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Synthesis and Characterization of the First Multiply Bonded Heteronuclear Edge-Sharing Bioctahedral Complex, MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$

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The heterobimetallic complex MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$·2THF·C$_6$H$_6$ (**1**) forms in the reaction between Mo$\overset{4}{-}$WCl$_4$(PMePh$_2$)$_4$ and bis(diphenylphosphino)methane (dppm) in a variety of hydrocarbon solvents. Red crystals were grown by slow diffusion of hexane into the reaction mixture. This complex crystallizes in the monoclinic space group $P2_1/a$, with the following unit cell dimensions: $a = 22.292$ (4) Å, $b = 12.938$ (7) Å, $c = 23.489$ (9) Å, $\beta = 113.70$ (2)°, $V = 6203$ (8) Å^3, and $Z = 4$. The structure was refined to $R = 0.0366$ ($R_w = 0.0606$) for 6306 data points with $F_o^2 > 3\sigma(F_o^2)$. The complex contains a (III, III) core in a distorted edge-sharing bioctahedral environment where the dppm ligands assume the bridging mode and are trans to one another. The Mo–W distance of 2.4932 (6) is consistent with some degree of multiple metal–metal bonding and is unusually short for a (III, III) core. The formation of this complex affords the first information concerning the reactivities of heteronuclear species relative to their homonuclear counterparts.

Introduction

The chemistry of edge-sharing bioctahedral complexes has recently been reviewed.[1] This class of complexes comprises a variety of metal cores and ligand environments. Despite this diversity, there are no previously known multiply bonded heteronuclear edge-sharing bioctahedral complexes. The title compound represents the first example of this class of complexes.

Only a few multiply bonded heteronuclear complexes of any kind have been reported in the literature.[2-4] This paucity and lack of diversity results from the difficult synthetic and purification procedures required to produce them. The recent development of a more convenient synthetic route to a suitable Mo–W precursor, Mo$\overset{4}{-}$WCl$_4$(PMePh$_2$)$_4$, has allowed a more thorough investigation of the chemistry and structural properties of these mixed-metal complexes.[3]

Attempts to obtain the heteronuclear analogue to the known M$\overset{4}{-}$MCl$_4$(μ-dppm)$_2$ complexes resulted in the formation of MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$. The formation of this heteronuclear complex has allowed for a comparison of its chemical, structural, and spectroscopic properties with those of W$_2$Cl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$.

Experimental Procedures

General Data. All manipulations were carried out under an atmosphere of argon unless otherwise specified. Standard Schlenk and vacuum-line techniques were used. Commercial grade solvents, except dichloromethane and deuterated chloroform, were dried over the freshly distilled from potassium/sodium benzophenone ketyl prior to use. Dichloromethane was dried over and freshly distilled from phosphorus pentoxide, and deuterated chloroform was dried over molecular seives prior to use. Mo$\overset{4}{-}$WCl$_4$(PMePh$_2$)$_4$ was prepared by the literature method involving the reaction of Mo(η^6-C$_6$H$_5$PMePh)(PMePh$_2$)$_3$ with WCl$_4$(PPh$_3$)$_2$ in benzene.[3] Bis(diphenylphosphino)methane (dppm) was purchased from Strem Chemicals and dried in vacuo prior to use. The IR and visible spectra were recorded on Perkin-Elmer 783 and Cary 17D spectrophotometers, respectively. The ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded on Varian XL-200 and XL-400 spectrometers, respectively. Mass spectra were obtained from the Mass Spectrometry Applications Laboratory sponsored by the Department of Chemistry at Texas A&M University. Samples were run on a Vestec VG Analytical 70S high-resolution double-focusing magnetic sector mass spectrometer in NBA/CH$_2$Cl$_2$ matrices.

Preparation of MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$ (1). Method 1. A 0.050-g (0.041-mmol) sample of Mo$\overset{4}{-}$WCl$_4$(PMePh$_2$)$_4$, 0.063 g (0.164 mmol) of dppm, and 20 mL of toluene were added to a 50-mL sidearm flask, and a reflux condenser was attached. The reaction mixture was stirred and heated at reflux for 3 h to give a pink precipitate and a blue solution. The precipitate was filtered from the solution, washed with toluene and hexanes, and dried in vacuo to give 0.036 g (64%) of MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$. The product may also be obtained in THF or CH$_2$Cl$_2$ at reflux, but longer reaction times (THF, 72 h; CH$_2$Cl$_2$, 48 h) are required. IR (Nujol, CsI; cm^{-1}): 1725 (w), 1585 (w), 1570 (w), 1480 (m), 1460 (s), 1435 (s), 1375 (m), 1340 (w), 1260 (m), 1103 (s), 1030 (m), 980 (w), 800 (m), 775 (w), 735 (m), 720 (w), 685 (m), 615 (w), 575 (w), 520 (w), 475 (m), 400 (w), 350 (m), 330 (w), 315 (m), 300 (w), 275 (w). Visible spectrum (CH$_2$Cl$_2$; nm): 820 (w), 590 (s), 400 (s). The molecular ion peak in the FABMS spectrum at 1226 amu corresponds to the MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2^+$ ion. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ −104 (t, 2 P, P–Mo, $J_{PP} \approx 150$ Hz), +108 (t, 2 P, P–W, $J_{PP} \approx 150$ Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 8.0–7.0 (m, 40 H, *Ph*P–M, M = Mo, W), 3.3 (m, 4 H, *CH$_2$*P–M, M = Mo, W), 2.0 (m, 1 H, H–M, M = Mo, W).

Method 2. A 0.050-g (0.041-mmol) sample of Mo$\overset{4}{-}$WCl$_4$(μ-dppm)$_2$[5] was placed in a 50-mL three-neck flask, and 20 mL of THF was added. HCl gas was then bubbled through this solution until all the green color had disappeared. The solvent was then removed in vacuo, and the oily residue was washed with methanol to remove any excess HCl. The residue was then redissolved in CH$_2$Cl$_2$, and hexanes were added to cause precipitation of 0.043 g (78%) of MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$. Visible spectrum (CH$_2$Cl$_2$; nm): 820 (w), 590 (s), 400 (s).

Preparation of MoWCl$_4$(μ-Cl)(μ-D)(μ-dppm)$_2$. A 0.050-g (0.041-mmol) sample of Mo$\overset{4}{-}$WCl$_4$(PMePh$_2$)$_4$, 0.063 g (0.164 mmol) of dppm, and 20 mL of CDCl$_3$ were added to a 50-mL sidearm flask, and a reflux condenser was attached. The reaction mixture was stirred and heated at reflux for 12 h to give a pink precipitate and an orange solution. The precipitate was filtered from the solution, washed with hexanes, and dried in vacuo to give 0.031 g (56%) of MoWCl$_4$(μ-Cl)(μ-D)(μ-dppm)$_2$. IR (Nujol, CsI; cm^{-1}): 1725 (w), 1570 (w), 1480 (m), 1460 (s), 1435 (s), 1375 (m), 1260 (m), 1135 (w), 1103 (s), 1095 (w), 1030 (w), 910 (w), 800 (m), 775 (w), 750 (w), 735 (m), 720 (w), 685 (m), 615 (w), 520 (w), 475 (m), 350 (m), 310 (m), 300 (w), 275 (w). Visible spectrum (CH$_2$Cl$_2$; nm): 820 (w), 580 (s), 400 (s). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ −104 (t, 2 P, P–Mo, $J_{PP} \approx 150$ Hz), +108 (t, 2 P, P–W, $J_{PP} \approx 150$ Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 8.0–7.0 (m, 40 H, *Ph*P–M, M = Mo, W), 3.3 (m, 4 H, *CH$_2$*P–M, M = Mo, W).

X-ray Crystallography

Single crystals of MoWCl$_4$(μ-Cl)(μ-H)(μ-dppm)$_2$ were obtained by layering the reaction mixture, in THF, with a solution composed of two parts of *n*-hexanes to one part of benzene in a long glass tube sealed under an argon atmosphere. The diffusion of the solvent mixture into the THF solution yielded several red crystals from which one of X-ray quality was chosen. The crystal was mounted on the tip of a quartz fiber with halocarbon grease.

Pertinent crystallographic information is given in Table I. Crystal quality was verified by means of a rotation photograph, and reflections suitable for indexing were found using the automatic search routine on an Enraf-Nonius CAD-4 diffractometer. A least-squares analysis of the setting angles of 25 reflections provided accurate unit cell parameters (Table I). Lattice dimensions and Laue symmetry were verified using axial photographs. Intensity data were collected by utilizing the options specified in Table I and the general procedures previously described.[6]

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Table I. Crystallographic Data for $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2\cdot 2THF\cdot C_6H_6$

chem formula	$WMoCl_5P_4O_2C_{64}H_{66}$
fw	1448.19
space group	$P2_1/a$ (No. 14)
a, Å	22.292 (4)
b, Å	12.938 (7)
c, Å	23.489 (9)
α, deg	90
β, deg	113.70 (2)
γ, deg	90
V, Å^3	6203 (8)
Z	4
T, °C	-60 ± 2
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.550
μ(Mo Kα), cm^{-1}	24.065
transm coeff	0.9995–0.8361
$R(F_o)$,[a] $R_w(F_o)$[b]	0.0366, 0.0626

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

Three standard reflections were measured every 1 h during data collection and displayed no systematic variation in intensity. Corrections were applied for Lorentz, polarization, and absorption effects. The later correction was based on azimuthal scans of several reflections with diffractometer angle χ near 90°.[7]

The heavy-atom positions were obtained from a three-dimensional Patterson function. Hybrid atoms composed of 50% Mo and 50% W were placed at the metal atom positions in the initial stages of the refinement. The positions for the remainder of the non-hydrogen atoms were found using a series of full-matrix refinements followed by difference Fourier syntheses. These were initially refined with isotropic thermal parameters and then with anisotropic thermal parameters to convergence. The hydrogen atoms, except the bridging hydride, were placed and fixed at calculated positions and their isotropic thermal parameters constrained to one variable, and this entire model refined to convergence. The difference Fourier map showed several peaks that could be ascribed to solvent molecules, namely two THF molecules and a benzene molecule. The atoms representing the two THF molecules were allowed to refine freely first with isotropic and then finally anisotropic thermal parameters. The atoms ascribed to the benzene molecule refined best as a regular hexagon. The isotropic thermal parameters of the "benzene carbon atoms" were constrained to and refined as one variable. The data were not of sufficient quality to unambiguously rule out the fact that the electron density maxima ascribed to the benzene molecule may, in fact, represent a severely disordered THF molecule. However, since benzene was used in the preparation of the crystal our assignment here is reasonable.

Because the mass spectral measurements on crystals from the same tube showed no evidence of the ditungsten or dimolybdenum compounds, the compositions of the metal atom positions were constrained so that the total Mo and total W occupancies for the two positions were equal to one. Final refinement employed the SHELX-76 package of programs with variation of occupancy factors used to determine the composition of the metal atom sites. The final refinement factors after convergence are listed in Table I. Table II contains positional and thermal parameters. Selected bond lengths and angles are listed in Table III. ORTEP diagrams of the molecular core are given in Figures 1 and 2, while tables of anisotropic thermal parameters, complete bond lengths and angles, and structure factors and a complete ORTEP drawing are available as supplementary material.

Results and Discussion

Synthesis. The oxidation of the MoW^{4+} core to a MoW^{6+} in refluxing toluene is the most interesting feature of the reaction between $Mo\overset{4}{-}WCl_4(PMePh_2)_4$ and dppm. The formation of $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$ demonstrates the susceptibility of the MoW^{4+} core to oxidative addition, even in nonhydridic media. While this is not the first example of a mixed-metal hydrido-bridged species, the other being $MoWCl_8H^{3-}$, it is the first to be formed under such mild conditions.[8] Unfortunately, there are few details known about the pathway by which this species is formed or the nature of the oxidizing agent which attacks the MoW^{4+} core. The formation of $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}D)(\mu\text{-}dppm)_2$ and the homologous ditungsten complex from deuterated solvents, $CDCl_3$ and CH_3OD, suggests that the solvent is the proton source.

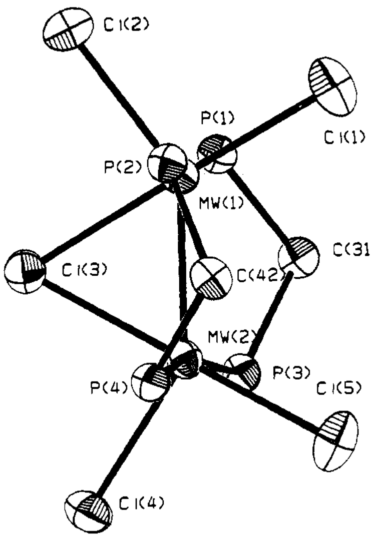

Figure 1. ORTEP drawing of $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$ (phenyl rings of dppm and bridging hydride omitted). Thermal ellipsoids are drawn at 50% probability.

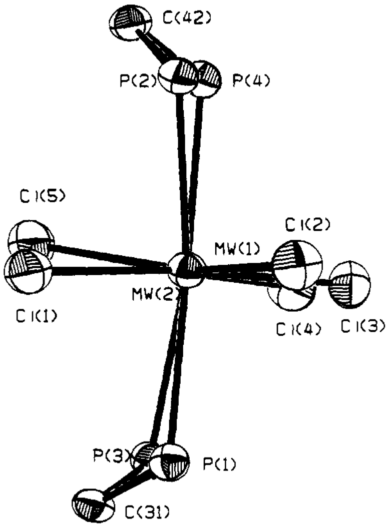

Figure 2. View down the Mo–W axis in $MoWCl_4(m\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$ (phenyl rings of dppm and bridging hydride omitted). Thermal ellipsoids are drawn at 50% probability.

The propensity of the WW^{4+} core to undergo oxidative addition under acidic as well as nonacidic conditions has been established.[9-12] Both complex **1** and its ditungsten analogue are synthesized under identical conditions,[11] but efforts to synthesize the dimolybdenum analogue under these conditions have been unsuccessful. This and other observations indicate that the chemistry of the mixed-metal compound is more closely related to that of the tungsten dimer than to that of the Mo_2^{4+} compound. There are other examples of the propensity of the MoW^{4+} core to undergo oxidative-addition reactions under very mild conditions. These include the formation of $MoWCl_6(L\text{-}L)_2$ complexes from CH_2Cl_2 solutions of $\beta\text{-}Mo\overset{4}{-}WCl_4(\mu\text{-}dppe)_2$, $\alpha\text{-}Mo\overset{4}{-}WCl_4$-

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Table II. Positional Parameters and Their Estimated Standard Deviations for $MoW(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(\mu\text{-dppm})_2 \cdot 2THF \cdot C_6H_6$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
MW^b(1)	0.05009 (2)	0.33947 (3)	0.24481 (2)	2.02 (1)	C(125)	0.0033 (2)	0.7126 (3)	0.1308 (2)	5.5 (3)
MW^c(2)	0.01313 (2)	0.15646 (3)	0.22217 (2)	2.01 (1)	C(126)	−0.0063 (2)	0.6192 (3)	0.1556 (2)	4.3 (3)
Cl(1)	0.11162 (8)	0.4136 (2)	0.19298 (8)	3.74 (5)	C(211)	0.1753 (2)	0.3060 (4)	0.4147 (2)	2.5 (2)
Cl(2)	0.05011 (8)	0.4918 (1)	0.30744 (8)	3.30 (5)	C(212)	0.2391 (2)	0.2990 (4)	0.4600 (2)	4.1 (2)
Cl(3)	−0.02317 (8)	0.2625 (1)	0.28971 (8)	2.86 (4)	C(213)	0.2502 (2)	0.3014 (4)	0.5229 (2)	4.8 (3)
Cl(4)	−0.05557 (8)	0.0198 (1)	0.23698 (8)	3.08 (5)	C(214)	0.1976 (2)	0.3108 (4)	0.5403 (2)	5.1 (3)
Cl(5)	0.05569 (9)	0.0534 (2)	0.16405 (8)	3.85 (5)	C(215)	0.1338 (2)	0.3178 (4)	0.4950 (2)	5.2 (3)
P(1)	−0.04607 (8)	0.4167 (1)	0.15171 (7)	2.16 (4)	C(216)	0.1227 (2)	0.3154 (4)	0.4321 (2)	3.9 (2)
P(2)	0.16150 (8)	0.2939 (1)	0.33282 (7)	2.19 (4)	C(221)	0.2311 (2)	0.3650 (3)	0.3297 (2)	2.4 (2)
P(3)	−0.08310 (8)	0.1956 (1)	0.11833 (7)	2.12 (4)	C(222)	0.2834 (2)	0.3155 (3)	0.3228 (2)	3.5 (2)
P(4)	0.10963 (8)	0.0783 (1)	0.31364 (7)	2.12 (4)	C(223)	0.3349 (2)	0.3735 (3)	0.3200 (2)	3.9 (2)
O(1)	0.3210 (3)	0.1185 (6)	0.9508 (3)	7.1 (2)	C(224)	0.3341 (2)	0.4810 (3)	0.3240 (2)	3.6 (2)
C(1)	0.6326 (7)	0.233 (1)	0.6676 (9)	9.5 (6)	C(225)	0.2817 (2)	0.5305 (3)	0.3308 (2)	3.8 (2)
C(2)	0.2515 (4)	0.100 (1)	0.9317 (4)	7.3 (4)	C(226)	0.2303 (2)	0.4725 (3)	0.3336 (2)	3.2 (2)
C(3)	0.2229 (6)	0.116 (2)	0.8680 (6)	12.6 (6)	C(311)	−0.0893 (2)	0.1044 (3)	0.0571 (2)	2.3 (2)
C(4)	0.2770 (5)	0.110 (1)	0.8422 (5)	9.1 (4)	C(312)	−0.0819 (2)	0.1333 (3)	0.0031 (2)	3.2 (2)
C(5)	0.3374 (5)	0.105 (1)	0.8983 (5)	8.5 (4)	C(313)	−0.0866 (2)	0.0591 (3)	−0.0417 (2)	3.5 (2)
C(6)	0.4568 (6)	0.143 (1)	0.444 (1)	18.9 (3)*	C(314)	−0.0987 (2)	−0.0440 (3)	−0.0323 (2)	3.5 (2)
C(7)	0.4145 (6)	0.089 (1)	0.392 (1)	18.9 (3)*	C(315)	−0.1062 (2)	−0.0728 (3)	0.0217 (2)	3.4 (2)
C(8)	0.3530 (6)	0.058 (1)	0.389 (1)	18.9 (3)*	C(316)	−0.1014 (2)	0.0014 (3)	0.0664 (2)	2.9 (2)
C(9)	0.3338 (6)	0.081 (1)	0.437 (1)	18.9 (3)*	C(321)	−0.1678 (2)	0.2000 (4)	0.1106 (2)	2.4 (2)
C(10)	0.3762 (6)	0.135 (1)	0.489 (1)	18.9 (3)*	C(322)	−0.2180 (2)	0.1979 (4)	0.0511 (2)	3.0 (2)
C(11)	0.4376 (6)	0.166 (1)	0.493 (1)	18.9 (3)*	C(323)	−0.2833 (2)	0.1990 (4)	0.0439 (2)	3.7 (2)
C(12)	0.6308 (7)	0.249 (1)	0.7236 (9)	11.2 (7)	C(324)	−0.2983 (2)	0.2023 (4)	0.0961 (2)	3.7 (2)
C(13)	0.5733 (8)	0.234 (1)	0.6190 (7)	11.7 (7)	C(325)	−0.2481 (2)	0.2044 (4)	0.1555 (2)	4.2 (2)
C(14)	0.5230 (6)	0.260 (1)	0.6432 (6)	10.1 (5)	C(326)	−0.1828 (2)	0.2033 (4)	0.1627 (2)	3.2 (2)
C(15)	0.5585 (5)	0.2367 (9)	0.7117 (6)	7.5 (4)	C(411)	0.1064 (2)	0.0650 (4)	0.3894 (2)	2.5 (2)
C(31)	−0.0691 (3)	0.3188 (5)	0.0893 (3)	2.2 (2)	C(412)	0.1638 (2)	0.0460 (4)	0.4418 (2)	3.6 (2)
C(42)	0.1809 (3)	0.1587 (5)	0.3244 (3)	2.3 (2)	C(413)	0.1614 (2)	0.0329 (4)	0.4998 (2)	4.4 (2)
C(111)	−0.1229 (2)	0.4532 (4)	0.1564 (2)	2.3 (2)	C(414)	0.1015 (2)	0.0387 (4)	0.5054 (2)	4.7 (3)
C(112)	−0.1763 (2)	0.4777 (4)	0.1015 (2)	3.5 (2)	C(415)	0.0441 (2)	0.0577 (4)	0.4530 (2)	4.6 (3)
C(113)	−0.2355 (2)	0.5076 (4)	0.1035 (2)	4.1 (2)	C(416)	0.0465 (2)	0.0709 (4)	0.3950 (2)	3.4 (2)
C(114)	−0.2413 (2)	0.5130 (4)	0.1604 (2)	4.3 (2)	C(421)	0.1336 (2)	−0.0517 (3)	0.3016 (3)	2.6 (2)
C(115)	−0.1879 (2)	0.4886 (4)	0.2153 (2)	4.7 (3)	C(422)	0.1833 (2)	−0.0702 (3)	0.2811 (3)	4.2 (3)
C(116)	−0.1286 (2)	0.4587 (4)	0.2133 (2)	3.4 (2)	C(423)	0.1966 (2)	−0.1711 (3)	0.2686 (3)	5.3 (3)
C(121)	−0.0287 (2)	0.5328 (3)	0.1173 (2)	2.8 (2)	C(424)	0.1603 (2)	−0.2533 (3)	0.2767 (3)	4.1 (2)
C(122)	−0.0413 (2)	0.5399 (3)	0.0542 (2)	3.6 (2)	C(425)	0.1107 (2)	−0.2347 (3)	0.2972 (3)	4.7 (3)
C(123)	−0.0317 (2)	0.6333 (3)	0.0294 (2)	4.1 (2)	C(426)	0.0973 (2)	−0.1339 (3)	0.3097 (3)	4.1 (3)
C(124)	−0.0093 (2)	0.7197 (3)	0.0678 (2)	4.7 (3)					

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred *B* values are for atoms that were refined isotropically. [b] Hybrid metal atom composed of 53.6 (2)% Mo and 46.4 (2)% W. [c] Hybrid metal atom composed of 46.4 (2)% Mo and 53.6 (2)% W.

$(dppe)_2$, and $Mo\overset{4}{—}WCl_4(\mu\text{-dppm})_2$.[5]

Structure and Bonding. Because of the disorder, which is typical for heteronuclear complexes with symmetric ligand environments, the metal–metal distance is the only exact distance which may be extracted from the crystallographic data.[3,13–15] The metal to ligand distances have been averaged by the random arrangement of the metal–metal vector. Despite this, structural comparisons are still useful and provide important information. It should be noted that the two metal atom positions are not crystallographically equivalent and, further, the metal occupancy ratio at each site is not 0.50 Mo/0.50 W. The final percentages, which are significantly different, were 53.6 (2)% Mo/46.4 (2)% W at one site and 46.4 (2)% Mo/53.6% W at the other.

The Mo–W bond distance of 2.4932 (6) Å is indicative of multiple metal–metal bond character and it is significantly longer than the M–M distances found in $W_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-dppm})_2$ (2.4830 (9) Å)[11] and $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(O_2CPh)_2(P\text{-}n\text{-}Bu_3)_2$ (2.429 [8] Å).[10] Observed bond distances in other mixed-metal complexes would suggest that the Mo–W distance should be shorter than the W–W distances and longer than Mo–Mo distance in analogous complexes.[2–5] The lengthening of the Mo–W bond distance may be due to the average torsional angle of 8.5 [1]° about the M–M′ vector found in the title complex and shown in Figure 2. The dependence of bond distance on torsional angle is a well-known phenomenon in quadruply bonded complexes,[16,17] but this has not been established in edge-sharing complexes because most are in the eclipsed conformation. The M–M′ distance in **1** is significantly shorter than other $MM'Cl_4(\mu\text{-}X)_2(L\text{-}L)_2$ species, where L-L represents bridging dppm ligands.[5,18] This is a general result of replacing a μ-Cl by μ-H and is probably both steric and electronic in origin.

No direct X-ray evidence for the μ-H atom was obtained. However, its presence is supported by the following spectroscopic evidence and by the following indirect structural evidence, especially the differences in the $M\text{–}Cl_t$ distances and the $M\text{–}M\text{–}Cl_t$ angles. For the two terminal chloride ligands trans to the bridging chloride atom the average $M\text{–}Cl_t$ distance is 2.367 [4] Å and the average $M\text{–}M\text{–}Cl_t$ angle is 118.95 [6]°. In contrast, the two terminal chloride ligands cis to the bridging chloride atom (trans to the bridging hydride atom) have an average $M\text{–}Cl_t$ distance of 2.457 [5] Å and have an average $M\text{–}M\text{–}Cl_t$ angle of 144.85 [7]°. Similar differences have been observed in the structures of $W_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-dppm})_2$,[11] $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(O_2CPh)_2(P\text{-}n\text{-}Bu_3)_2$,[10] and $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(4\text{-Etpy})$.[19] The $M\text{–}Cl_b$ distances for **1** of 2.481 (2) and 2.467 (2) Å are similar to the comparable distances in all three of the aforementioned structures. The two distances are significantly different, and the shorter one occurs in the case of the Cl_b attached to the metal atom site refined as consisting of more W than Mo.

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Table III. Selected Bond Distances (Å) and Angles (deg) for $MoW(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(\mu\text{-}dppm)_2\cdot 2THF\cdot C_6H_6$[a]

Distances

MW^b(1)–MW^c(2)	2.4932 (6)	P(1)–C(111)	1.821 (5)
MW(1)–Cl(1)	2.372 (2)	P(1)–C(121)	1.821 (5)
MW(1)–Cl(2)	2.460 (2)	P(2)–C(42)	1.832 (6)
MW(1)–Cl(3)	2.481 (2)	P(2)–C(211)	1.828 (5)
MW(1)–P(1)	2.571 (1)	P(2)–C(221)	1.831 (5)
MW(1)–P(2)	2.581 (1)	P(3)–C(31)	1.810 (7)
MW(2)–Cl(3)	2.467 (2)	P(3)–C(311)	1.823 (5)
MW(2)–Cl(4)	2.454 (2)	P(3)–C(321)	1.823 (5)
MW(2)–Cl(5)	2.363 (2)	P(4)–C(42)	1.829 (7)
MW(2)–P(3)	2.569 (1)	P(4)–C(411)	1.818 (5)
MW(2)–P(4)	2.560 (1)	P(4)–C(421)	1.820 (5)
P(1)–C(31)	1.847 (6)		

Angles

MW(2)–MW(1)–Cl(1)	118.96 (5)	MW(1)–MW(2)–Cl(3)	60.03 (5)
MW(2)–MW(1)–Cl(2)	144.03 (5)	MW(1)–MW(2)–Cl(4)	145.66 (5)
MW(2)–MW(1)–Cl(3)	59.45 (4)	MW(1)–MW(2)–Cl(5)	118.95 (6)
MW(2)–MW(1)–P(1)	95.55 (4)	MW(1)–MW(2)–P(3)	95.36 (4)
MW(2)–MW(1)–P(2)	94.77 (4)	MW(1)–MW(2)–P(4)	95.86 (4)
Cl(1)–MW(1)–Cl(2)	97.00 (7)	Cl(3)–MW(2)–Cl(4)	85.68 (7)
Cl(1)–MW(1)–Cl(3)	174.71 (5)	Cl(3)–MW(2)–Cl(5)	175.61 (5)
Cl(1)–MW(1)–P(1)	82.11 (6)	Cl(3)–MW(2)–P(3)	97.84 (6)
Cl(1)–MW(1)–P(2)	86.25 (6)	Cl(3)–MW(2)–P(4)	93.56 (6)
Cl(2)–MW(1)–Cl(3)	84.81 (6)	Cl(4)–MW(2)–Cl(5)	95.38 (7)
Cl(2)–MW(1)–P(1)	89.82 (5)	Cl(4)–MW(2)–P(3)	86.92 (5)
Cl(2)–MW(1)–P(2)	86.28 (5)	Cl(4)–MW(2)–P(4)	87.59 (5)
Cl(3)–MW(1)–P(1)	92.95 (6)	Cl(5)–MW(2)–P(3)	86.49 (6)
Cl(3)–MW(1)–P(2)	98.84 (6)	CL(5)–MW(2)–P(4)	82.23 (6)
P(1)–MW(1)–P(2)	167.18 (6)	P(3)–MW(2)–P(4)	166.93 (6)
C(31)–P(1)–C(111)	104.9 (3)	C(31)–P(3)–C(311)	104.1 (3)
C(31)–P(1)–C(121)	104.7 (3)	C(31)–P(3)–C(321)	105.3 (3)
C(111)–P(1)–C(121)	100.7 (2)	C(311)–P(3)–C(321)	101.2 (2)
C(42)–P(2)–C(211)	104.3 (3)	C(42)–P(4)–C(411)	107.0 (3)
C(42)–P(2)–C(221)	103.6 (3)	C(42)–P(4)–C(421)	104.7 (3)
C(211)–P(2)–C(221)	102.3 (2)	C(411)–P(4)–C(421)	101.2 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Hybrid metal atom composed of 53.6 (2)% Mo and 46.4 (2)% W. [c] Hybrid metal atom composed of 46.4 (2)% Mo and 53.6 (2)% W.

Spectroscopic Properties. Definitive proof of the existence of the μ-H atom in $MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2$ was obtained in a comparison of the IR spectra of **1** and the analogue containing a μ-D atom (**2**). The spectra obtained as Nujol mulls show features for ν(sym) at 1585 cm^{-1} (m) and ν(asym) at 980 cm^{-1} (m) for **1**, which shift to 1135 (w) and 910 cm^{-1} (m) for the deuterated analogue. While the latter band overlaps with that of dppm, it is discernible. These shifts match those reported for $MoWCl_8H^{3-}$ and $MoWCl_8D^{3-}$, respectively.[8]

The electronic absorption spectrum of **1** in CH_2Cl_2 has bands at 820 (w), 590 (s), and 400 nm (s). These are similar to those reported for the ditungsten species, which has features at 790 (w), 602 (s), and 464 nm (s).[11] In general, complexes of the form $MM'Cl_4(\mu\text{-}X)_2(L\text{-}L)_2$ display absorptions in these regions.[1]

As a result of the thermal population of a low-lying paramagnetic excited state at room temperature,[11,18] the $^{31}P\{^1H\}$ NMR spectra of **1** and **2** are observed only at temperatures below −80 °C. This behavior is consistant with the value of χ_{mol}, measured at 297 K, of 5.2×10^{-4} emu/mol,[20] which is comparable to magnetic susceptibilities recorded for similar $M_2X_6(L\text{-}L)_2$ type complexes.[18] The two similiar spectra for **1** and **2** were recorded in saturated CH_2Cl_2 solutions at −100 °C. Each spectrum consists of two broad triplets of equal intensities with P–P couplings of approximately 150 Hz, one at approximately +108 ppm and the other at approximately −104 ppm. The resonances due to $^{31}P\text{–}^{183}W$ coupling were not observed, and therefore, a definitive assignment of these resonances is not feasible. However, on the basis of previously reported chemical shift data, one may tentatively assign the low-field triplet (+108 ppm) to the phosphorus atoms on tungsten and the high-field triplet (−104 ppm) to the phosphorus atoms on molybdenum.[3] The spectrum of complex **2** displayed greater line widths by approximately 40% relative to those in the spectrum of complex **1**. This increase in line widths is presumably due to the coupling of μ-D to the phosphorus atoms on the metal centers. Attempts to obtain higher resolution spectra in order to determine the P–D couplings were unsuccessful.

Although complex **1** is only sparingly soluble in CD_2Cl_2 and is slightly paramagnetic at room temperature, an acceptable ^1H NMR spectrum was obtained. The phenyl protons of the dppm ligands are seen as multiplets with δ 7–8 ppm. The methylene resonance appears as a multiplet at δ 3.3 ppm with no observable P–H coupling. From a comparison of the spectra of the μ-H and μ-D species and the chemical shifts reported for other bridging hydrides,[10] a resonance centered at δ 2.0 ppm has been assigned to the bridging hydride.

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Registry No. $1\cdot 2THF\cdot C_6H_6$, 136660-27-0; **2**, 136675-80-4; $MoWCl_4(PMePh_2)_4$, 93304-09-7; $MoWCl_4(\mu\text{-}dppm)_2$, 136632-27-4; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Full lists of crystallographic data, bond distances, bond angles, torsion angles, anisotropic thermal parameters, and hydrogen atom coordinates and a complete ORTEP drawing (15 pages); a list of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

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(20) χ_{mol} was determined by the Faraday method and corrected for the diamagnetism of the constituent atoms using Pascal's constants.