medium to strong intensity occur between 400 and 200 cm^{-1}. These are presumably due to Re–Cl stretching modes,[2,4] and a symmetry analysis of the metal–halogen stretching vibrations in the C_{2h} point group predicts two infrared-active species (A_u and B_u symmetry). Of particular interest is the shift of these bands to lower energy relative to those observed for $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(PEt_3)_4$ in this region. A possible cause of the frequency decrease may lie with the trans-effect lengthening of the Re–Cl bonds in $Re_2Cl_4(dppp)_2$ (vide infra). The electronic spectra of all three compounds in the solid state

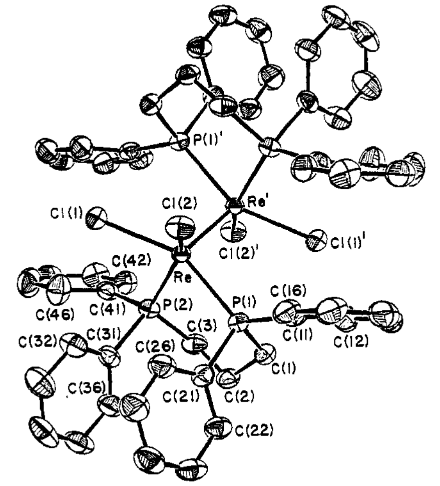

Figure 1. Molecular structure of $Re_2Cl_4(dppp)_2$. Numbers for unlabeled ring atoms follow from those given by an obvious pattern.

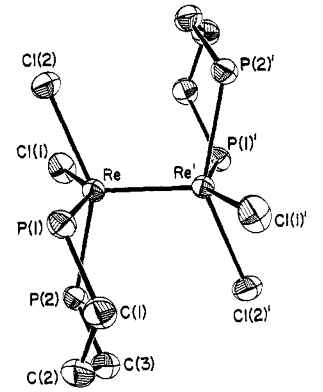

Figure 2. View of the central part of the $Re_2Cl_4(dppp)_2$ molecule emphasizing the eclipsed conformation and the chair form of the six-membered rings.

are quite dissimilar, which is a reflection of the different symmetries about the $Re_2Cl_4(Phos)_4$ chromophores. Given the large number of bands observed for $Re_2Cl_4(dppp)_2$, no detailed spectral assignments seem feasible at this stage.

Discussion of the Structure. Figure 1 illustrates the complete molecular geometry and atom-labeling scheme for the nonhydrogen atoms of $Re_2Cl_4(dppp)_2$. One dppp ligand is chelated to each metal atom to form two six-membered rings that have a chair conformation. The molecule resides on a crystallographic center of inversion and possesses idealized C_{2h} symmetry with a mirror plane passing through the two rhenium atoms and the central carbon atoms, C(2) and C(2)′, of the dppp ligands, and a C_2 axis perpendicularly bisecting the Re–Re bond.

The chair conformation of the chelate ring can be described as follows. Atoms P(1), P(2), C(1), and C(3) are coplanar with the largest deviation from a least-squares mean plane being 0.016 (5) Å, while atoms Re and C(2) are 1.077 (1) and 0.674 (5) Å, respectively, above and below this plane. This chair conformation is better illustrated in the view of the central portion of the molecule given in Figure 2.

One might expect from steric considerations that the overall ligand arrangement in $Re_2Cl_4(dppp)_2$ would be eclipsed. Indeed, the rotational conformation in this dimer is almost perfectly eclipsed with the two independent torsion angles being only 0.2 (1) and 1.0 (1)°. The presence of an inversion center requires the algebraic mean torsion angle to be zero.

To our knowledge, $Re_2Cl_4(dppp)_2$ is the first structurally characterized example of a triply bonded $Re_2X_4(LL)_2$ compound in which the bidentate ligands (LL) are chelating rather than bridging. It is also, therefore, the first example of an $Re_2X_4(Phos)_4$-type molecule in which the $ReX_2(Phos)_2$ units have *cis* rather than *trans* configurations. A comparison of the available structural data for molecules possessing these different arrangements follows presently.

Table V. Summary of Structural Data for $M_2X_4(Phos)_4$-Type Compounds with M = Re, W

compound	effective molecular symmetry	MX_2-$(Phos)_2$ confign	M–M bond length, Å
$Re_2Cl_4(dppp)_2$ [a]	C_{2h}	cis	2.266 (1)
$Re_2Cl_4(dppe)_2$ [b]	D_2	trans	2.244 (1)
$Re_2Cl_4(PMe_2Ph)_4$ [c]	D_{2d}	trans	2.241 (1)
$Re_2Cl_4(PEt_3)_4$ [d]	D_{2d}	trans	2.232 (5)
$W_2Cl_4(PMe_3)_4$ [e]	D_{2d}	trans	2.262 (1)
$W_2Cl_4(dmpe)_2$ [e]	C_{2h}	cis	2.287 (1)
$W_2Cl_4(dppe)_2$ [f]	C_{2h}	cis	2.281 (1)

[a] This paper. [b] Reference 6. [c] Reference 7. [d] Reference 3. [e] Reference 14. [f] Reference 13.

The only other $Re_2X_4(LL)_2$ compound that has been characterized by X-ray crystallography is $Re_2Cl_4(dppe)_2$, where dppe = 1,2-bis(diphenylphosphino)ethane.[6] In this compound, the rotational conformation is staggered and each $ReCl_2(Phos)_2$ unit has a trans arrangement. A comparison of the Re–P and Re–Cl bond distances in $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(dppp)_2$ reveals the presence of a structural trans influence. For the former molecule, in which Re–P bonds are trans to Re–P bonds and Re–Cl are trans to Re–Cl, the average Re–P and Re–Cl distances are 2.438 [7][12] and 2.370 [8] Å, respectively. In the dppp compound, in which Re–P bonds and Re–Cl bonds are trans to each other, the Re–P and Re–Cl distances are 2.401 [1] and 2.392 [8] Å, respectively. Thus, there exist differences of 0.037 (7) Å in the Re–P bond lengths and 0.022 (11) Å in the Re–Cl bond lengths. This result agrees well with a previous study of the trans influence in $M_2X_2L_4$- and $M_2X_6L_2$-type complexes for M = W and Re.[13]

A comparison of the Re–Re bond lengths in the two preceding compounds reveals a more interesting phenomenon. The Re–Re triple-bond distances in $Re_2Cl_4(dppe)_2$ and $Re_2Cl_4(dppp)_2$ are 2.244 (1) and 2.266 (1) Å, respectively. The metal–metal bond lengthens 0.022 (2) Å upon going from a trans to a cis arrangement in the $ReCl_2(Phos)_2$ unit. One might argue that this difference in bond lengths is due to the presence of bridging ligands in one molecule and the absence of bridging in the other. However, it may be more related to the cis or trans $MCl_2(Phos)_2$ configurations, since a similar effect was noted previously for two tungsten dimers $W_2Cl_4(PMe_3)_4$ and $W_2Cl_4(dmpe)_2$ (where dmpe = 1,2-bis(dimethylphosphino)ethane), neither of which contain bridging ligands.[14]

A summary of the molecular symmetry, ligand configuration, and metal–metal bond length for several similar rhenium and tungsen dimers is given in Table V. Clearly, the W–W bond length for $W_2Cl_4(PMe_3)_4$ lengthens 0.025 (2) Å in $W_2Cl_4(dmpe)_2$ and 0.019 (2) Å in $W_2Cl_4(dppe)_2$. The phosphines PMe_3 and dmpe are very similar, both electronically and sterically, as are dppe and dppp. Even though PMe_3 and dppe are quite different ligands, weakening of the W–W bond occurs to essentially the same extent. The other rhenium dimers are included in Table IV to accentuate the significance of this lengthening effect. The Re–Re bond lengths in all of the rhenium dimers with a *trans*-$ReCl_2(Phos)_2$ unit are es-

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[12] Throughout this paper, a number in parentheses is an esd for a given individual value, while a number in brackets is equal to$[\sum_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th of *n* values from the arithmetic mean of the *n* values.

[13] Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 3880.

[14] Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

sentially the same, while the Re–Re distance in the $Re_2Cl_4(dppp)_2$ molecule (with a cis arrangement) is notably longer.

Interestingly, the magnitudes of the lengthening of the W–W and Re–Re bonds are the same, i.e., 0.022 [3] Å. [It is noteworthy that the W_2^{4+} dimers possess $\sigma^2\pi^4\delta^2$ electronic configurations and quadruple M–M bonds, while the Re_2^{4+} dimers possess $\sigma^2\pi^4\delta^2\delta^{*2}$ configurations and triple bonds. This would seem to indicate that the lengthening of M–M distances on going from trans to cis $MX_2(Phos)_2$ geometry is *not* due to a weakening of the δ bond. Most likely, the origin is a destabilization of metal–metal π-bonding orbitals. It would be worthwhile to determine whether or not this phenomenon also exists in quadruply bonded molybdenum dimers.

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Registry No. $Re_2Cl_4(dppp)_2$, 86436-61-5; Re, 7440-15-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, least-squares planes for all phenyl rings, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Structural Characterization of the Nonachloroditungsten(II,III) Ion

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The reduction of WCl_4 by Na/Hg in THF, in the presence of $(Ph_3PNPPh_3)Cl$, produces a 40–50% yield of $(Ph_3PNPPh_3)_2[W_2Cl_9]$, which can be recrystallized from CH_2Cl_2/Et_2O to give dark violet crystals. The structure was solved and refined in the space group *I*2/*a* with the following unit cell dimensions: $a = 21.258$ (10) Å; $b = 12.962$ (5) Å; $c = 25.684$ (12) Å; $\beta = 101.04$ (4)°; $V = 6946$ (6) Å^3; $Z = 4$. The $[W_2Cl_9]^{2-}$ anions are disordered about the twofold axis. The structure was refined to $R_1 = 0.0438$ and $R_w = 0.0566$ with a quality-of-fit indicator of 1.103. The $[W_2Cl_9]^{2-}$ ion has the following principal dimensions: W–W = 2.540 (1) Å; W–Cl$_t$(av) = 2.358 [6] Å; W–Cl$_b$(av) = 2.453 [5] Å, W–Cl–W(av) = 62.4 [2]°. The increase in the W–W distance of 0.122 (9) Å compared to that in the $[W_2Cl_9]^{3-}$ ion is attributed mainly to the increased mean oxidation state of the metal atoms whereby the metal d orbitals are contracted, thus weakening the W–W σ bond. Support for this view is provided by the $[Re_2Cl_9]^-$ ion, which is isoelectronic with the $[W_2Cl_9]^{3-}$ ion but has a metal–metal distance about 0.29 Å greater than that in $[W_2Cl_9]^{3-}$.

Introduction

While we were searching for a preparative route to isolable salts of the $[W_2Cl_8]^{4-}$ ion (a goal that has subsequently been attained[2]), reduction of WCl_4 by sodium amalgam was carried out under a variety of conditions. With tetrahydrofuran as solvent at room temperature and with the very large cation $[Ph_3PNPPh_3]^+$ (PNP^+) present, a violet solid was formed. Upon recrystallization, this gave crystals suitable for X-ray study, and such a study was undertaken in hope of showing the presence of the $[W_2Cl_8]^{4-}$ ion. However, the initial phases of the X-ray work gave results at variance with this, and an elemental analysis was obtained that also disagreed with the postulated formula, $(PNP)_4[W_2Cl_8]$. Further work has shown that the compound obtained, in 40–50% yield, is the PNP salt of the $[W_2Cl_9]^{2-}$ ion, a species that had previously been made and characterized (except structurally) by Saillant and Wentworth.[3] In this paper we report and discuss the structure of this ion in the compound $(PNP)_2[W_2Cl_9]$.

Experimental Procedures

Preparation. A mixture of WCl_4 (3.26 g, 10 mmol), Na/Hg (100 g, 0.46%), and $(Ph_3PNPPh_3)Cl$ (11.5 g, 20 mmol) in THF (40 mL) was shaken at room temperature for 0.75 h. A dark red to purple product precipitated along with sodium chloride. The reaction mixture was poured over a column of Celite, leaving most of the mercury behind. The column, with reaction solids on top, was then washed through with several portions of CH_2Cl_2 to extract all of the colored material, and the extracts were filtered. The combined liquid was taken to dryness under vacuum and the solid residue recrystallized from a 1:1 mixture of CH_2Cl_2/Et_2O. The yield was 3.76 g (43% on WCl_4) of dark crystals, appearing red or blue depending on size and orientation. We believe that the presence of the PNP^+ ion is critical to obtaining a product containing the $W_2Cl_9^{2-}$ ion, since the preparation conditions are otherwise similar to those reported for preparing $Na_4(TMEDA)_4W_2Cl_8$.[2]

Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $(PNP)_2[W_2Cl_9]$

formula	$W_2Cl_9P_4C_{72}H_{60}N_2$
formula weight	1764.0
space group	*I*2/*a*
a, Å	21.258 (10)
b, Å	12.962 (5)
c, Å	25.684 (12)
β, deg	101.04 (4)
V, Å^3	6946 (6)
Z	4
d_{calcd}, g/cm^3	1.686
cryst size, mm	0.50 × 0.30 × 0.25
μ(Mo Kα), cm^{-1}	39.8
data collection instrument	Syntex P$\bar{1}$
radiation	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å); graphite monochromated
scan method	ω-scan
data collection range	$4 \leqslant 2\theta \leqslant 50°$; $+h, +k, \pm l$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	3312
no. of parameters refined	441
R^a	0.0438
$R_w{}^b$	0.0566
quality-of-fit indicator^c	1.103
largest shift/esd, final cycle	0.25

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

Anal. Calcd for $C_{72}H_{60}P_4N_2Cl_9W_2$: C, 49.03; H, 3.43; Cl, 18.09. Found: C, 50.7; H, 3.65; Cl, 20.5.

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[1] (a) Texas A&M University. (b) Massachusetts Institute of Technology.

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