(No. 33) and *Pnam* (No. 62), but the former was indicated by the shape of a Patterson function and confirmed by structure analysis.

Intensities of 9704 reflections (*hkl* with $2 < \theta < 27°$ and $\bar{h}kl$ with $2 < \theta < 18°$) were measured by continuous $\theta/2\theta$ scans of $(0.70 + 0.35 \tan \theta)°$ in θ; background was estimated by extending scans at both ends by 25%. The scan speeds were adjusted to give $\sigma(E)/I < 0.02$, subject to a time limit of 90 s. Two strong reflections were remeasured every 2 h, but their intensities displayed only random fluctuations not exceeding 3.4% of the mean values.

The integrated intensities of reflections, derived in the usual manner ($q = 0.03$),[31] were corrected for Lorentz, polarization, and absorption effects. The last correction, made by an empirical method,[32] yielded absorption factors (on F) of 0.78-1.47. Averaging 4604 symmetry-related structure amplitudes to get 2302 unique ones gave R(internal) of 0.032. Rejection of 2960 reflections with $I < 3\sigma(E)$ led to 4442 unique structure amplitudes, and only these were used in further analysis.

The positions of the platinum and gold atoms were determined from a Patterson function, and those of the remaining non-hydrogen atoms, from difference electron density syntheses. The dppm hydrogen atoms were included in the structural model in calculated positions and constrained so that $U(\mathrm{H}) = U(\mathrm{C})$ with C-H bonds of 1.0 Å. The CH_2 hydrogens were allowed to ride on the carbon atoms to which they are bonded, and the phenyl groups were treated as rigid bodies of D_{6h} symmetry (C-C = 1.38 Å). Only Au, Pt, I, and P atoms were allowed anisotropic displacement parameters. The structure was refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(|F_o|)$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 33. The refinement of 225 parameters, including the polarity factor η,[34] converged at $R = 0.040$ and $R_w = 0.050$,[35] with $\eta = 0.94$ (6), the largest parameter-shift/error ratio of 0.19, and the error in observation of unit weight of 2.6. In the final difference electron density synthesis the function values were -0.19 to $+0.18$ e Å^{-3}. Disorder of the methyl carbon atoms C(6) to C(8) and C(12) to C(14) is possible in view of their large displacement parameters (Table V). Attempts to model the disorder were unsuccessful, and this may explain the large error in observation of unit weight and discrepancies between $|F_o|$ and $|F_c|$ for about 20 low-angle reflections. All calculations were performed on a GOULD SEL 32/27 minicomputer, using the locally developed GX program package.[36]

The final atomic parameters are listed in Table V. The calculated coordinates of hydrogen atoms, anisotropic displacement parameters of Pt, Au, I, and P atoms, complete lists of bond lengths and angles, and the observed and calculated structure amplitudes are presented as supplementary material (Tables VI-X).

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Supplementary Material Available: Calculated coordinates of hydrogen atoms, anisotropic displacement parameters of Pt, Au, I, and P atoms, and complete bond lengths and angles (Tables VI-IX) (6 pages); observed and calculated structure amplitudes (Table X) (20 pages). Ordering information is given on any current masthead page.

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Complexes Containing Unbridged Homonuclear or Heteronuclear Quadruple Bonds. Crystal and Molecular Structures of $MoWCl_4(PMePh_2)_4$, $MoWCl_4(PMe_3)_4$, and $Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$

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The reactions of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ with $MoCl_4(THF)_2$ yield the homonuclear unbridged quadruply bonded complexes $Mo_2Cl_4(PR_3)_4$ ($PR_3 = PMePh_2$ (**1**), PMe_2Ph (**2**)). Complex **1** readily undergoes phosphine substitution with PMe_3 to yield $Mo_2Cl_4(PMe_3)_4$ (**3**). The reactions of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ with $WCl_4(PPh_3)_2$ yield the complexes $MoWCl_4(PR_3)_4$ ($PR_3 = PMe_2Ph$ (**4**), $PMePh_2$ (**5**)), which are among the first to contain an unbridged quadruple bond between two different elements. Complex **5** undergoes phosphine substitution reactions with PMe_3 to give sequentially $Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$ (**6**) and then $MoWCl_4(PMe_3)_4$ (**7**). Complex **4** can also be synthesized by reacting **5** with PMe_2Ph. The ^{31}P and ^1H NMR spectra, electronic and visible spectra, and cyclic voltammograms of these complexes are interpreted, and the crystal and molecular structures of **5**-**7** are reported. Compounds **5** and **7** were found to have disordered arrangements of the metal atoms; compound **6** with the different phosphine ligands on the metal atoms is, however, ordered with a $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ bond length of 2.207 (1) Å. In **6** and **7** the molecules have crystallographic 2-fold symmetry. In all three structures the ligand arrangement over the metal-metal bond defines an eclipsed geometry with chlorine next to phosphine across the bond in a pseudo-D_{2d} arrangement. The metal-metal distances in **5** and **7** are 2.208 (4) (average) and 2.2092 (7) Å, respectively. These values are close to distances expected on the basis of homonuclear $\mathrm{M}\overset{4}{-}\mathrm{M}$ bonds, and therefore there is no extra shortening of these bonds due to electronegativity differences. Crystal data: **5**, monoclinic, space group $P2_1/a$, $a = 21.511$ (4) Å, $b = 12.176$ (6) Å, $c = 40.863$ (8) Å, $\beta = 92.65$ (2)°, $V = 10692$ Å^3, $D_{\text{calcd}} = 1.52$ g cm^{-3} for $Z = 8$, $R = 0.0957$ for 3554 observed ($I > 3\sigma(I)$) reflections; **6**, monoclinic, space group $I2/a$, $a = 16.817$ (4) Å, $b = 11.925$ (3) Å, $c = 19.685$ (5) Å, $\beta = 103.87$ (2)°, $V = 3832.4$ Å^3, $D_{\text{calcd}} = 1.69$ g cm^{-3} for $Z = 4$, $R = 0.0364$ for 2203 observed reflections; **7**, monoclinic, space group $I2/a$, $a = 17.312$ (4) Å, $b = 9.193$ (1) Å, $c = 19.085$ (3) Å, $\beta = 119.69$ (2)°, $V = 2638.9$ Å^3, $D_{\text{calcd}} = 1.57$ g cm^{-3} for $Z = 4$, $R = 0.0312$ for 2084 observed reflections.

All of the compounds known to contain heteronuclear quadruple bonds involve combinations of the chromium group metals.[1] Two classes of complexes containing quadruple bonds between molybdenum and tungsten are now known in which the $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ bond is either supported by bridging ligands or is free of bridging ligands. The members of the first class are $MoW(O_2CCMe_3)_4$[2,3] and $MoW(mhp)_4$, [mhp = 2-hydroxy-6-methylpyridine anion].[4,5]

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These complexes appear to have enhanced stability above that expected from the average of the properties of the homonuclear congeners, Mo_2 and W_2. The dimer $MoW(O_2CCMe_3)_4$ has a shorter quadruple bond (2.080 (1) Å)[3] than the homonuclear dimer $Mo_2(O_2CCMe_3)_4$ (2.088 (1) Å)[6] despite the fact that tungsten normally has a greater quadruple bond radius than molybdenum. Similarly $MoW(mhp)_4$ is reported to have a higher force constant for its quadruple bond than the complexes $Mo_2(mhp)_4$ and $W_2(mhp)_4$[5] and has a bond which is shorter than that expected on the basis of homonuclear distances.[4] In addition the conditions of the preparation of these $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ complexes suggest that they might be thermodynamically favored over the usually very stable $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ congeners since the yield of $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ compounds exceeds that of the homonuclears when a mixture of $Mo(CO)_6$ and $W(CO)_6$ is heated with the acid form of the respective ligands.[2,4] The only effective method of separation of these $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ compounds from their $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ congeners is the selective oxidation of the former with iodine. The iodine adduct can be separated by precipitation and then reduced with zinc to give the pure $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ complexes.[2,4]

We have recently reported the synthesis of members of the second class: $MoWCl_4(PR_3)_4$ ($PR_3 = PMe_2Ph$ (**4**), $PMePh_2$ (**5**), PMe_3 (**7**)) as well as $Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$ (**6**).[7] Carlin and McCarley have described a different synthesis of $MoWCl_4(PMe_3)_4$ starting from $MoW(O_2CCMe_3)_4$.[8,9] In this paper we describe the complete syntheses and some properties of the heteronuclears as well as further details of the syntheses of the homonuclears $Mo_2Cl_4(PR_3)_4$ ($PR_3 = PMePh_2$ (**1**), PMe_2Ph (**2**), PMe_3 (**3**)). The crystal structures for **5**–**7** are also reported.

In the structural determinations of $MoW(O_2CCMe_3)_4$[3] and $MoW(mhp)_4$[4] the two metal sites are equally occupied by Mo and W because the two ends of the molecules are so similar. Crystals of **5** and **7** are also disordered. The crystal structure of **6** is significant because there is no disorder of the two metal atoms. In complex **6** the two metals are "labeled" with different phosphine ligands, and thus the molybdenum to tungsten and metal to ligand distances can be measured accurately. An interesting question is whether these unbridged $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ complexes show signs of enhanced stability relative to the homonuclear complexes $M_2Cl_4(PR_3)_4$ (M = Mo, W). We find that unbridged $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ bonds have properties close to those of the average of their Mo_2 and W_2 congeners and do not appear to have extra stability.

Experimental Section

General Data. Oxygen and water were excluded during all operations by using vacuum lines or a glovebox supplied with purified nitrogen. Solvents apart from dichloromethane were dried over and distilled from sodium benzophenone ketyl and were degassed before use. Dichloromethane was dried over phosphorus pentoxide. NMR spectra were recorded on a Varian XL-200 (200 MHz for ^1H and 81 MHz for ^{31}P NMR) or on a Bruker WP-80 (80 MHz for ^1H and 32.3 MHz for ^{31}P NMR) spectrometer. ^{31}P chemical shifts were measured relative to 1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries. They are reported relative to 85% H_3PO_4 by using the chemical shift difference, $\delta = -140.4$ ppm. Visible absorption spectra were recorded by using a Perkin-Elmer Lambda 3B UV/vis spectrophotometer and a Perkin-Elmer R100 recorder. Cyclic voltammetric measurements were performed on a BAS CV 1B instrument and a Houston Instruments 100 recorder with use of tetrahydrofuran solutions that were 0.002 M in the quadruply bonded complexes and 0.2 M in $(n\text{-}Bu)_4NBF_4$. Voltammograms were obtained by using a glassy-carbon electrode referenced to a Ag/AgCl electrode but are reported relative to the saturated calomel electrode (SCE). Microanalyses were performed on samples handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver, Canada. The phosphine ligands and metal chlorides $CrCl_3$ and $ReCl_5$ were used as purchased from Strem and Morton/Thiokol-Alfa Chemicals. The preparations of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$,[10] $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$,[11] $Mo(\eta^6\text{-}PhPEt_2)(PPh_2CH_2CH_2PPh_2)(PEt_2Ph)$,[12] $Mo(\eta^6\text{-}PhPMePh)(PPh_2CH_2CH_2PPh_2)(PMePh_2)$,[12] $MoCl_4(CH_3CN)_2$,[13] $MoCl_4(THF)_2$,[13] $NbCl_4(THF)_2$,[14] $[NbCl_3(THF)_2]_2(\mu\text{-}N_2)$,[15] and $WCl_4(PPh_3)_2$[16] were reported elsewhere.

Preparation of $Mo_2Cl_4(PMePh_2)_4$ (1). A solution of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (400 mg, 0.4 mmol) in 10 mL of dry tetrahydrofuran (THF) was added to a slurry of $MoCl_4(THF)_2$ (170 mg, 0.4 mmol) in 5 mL of THF. The mixture was stirred for 10 h and filtered through Celite. Concentrating to 2 mL and adding 10 mL of hexanes effected the precipitation of green **1** (390 mg, 78%). Subsequent recrystallizations with benzene/hexanes resulted in a blue isomer of **1**.[17,18] ^1H NMR (C_6D_6) δ 7.6 (br, 16 H, *o-Ph*P–Mo), 7.0 (br, 24 H, *m,p-Ph*P–Mo), 2.0 (br, 12 H, CH_3P–Mo); ^{31}P NMR (C_6H_6) δ 5.9 (s, 4 P, P–Mo); Raman ν(MoMo) 349 cm^{-1}. Anal. Calcd for $C_{52}H_{52}Cl_4Mo_2P_4$: C, 55.05; H, 4.62. Found: C, 54.73; H, 4.90.

Preparation of $Mo_2Cl_4(PMe_2Ph)_4$ (2). A solution of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ (50 mg, 0.1 mmol) in 2 mL of C_6H_6 was added to a slurry of $MoCl_4(THF)_2$ (29 mg, 0.1 mmol) in 1.5 mL of C_6H_6. The mixture was stirred for 2 h and filtered. The resulting green solution was concentrated to 1 mL, and hexanes (5 mL) were added. This was cooled for 3 h at −20 °C and filtered to yield the extremely soluble green-blue **2** (37 mg, 55%): ^1H NMR (C_6D_6) δ 7.4 (m, 8 H, *o-Ph*P–Mo), 7.0 (m, 12 H, *m,p-Ph*P–Mo), 1.8 (t, virtual coupling, 24 H, CH_3P–Mo); ^{31}P NMR (C_6H_6) δ −2.3 (s, 4 P, P–Mo). Anal. Calcd for $C_{32}H_{44}Cl_4Mo_2P_4\cdot 0.25C_6H_6$: C, 44.42; H, 5.06. Found: C, 44.19; H, 5.14.

Preparation of $Mo_2Cl_4(PMe_3)_4$ (3). An excess of PMe_3 (175 mg, 2.3 mmol) was added to a solution of **1** (500 mg, 0.4 mmol) in 10 mL of C_6H_6. This was heated at 40 °C for 1 h, then concentrated to 2 mL, and treated with pentane (ca. 15 mL) to precipitate blue **3**.[19] This product appeared to be pure by ^1H NMR (200 mg, 70%): ^1H NMR (C_6D_6) δ 1.4 (t, virtual coupling, 12 H, CH_3P–Mo); ^{31}P NMR (C_6H_6) δ −10.5 (s, 4 P, P–Mo).

Preparation of $MoWCl_4(PMe_2Ph)_4$ (4). (a) A solution of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ (50 mg, 0.1 mmol) in 10 mL of C_6H_6 was added to a slurry of complex $WCl_4(PPh_3)_2$ (66 mg, 0.1 mmol) stirring in C_6H_6 (10 mL). This was stirred for 2.5 h and then filtered to yield a green solution of complex **4**. The solution was concentrated to 3 mL, and 10 mL of hexanes was added. After being cooled at −20 °C for 1 h, the solution was filtered to yield **4** (45 mg, 60%). (b) Alternatively, to a solution of complex **5** (50 mg, 0.04 mmol) in 3 mL of C_6H_6 was added PMe_2Ph (28 mg, 0.20 mmol). This was heated at 45 °C for 3 h. The ^{31}P NMR spectrum of this solution verified the formation of complex **4**. ^1H NMR (C_6D_6): δ 7.3 (m, 8 H, *o-Ph*P–M, M = Mo, W), 7.0 (m, 12 H, *m,p-Ph*P–M, M = Mo, W), 1.9 (t, virtual coupling, 12 H, CH_3P–W, $J = 4.0$ Hz), 1.8 (t, virtual coupling, 12 H, CH_3P–Mo, $J = 3.6$ Hz). ^{31}P NMR (C_6H_6): δ −20.1 (t, 2 P, P–Mo, $^3J_{PP} = 24.0$ Hz), 17.4 (t, 2 × 0.86 P, P–W ($I = 0$), $^3J_{PP} = 24.0$ Hz), 17.4 (dt, 2 × 0.14 P, P–^{183}W ($I = {}^1/_2$), $^1J_{PW} = 280$ Hz, $^3J_{PP} = 24.0$ Hz). Anal. Calcd for $C_{32}H_{44}Cl_4MoP_4W\cdot 0.5C_6H_6$: C, 41.49; H, 4.68. Found: C, 41.61; H, 4.68.

Preparation of $MoWCl_4(PMePh_2)_4$ (5). A solution of $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ (100 mg, 0.1 mmol) in 5 mL of C_6H_6 was added dropwise over a 1-min period to a yellow suspension of the complex $WCl_4(PPh_3)_2$ (250 mg, 0.3 mmol) in 10 mL of C_6H_6. After 5 min the resulting green suspension was filtered, and the filtrate was concentrated under vacuum to 5 mL. A ^{31}P NMR spectrum of this green solution revealed the presence of **5**, free PPh_3, and small amounts of **1** and

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Table I. Crystal Data, Details of Data Collections,[a] and Structure Refinements

	$C_{52}H_{52}Cl_4P_4MoW^b$ (**5**)	$C_{32}H_{44}Cl_4P_4MoW$ (**6**)	$C_{12}H_{36}Cl_4P_4MoW^b$ (**7**)
systems	monoclinic	monoclinic	monoclinic
a, Å	21.511 (4)	16.817 (4)	17.312 (4)
b, Å	12.176 (6)	11.925 (3)	9.193 (1)
c, Å	40.863 (8)	19.685 (5)	19.085 (3)
β, deg	92.65 (2)	103.87 (2)	119.69 (2)
V, Å^3	10692	3832.4	2638.9
fw^b	1222.5	974.2	725.9
Z	8	4	4
D_{calcd},^{b} g cm^{-3}	1.519	1.688	1.570
μ(Mo K$\bar{\alpha}$),^{b} cm^{-1}	27.8	38.5	55.6
space group	$P2_1/a$	$I2/a$	$I2/a$
no. of reflcns used in cell detmn (θ range, deg)	24 ($8.6 < \theta < 12.1$)	25 ($10.8 < \theta < 19.7$)	25 ($10.9 < \theta < 17.3$)
scan range,^{c} deg	($0.80 + 0.35 \tan \theta$)	($0.90 + 0.35 \tan \theta$)	($0.75 + 0.35 \tan \theta$)
max scan time, s	65	70	70
max 2θ, deg	40	50	55
quadrants collcd	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
std. reflns: no./interval, s	2/8500	3/9000	3/9000
no. data colld.	11 136	3583	3733
cryst shape	plate	needle	rhomb
cryst faces: d, cm	{010}: 0.011 25 {100}: 0.008 75 {001}: 0.002 75	{100}: 0.0037 {001}: 0.0044 {010}: 0.0119	{001}: 0.0044 (110), ($\bar{1}\bar{1}0$): 0.0050 ($1\bar{1}0$), ($\bar{1}10$): 0.0056
grid	10 × 10 × 6	6 × 10 × 8	10 × 8 × 8
T	0.627–0.860	0.704–0.834	0.623–0.674
structure soln	direct methods	Patterson	Patterson
no. of nonzero data	8078	3113	2825
no. of obsd data	3554	2203	2084
final R factors			
R	0.0957	0.0364	0.0312
R_w	0.0912	0.0392	0.0322
max shift/error	0.64	0.07	0.76
weighting scheme	$(\sigma^2(F) + 0.00074F^2)^{-1}$	$4F^2\{\sigma^2(I) + (0.04F^2)^2\}^{-1}$	$(\sigma^2(F) + 0.0005F^2)^{-1}$
max peak in final difference Fourier, e Å^{-3}	1.25 (near Mo(2))	1.16 (near W)	1.14 (between M(1) and M(2))

[a] Enraf-Nonius CAD-4 diffractometer (graphite monochromater) using Mo K$\bar{\alpha}$ radiation (λ = 0.710 69 Å) in the ω:2θ mode. [b] Assuming formulas for compounds **5** and **7** correctly represent the molecular composition of these two compounds. [c] Backgrounds were measured by extending the scan by 25% on either side of the scan and were collected for half the time taken to collect the peak.

$WOCl_2(PMePh_2)_3$.[7] Addition of hexanes gave crude **5**, which was recrystallized from benzene/hexanes to give the product (100 mg, 74%) contaminated with approx. 5% of complex **1**. Complex **1** can be removed by allowing the mixture (100 mg; contains 0.004 mmol **1**) to react with 6 μL of PMe_3 for 2 h. Pure **5** was then precipitated with hexanes (81 mg, 60%): ^{1}H NMR (C_6D_6) δ 8.0–7.5 (m, 16H, *o-Ph*P–M, M = Mo, W), 7.0–6.8 (m, 24 H, *m,p-Ph*P–M, M = Mo, W), 2.1 (t, virtual coupling, 6 H, CH_3P–W, J = 4 Hz), 1.9 (t, virtual coupling, 6 H, CH_3P–Mo, J = 3 Hz); ^{31}P NMR (C_6H_6) δ −13.1 (t, 2 × 0.86 P, P–Mo$\overset{4}{-}$W (I = 0), $^3J_{PP}$ = 23.5 Hz), −13.1 (dt, 2 × 0.14 P, P–Mo$\overset{4}{-}$^{183}W, $^2J_{PW}$ = 47 Hz, $^3J_{PP}$ = 23.5 Hz), 21.9 (t, 2 × 0.86 P, P–W (I = 0), $^3J_{PP}$ = 23.5 Hz), 21.9 (dt, 2 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 266 Hz, $^3J_{PP}$ = 23.5 Hz). Anal. Calcd for $C_{52}H_{52}Cl_4MoP_4W{\cdot}0.2C_6H_6$: C, 51.60; H, 4.33. Found: C, 51.62; H, 4.51.

Preparation of $(Me_3P)_2Cl_2MoWCl_2(PMePh_2)_2$ (6). To a solution of complexes **5** (438 mg, 0.4 mmol) in 10 mL of C_6H_6 was added PMe_3 (0.272 mg, 3.5 mmol). The mixture was stirred for 2 h at ambient temperature, whereupon the volume was concentrated under vacuum to ca. 2 mL and hexanes (ca. 3 mL) were added to effect the precipitation of blue-green complex **6** (171 mg, 49%): ^{1}H NMR (C_6D_6) δ 7.7–7.4 (m, 8 H, *o-Ph*P–W), 7.0–6.8 (m, 12 H, *m,p-Ph*P–W), 2.8 (t, virtual coupling, 6 H, CH_3P–W, J = 4 Hz), 1.1 (br, 18 H, CH_3P–Mo); ^{31}P NMR (C_6H_6) δ −28.0 (t, 2 P, P–Mo, $^3J_{PP}$ = 24.4 Hz), 21.8 (t, 2 × 0.86 P, P–W (I = 0), $^3J_{PP}$ = 24.4 Hz), 21.8 (dt, 2 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 273 Hz, $^3J_{PP}$ = 24.4 Hz). Anal. Calcd for $C_{32}H_{44}Cl_4MoP_4W$: C, 39.45; H, 4.55. Found: C, 38.54; H, 4.54.

Preparation of $MoWCl_4(PMe_3)_4$ (7). To a solution of complex **5** (650 mg, 0.5 mmol) in 20 mL of C_6H_6 was added PMe_3 (200 mg, 2.6 mmol). The mixture was sealed under vacuum and heated at 60 °C for 3 h. The solvent plus excess PMe_3 was then pumped off under vacuum, and the dissociated $PMePh_2$ was removed by means of vacuum distillation from the reaction flask, which was heated at 55 °C for 2 h onto a water-cooled sublimation probe. A small glass cup attached to the bottom of the probe collected the $PMePh_2$. The resulting blue-green residue was taken up in a minimum amount of C_6H_6, ca. 0.5 mL, and hexanes were added. This mixture was cooled at −20 °C for 2 h and complex **7**[8,9] was filtered off and washed with pentanes. This product appeared to be pure by ^{1}H and ^{31}P NMR (127 mg, 33%): ^{1}H NMR (C_6D_6) δ 1.4 (m, 36 H, CH_3P–M, M = Mo, W); ^{31}P NMR (C_6H_6) δ −28.9 (t, 2 P, P–Mo, $^3J_{PP}$ = 24.4 Hz), 9.6 (t, 2 × 0.86 P, P–W (I = 0), $^3J_{PP}$ = 24.4 Hz), 9.6 (dt, 2 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 269 Hz, $^3J_{PP}$ = 24.4 Hz). The photoelectron spectrum of this complex has recently been discussed.[20]

Attempted Preparations of Other Quadruply Bonded Dimers. 1. Mo(η^6-PhPMePh)($PPh_2CH_2CH_2PPh_2$)($PMePh_2$) (50 mg, 0.05 mmol) was dissolved in 1 mL of C_6H_6 and added to a slurry of $WCl_4(PPh_3)_2$ (143 mg, 0.16 mmol) in 0.5 mL of C_6H_6. After the mixture was stirred for 1 h, the ^{31}P NMR spectrum was obtained. Besides dissociated PPh_3 the only other species apparent was the heteronuclear **5**.

2. Orange Mo(η^6-PhPEt$_2$)($PPh_2CH_2CH_2PPh_2$)(PEt_2Ph) (50 mg, 0.06 mmol) was dissolved in 0.5 mL of C_6H_6 and added to a suspension of $WCl_4(PPh_3)_2$ (51 mg, 0.06 mmol) in 1 mL of C_6H_6. After the mixture was stirred for 1 h, the ^{31}P NMR spectrum obtained on the solution, which was now green, provided evidence that $MoWCl_4(PEt_2Ph)_4$ was the major species: ^{31}P NMR (C_6H_6) δ −4.0 (t, 2 P, P–Mo, $^3J_{PP}$ = 22.0 Hz), 32.2 (t, 2 × 0.86 P, P–W (I = 0), $^3J_{PP}$ = 22.0 Hz), 32.2 (dt, 2 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 290 Hz, $^3J_{PP}$ = 22.0 Hz).

3. Orange Mo(η^6-PhPEt$_2$)($PPh_2CH_2CH_2PPh_2$)(PEt_2Ph) (100 mg, 0.12 mmol) was dissolved in 2.0 mL of THF and added to a suspension of $MoCl_4(CH_3CN)_2$ (38 mg, 0.12 mmol) in 5.0 mL of THF. The mixture was stirred for 1 h and evaporated to dryness. The resulting residue was dissolved in C_6H_6 to form a green-blue solution, and the ^{31}P NMR spectrum was obtained. The major species evident was the homonuclear $Mo_2Cl_4(PEt_2Ph)_4$: ^{31}P NMR (C_6H_6) δ 16.0 (s, 4 P, P–Mo).

4. Stoichiometric equivalents of Mo(η^6-PhPMePh)($PMePh_2$)$_3$ were allowed to react with other metal halides such as $NbCl_4(THF)_2$, $[NbCl_3(THF)_2]_2(\mu\text{-}N_2)$, $CrCl_3$, and $ReCl_5$ in dry C_6H_6. No readily identifiable products were obtained.

X-ray Structure Determinations. Crystals of complexes **5**–**7** were obtained by slow diffusion of hexanes into a benzene solution of the respective complex in a long glass tube. Suitable crystals were wedged into 0.2–0.3-mm Lindemann capillaries and sealed under nitrogen. All

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(20) Bancroft, G. M.; Bice, J.; Morris, R. H.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 898–899.

Table II. Final Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] and Their Estimated Standard Deviations

atom	x	y	z	U_{eq}[a]	atom	x	y	z	U_{eq}[a]
Compound **5**[b]									
W(1)[c]	0.3372 (1)	0.4262 (3)	0.4116 (1)	51 (2)	Cl(7)	0.2071 (5)	0.5914 (10)	0.9238 (3)	57 (10)
W(2)[c]	0.1480 (1)	0.4308 (2)	0.9106 (1)	52 (2)	Cl(8)	0.0663 (5)	0.3252 (10)	0.9327 (3)	53 (9)
Mo(1)[c]	0.2975 (1)	0.3536 (3)	0.3657 (1)	49 (3)	P(1)	0.2756 (6)	0.3242 (10)	0.4552 (3)	45 (10)
Mo(2)[c]	0.1798 (1)	0.3588 (3)	0.8647 (1)	45 (3)	P(2)	0.4158 (6)	0.5634 (13)	0.3891 (4)	64 (11)
Cl(1)	0.4220 (6)	0.3208 (11)	0.4339 (3)	67 (11)	P(3)	0.3708 (7)	0.1883 (12)	0.3584 (4)	69 (12)
Cl(2)	0.2799 (6)	0.5885 (11)	0.4245 (3)	62 (10)	P(4)	0.2008 (6)	0.4740 (13)	0.3522 (4)	66 (13)
Cl(3)	0.3492 (6)	0.4240 (15)	0.3201 (4)	106 (13)	P(5)	0.1046 (7)	0.1940 (12)	0.8561 (4)	66 (12)
Cl(4)	0.2205 (6)	0.2189 (11)	0.3755 (3)	68 (11)	P(6)	0.2748 (7)	0.4803 (13)	0.8533 (4)	78 (14)
Cl(5)	0.1245 (6)	0.4343 (13)	0.8175 (3)	75 (11)	P(7)	0.2171 (6)	0.3262 (11)	0.9537 (3)	49 (11)
Cl(6)	0.2589 (6)	0.2248 (11)	0.8752 (3)	69 (11)	P(8)	0.0636 (6)	0.5644 (12)	0.8887 (3)	50 (10)
Compound **6**									
W	0.2500	0.02988 (4)	0.0000	31.3 (1)	C(112)	0.2139 (6)	−0.2458 (8)	−0.0940 (5)	60 (3)
Mo	0.2500	0.21498 (8)	0.0000	30.6 (3)	C(113)	0.2302 (7)	−0.3592 (8)	−0.0940 (6)	72 (4)
Cl(1)	0.3847 (1)	−0.0359 (2)	0.0047 (1)	47.9 (5)	C(114)	0.2815 (7)	−0.3986 (8)	−0.1313 (5)	71 (4)
Cl(2)	0.2301 (1)	0.2950 (2)	−0.1161 (1)	51.5 (6)	C(115)	0.3182 (6)	−0.3279 (9)	−0.1679 (5)	67 (3)
P(1)	0.2285 (1)	−0.0189 (2)	−0.1287 (1)	37.2 (5)	C(116)	0.3032 (5)	−0.2122 (8)	−0.1684 (5)	52 (3)
P(2)	0.4010 (1)	0.2562 (2)	0.0154 (1)	44.8 (6)	C(121)	0.1281 (5)	−0.0038 (7)	−0.1890 (4)	42 (3)
C(11)	0.2980 (5)	0.0435 (8)	−0.1751 (4)	51 (3)	C(122)	0.1117 (6)	0.0871 (9)	−0.2351 (5)	66 (3)
C(21)	0.4732 (5)	0.2049 (9)	0.0928 (5)	63 (3)	C(123)	0.0338 (7)	0.099 (1)	−0.2784 (5)	81 (4)
C(22)	0.4478 (5)	0.225 (1)	−0.0558 (5)	68 (4)	C(124)	−0.0269 (6)	0.022 (1)	−0.2769 (5)	76 (4)
C(23)	0.4131 (6)	0.4079 (9)	0.0264 (6)	76 (4)	C(125)	−0.0103 (6)	−0.0662 (9)	−0.2328 (5)	68 (4)
C(111)	0.2492 (5)	−0.1697 (7)	−0.1311 (4)	40 (3)	C(126)	0.0660 (5)	−0.0783 (8)	−0.1880 (5)	53 (3)
Compound **7**									
W(1)[d]	0.2500	0.59836 (5)	0.0000	24.1 (3)	C(11)	0.3069 (5)	0.5956 (9)	0.2171 (4)	45 (4)
Mo(1)[d]	0.2500	0.83866 (6)	0.0000	20.4 (3)	C(12)	0.2221 (7)	0.3425 (9)	0.1243 (6)	62 (7)
Cl(1)	0.3959 (1)	0.5024 (2)	0.0853 (1)	40.3 (10)	C(13)	0.1172 (5)	0.5957 (9)	0.1084 (5)	54 (6)
Cl(2)	0.2236 (1)	0.9364 (2)	0.1032 (1)	40.1 (11)	C(21)	0.4221 (6)	1.0937 (9)	0.1000 (5)	53 (6)
P(1)	0.2226 (1)	0.5431 (2)	0.1153 (1)	32.2 (10)	C(22)	0.4950 (5)	0.8386 (9)	0.0683 (6)	56 (6)
P(2)	0.4122 (1)	0.8940 (2)	0.0956 (1)	35.4 (10)	C(23)	0.4622 (5)	0.8426 (10)	0.2018 (4)	63 (6)

[a] Atoms refined anisotropically: $U_{eq} = {}^1/_3$ Tr U. [b] Positional parameters of phenyl ring carbon atoms are given in the supplementary materials. [c] Population parameters obtained by scaling down the W scattering curves or scaling up the Mo scattering curves were W(1), 0.777 (6); W(2), 0.812(6); Mo(1), 1.344(12); and Mo(2), 1.385 (11), which correspond to compositions in % W [% Mo] of 48 (1) [52 (1)], 57 (1) [43 (1)], 45 (2) [55 (2)] and 51 (2) [49 (1)], respectively. Thus the metal compositions of the two independent molecules are $W_{0.93(3)}Mo_{1.07(3)}$ [W(1)–Mo(1)] and $W_{1.08(3)}Mo_{0.92(3)}$ [W(2)–Mo(2)]. (Esd's on population parameters are somewhat conservative.) [d] Population parameters obtained by scaling down the W scattering curve or scaling up the Mo scattering curve were W = 0.766 (2) and Mo = 1.318 (4) corresponding to 45.9 (3)% W [54.1 (3)% Mo] and 41.9 (6)% W [58.1 (6)% Mo], respectively, that is, an overall metal composition of $W_{0.88(1)}Mo_{1.12(1)}$. (Esd's on population parameters are somewhat conservative.)

relevant crystallographic information is given in Table I. Precession photographs were used to obtain preliminary cell and symmetry information. Intensity data on each compound were collected on an Enraf-Nonius CAD-4 diffractometer utilizing the options specified in Table I. For each reflection, stationary background counts were recorded at each end of the scan, each for one-fourth of the scan time. Lorentz and polarization corrections were applied to all data. Absorption corrections were applied after the composition of each crystal had been established. The crystal quality of **5** was not as high as that of **6** and **7**, leading to fewer observed reflections for the criterion $I \geq 3\sigma(I)$. All three structures were solved as indicated in Table I, and least-squares refinements (blocked for compound **5**) have converged to the residuals indicated. In the case of compound **5** and that of **7** refinement of the site occupancy factor of the central metal atoms indicated disorder (Table II). For **6** and **7** hydrogen atoms were located in difference Fourier maps or were placed in calculated positions. In the final refinement of **7** the CH_3 atoms were refined as rigid groups. Neutral-atom scattering factors were taken from the *International Tables* for *X-Ray Crystallography* or were stored in the program (SDP package). Calculations were performed on PDP 11/23 and Gould SEL computers using programs in the SDP package and SHELX, respectively. Final positional parameters and their estimated standard deviations for non-hydrogen atoms and selected bond lengths and bond angles are given in Tables II and III, respectively. An ORTEP view of complex **6** is presented in Figure 1, and a view of the crystal packing of **6** is given in Figure 2 (supplementary material).

Results and Discussion

Synthesis. A new route to quadruply bonded species has been discovered (Scheme I). This involves the use of (η^6-arylphosphine)molybdenum complexes where the "dangling" phosphorus atom contained in these species appears to assist in the formation of the quadruple bond. Reacting complexes Mo(η^6-L)(L)$_3$ (L = PMe_2Ph or $PMePh_2$) with either $MoCl_4(THF)_2$ or $WCl_4(PPh_3)_2$ yields the unbridged quadruply bonded complexes **1**, **2**, **4**, and **5** in high yields.

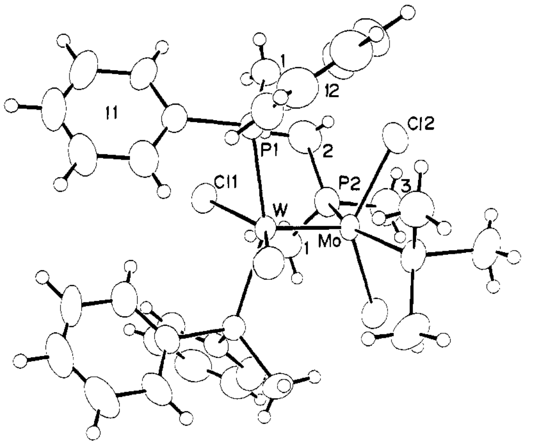


Figure 1. ORTEP view of compound **6** showing the atomic numbering scheme used. Thermal ellipsoids are drawn at the 50% probability level.

Our synthetic route to the quadruple bonds is unique in two respects: first, molybdenum(0) complexes are used to reduce molybdenum(IV) or tungsten(IV) complexes to produce the Mo(II)$\overset{4}{-}$M(II) (M = Mo or W) products; second, in heteronuclear formation the reaction gives almost exclusively the desired Mo$\overset{4}{-}$W products at 22 °C in a regioselective reaction. The preparation of **1** is unusual in that a green isomer is first produced, which upon recrystallization isomerizes to a blue form.

In a preliminary report on this work,[7] we reported that Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ reacted with $WCl_4(PPh_3)_4$ to produce complex **4**. The former complex was prepared in a low-yield

Table III. Selected Bond Distances (Å) and Bond Angles (deg)

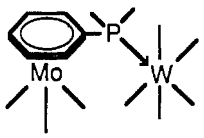
	$Mo_2Cl_4(PMe_3)_4$[a]	$MoWCl_4(PMePh_2)_4$ (**5**)	$Cl_2(PMe_3)_2MoWCl_2$-$(PMePh_2)_2$ (**6**)	$MoWCl_4(PMe_3)_4$ (**7**)	$W_2Cl_4(PMe_3)_4$[a]
Bond Distances					
M(1)–M(2)[b]	2.130 (1)[c]	2.210 (4), 2.207 (4)[c]	2.207 (1)[c]	2.2092 (7)[c]	2.262 (1)[c]
M(1)–P(1)	2.546 (1)	2.592 (14), 2.584 (16) 2.579 (14), 2.560 (14)	2.539 (2)	2.522 (2)	2.509 (2)
M(2)–P(2)	2.544 (1)	2.577 (16), 2.587 (16) 2.593 (16), 2.580 (16)	2.532 (2)	2.529 (2)	2.506 (2)
M(1)–Cl(1)	2.415 (1)	2.382 (13), 2.399 (14) 2.381 (13), 2.384 (13)	2.378 (2)	2.395 (2)	2.395 (2)
M(2)–Cl(2)	2.413 (1)	2.361 (17), 2.373 (14) 2.410 (13), 2.384 (14)	2.424 (2)	2.406 (2)	2.389 (2)
Bond Angles					
M(2)–M(1)–Cl(1)	112.37 (2)	111.6 (4), 109.8 (3) 109.5 (3), 111.8 (3)	109.27 (6)	111.62 (5)	111.74 (6)
M(2)–M(1)–P(1)	102.23 (2)	101.6 (3), 100.8 (4) 101.2 (3), 101.6 (3)	103.24 (6)	101.62 (4)	101.18 (5)
Cl(1)–M(1)–Cl(1)′	135.27 (4)	138.6 (5), 138.7 (5)	141.5 (1)	136.77 (6)	136.9 (1)
Cl(1)–M(1)–P(1)	85.27 (2)	83.1 (4), 88.0 (4) 87.7 (4), 83.8 (4)	82.48 (7)	85.61 (6)	85.88 (7)
Cl(1)–M(1)–P(1)′	85.48 (2)	89.3 (5), 85.3 (4) 84.1 (5), 87.0 (4)	88.83 (7)	85.87 (6)	85.88 (7)
P(1)–M(1)–P(1)′	155.55 (4)	157.6 (5), 157.2 (5)	153.5 (1)	156.76 (6)	157.7 (1)
M(1)–M(2)–Cl(2)	112.07 (2)	109.9 (4), 112.0 (4) 111.7 (4), 111.4 (4)	113.19 (6)	111.93 (5)	111.55 (6)
M(1)–M(2)–P(2)	102.41 (2)	101.1 (4), 103.2 (4) 102.1 (4), 101.6 (4)	101.18 (6)	101.59 (5)	101.10 (5)
Cl(2)–M(2)–Cl(2)′	135.85 (4)	137.9 (5), 136.8 (5)	133.6 (1)	136.14 (6)	136.9 (1)
Cl(2)–M(2)–P(2)	85.24 (2)	83.2 (6), 84.3 (5) 85.4 (5), 85.9 (5)	86.79 (8)	85.82 (6)	85.83 (6)
Cl(2)–M(2)–P(2)′	85.49 (2)	91.7 (5), 90.4 (5) 82.4 (5), 82.0 (5)	84.45 (8)	85.54 (6)	86.06 (7)
P(2)–M(2)–P(2)′	155.18 (4)	155.4 (5), 157.2 (5)	157.6 (1)	156.80 (6)	157.8 (1)

[a] Reference 19. [b] M(1) = W(1) (or W(2)) and M(2) = Mo(1) (or Mo(2)) in **5**–**7**. [c] Numbers in parentheses are the estimated standard deviations.

reaction by the photolysis of $MoH_4(PMe_2Ph)_4$ in pentane in the presence of *tert*-butylethylene.[21] We have recently developed a more efficient preparation of this complex involving the reduction of Mo_2Cl_{10} by Mg in a THF solution of PMe_2Ph at 70 °C under Ar.[10]

Water and oxygen must be excluded at all stages of the preparations of **4** and **5** to avoid the formation of a side product identified as $WOCl_2(PR_3)_3$ (PR_3 = PMe_2Ph or $PMePh_2$).[7,22] When these precautions are taken, the reaction of stoichiometric equivalents of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and $WCl_4(PPh_3)_2$ yields **4** in close to 100% yield according to the ^{31}P NMR spectrum of the reaction mixture. This can be compared to the reaction to give **5**, where even if $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $WCl_4(PPh_3)_2$ are used in a 1:5 ratio in order to minimize the formation of **1**, small amounts of the homonuclear **1** (~5%) are a persistent contaminant of the desired $Mo\overset{4}{-}W$ complex. Various attempts to separate this mixture by chromatography were not successful. The experimental conditions reported above minimize the amount of this impurity. Complex **1** can be removed completely by titrating the mixture of $Mo\overset{4}{-}W$ and $Mo\overset{4}{-}Mo$ with trimethylphosphine until the ^{31}P resonance for **1** disappears. Then **5** can be crystallized out selectively in 60% yield overall. Reasons for the difference in selectivity between $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ in these reduction reactions are not readily apparent, although the second compound is known to be more sterically hindered and undergoes substitution reactions much more readily than the first.[10]

The THF and phosphine ligands in $MoCl_4(THF)_2$ and $WCl_4(PPh_3)_2$, respectively, are known to be rapidly substituted by a variety of phosphines. We have demonstrated elsewhere that a variety of η^6-phosphine complexes of Mo(0) can be used as phosphine-like ligands in complexes of rhodium(I),[23] molybdenum(0)[24] and group VI (group 6[25]) metal carbonyls.[10] Thus the coordination of the η^6-phosphine complex to the metal halide could easily give an intermediate binuclear complex that would facilitate metal–metal bond formation and enhance the selectivity of this reaction, particularly in the heteronuclear case.



Roberts and Geoffroy have classified this type of reaction that leads to metal–metal bond formation as a "bridge-assisted" reaction and have reviewed many examples.[26]

The high yields of the desired product in the heteronuclear synthesis reactions contrast sharply to the result obtained by using $Mo(N_2)_2(PMePh_2)_4$ as the reducing agent. Here yields of only 20% of the heteronuclear **5** are obtained as well as the undesired products **1**, (35%) and $WOCl_2(PMePh_2)_3$, (30%), as indicated by the ^{31}P NMR spectrum of the reaction mixture.[7] Thus the η^6-arylphosphine does appear to have a role to play as bridging ligand in the formation of **4** and **5**.

Unfortunately the capacity of (η^6-phosphine)molybdenum complexes to react with metal halides to produce metal to metal bonds may have limited scope. Attempts to synthesize mixed-ligand quadruply bonded species by using $Mo(\eta^6\text{-}PhPMePh)(PPh_2CH_2CH_2PPh_2)(PMePh_2)$ and $Mo(\eta^6\text{-}PhPEt_2)$-

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(21) Zubkowski, J. D. Ph.D. Thesis, Indiana University, 1983.

(22) $WOCl_2(PMe_2Ph)_3$ was identified by ^{31}P NMR (C_6H_6): δ −24.0 (t, 1 × 0.86 P, P–W(I = 0), $^2J_{PP}$ = 3.4 Hz), −24.0 (dt, 1 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 445, $^2J_{PP}$ = 3.4 Hz), −14.7 (d, 2 × 0.86 P, P–W(I = 0), $^2J_{PP}$ = 3.7 Hz), −14.7 (dd, 2 × 0.14 P, P–^{183}W, $^1J_{PW}$ = 346, $^2J_{PP}$ = 3.7 Hz).

(23) Luck, R. L.; Morris, R. H. *J. Organomet. Chem.* **1983**, *255*, 221–230.

(24) Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Organometallics* **1984**, *3*, 1009–1014.

(25) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

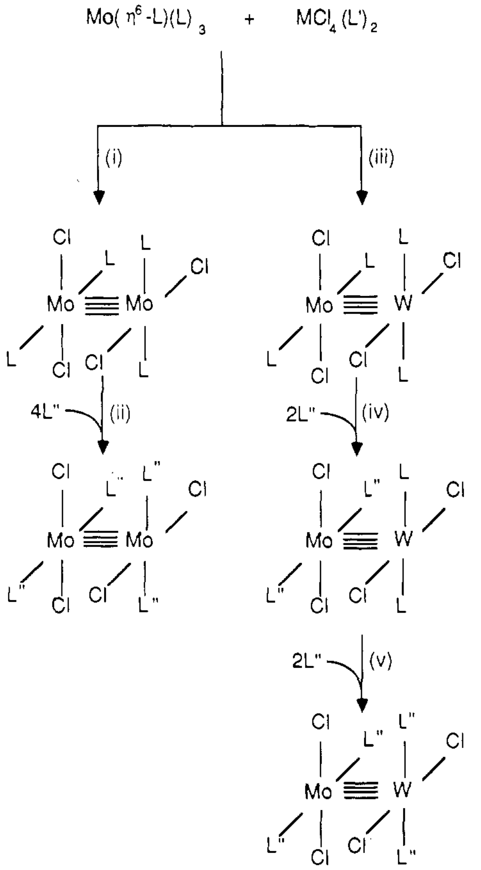
(26) Roberts, D. A.; Geoffroy, G. L. *Comprehesive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon: Oxford, England, 1982, Chapter 40.

Table IV. ^{31}P NMR Chemical Shift Data Referenced to H_3PO_4 for Complexes Containing Quadruple Bonds

	$MoWCl_4L_4$			$Mo_2Cl_4L_4$	$W_2Cl_4L_4$	
	δ(P-Mo)	δ(P-W)	δ(P-W) - δ(P-Mo)	δ(P-Mo)	δ(P-W)	|δ(P-Mo) - δ(P-W)|
L = $PMePh_2$	-13.1	21.9	35.0	5.9	2.0[a]	3.9
L = PMe_2Ph	-20.1	17.4	37.5	-2.3		
L = PMe_3	-28.9	9.6	38.5	-10.5	-7.3[b]	3.2
L = PEt_2Ph	-4.0	32.2	36.2	16.0		
$Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$	-28.0	21.8				

[a] Reference 34. [b] Reference 9.

Scheme I. Synthetic Route to New Complexes Containing Quadruple Bonds[a]



[a] Reaction conditions: (i) M = Mo, L = $PMePh_2$, L′ = THF gives **1**; M = Mo, L = PMe_2Ph, L′ = THF gives **2**. (ii) L = $PMePh_2$, L″ = PMe_3, 1 h, 40 °C gives **3**. (iii) M = W, L = PMe_2Ph, L′ = PPh_3 gives **4**; M = W, L = $PMePh_2$, L′ = PPh_3 gives **5**. (iv) L = $PMePh_2$, L″ = PMe_3, 1 h, 40 °C gives **6**. (v) L = $PMePh_2$, L″ = PMe_3, 3 h, 60 °C gives **7**.

$(PPh_2CH_2CH_2PPh_2)(PEt_2Ph)$ as reductants for $WCl_4(PPh_3)_2$ have not been successful. In these reactions the major products as seen in the ^{31}P NMR were the complexes $MoWCl_4(PR_3)_4$ (PR_3 = $PMePh_2$ and PEt_2Ph, respectively). The reaction of Mo(η^6-$PhPEt_2$)$(PPh_2CH_2CH_2PPh_2)(PEt_2Ph)$ and $MoCl_4(CH_3CN)_2$ also did not yield the mixed-ligand complex. Here the complex $Mo_2Cl_4(PEt_2Ph)_4$ was the major product. Reactions using Mo(η^6-PhPMePh)$(PMePh_2)_3$ and other metal chlorides such as $NbCl_4(THF)_2$, $[NbCl_3(THF)_2]_2(\mu-N_2)$, $CrCl_3$, and $ReCl_5$ did not yield identifiable products. Therefore this synthetic route does not appear to be generally applicable. Clearly other factors in addition to initial coordination of the molybdenum complex are required for specific ligand retention or heteronuclear bond formation in general.

Substitution Reactions. The phosphine ligands on complexes **1** and **5** are easily substituted in reactions with phosphines that have smaller Tolman's cone angles (θ)[27] such as PMe_2Ph (θ = 122°) and PMe_3 (θ = 118°). The reaction of **1** with 4 equiv of PMe_3 at room temperature leads to the formation of complex **3**. This represents a relatively easy and high-yield route to this complex.[19] The phosphine ligands on the tungsten atom in complex **5** are substituted with PMe_3 only at temperatures of about 45 °C. We took advantage of this fact to produce a disubstituted heteronuclear complex **6** where only the phosphines on the molybdenum atom in complex **5** were substituted with PMe_3 in a reaction carried out at room temperature. This reactivity sequence is consistent with the expected trend in metal-phosphorus bond strengths: Mo-P < W-P. This differs from the substitution reactions of $Mo_2Me_4(PEt_3)_4$ with PMe_3 where the second phosphine to be substituted is on the molybdenum next to the one that is substituted first.[28]

A similar reaction between **5** and PMe_2Ph at room temperature gave a complicated and inseparable mixture of products substituted at both metals even if only 2 equiv of PMe_2Ph are used. It was possible to produce the tetraphosphine substituted complexes **4** and **7** by the use of 4 equiv of PMe_2Ph and PMe_3, respectively. There is no reaction of **4** or **5** with PCy_3 (θ = 175°) or PPh_3 (θ = 145°).

^{1}H NMR Data. A broad singlet was obtained for the methyl groups on **1** and a virtual triplet pattern for those on **2** and **3** at 200 MHz. The spectra of **4** and **5** show two methyl resonances as virtual triplets consistent with two types of phosphines. The downfield triplets have been assigned to the methyl groups on the phosphines on the tungsten end of the molecules and the upfield triplets to those on molybdenum. These assignments were based on the results from the ^{31}P NMR spectra of these complexes (where the phosphines on the tungsten atoms were less shielded with respect to those on molybdenum atoms) as the tungsten satellites were not observed. Also in the spectra for both **4** and **5**, the downfield triplets had lower intensities due to unresolved ^{183}W coupling than the upfield ones, in agreement with the above assignments.

The ^{1}H NMR of **6** is interesting in that the protons of the methyl groups on the phosphine ligands on the tungsten atom experience a significant downfield shift (Δδ = 0.8) in comparison with data for complex **5**. This is due to a diamagnetic anisotropy effect attributable to the Mo$\overset{4}{-}$W bond.[29]

^{31}P NMR Data. The ^{31}P NMR spectra of **1**–**3** consist simply of singlets as would be predicted. The identities of the heteronuclear complexes are also readily established by their distinctive ^{31}P NMR spectra. The spectrum of **5** (Figure 3) shows the features expected for the isotopomers present. The isotopomers containing tungsten isotopes with $I = 0$ give two intense triplets due to equivalent ^{31}P nuclei coupling across the quadruple bond. The isotopomer containing ^{183}W gives a doublet of triplets with coupling $^1J_{PW}$ = 266 Hz for the ^{31}P nuclei on W and a doublet of triplets (only the outer two peaks are observed) with coupling $^2J_{PW} \sim 47$ Hz for those on Mo. The satellite peaks due to the $^2J_{^{31}P^{183}W}$ coupling are not resolved in the spectra for **4**, **6**, and **7**.

One observation also noted by Carlin[9] is the magnitude of the chemical shift difference between the phosphorus ligands on the different metals [δ(P-W) - δ(P-Mo) = 35.0–38.5 (Table IV)]. The absolute differences between such chemical shifts for homonuclear complexes with similar ligands, specifically $M_2Cl_4(PMePh_2)_4$ and $M_2Cl_4(PMe_3)_4$ (M = Mo or W), are only 3.9 and

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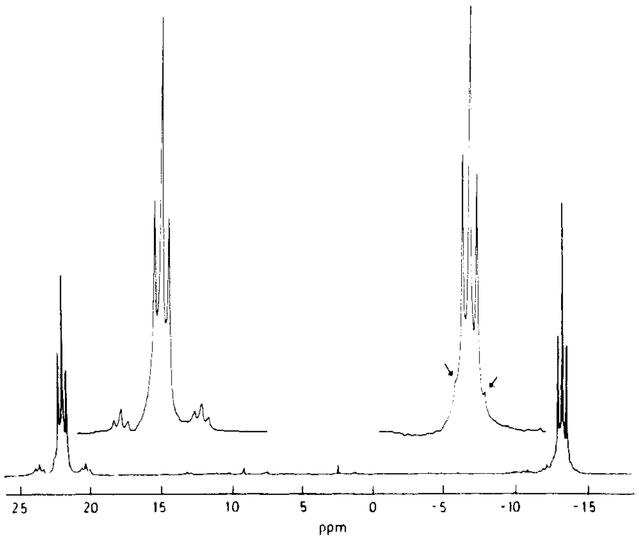

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of **5** at 81 MHz. The arrows indicate the outer peaks of the doublet of triplets associated with the ^{31}P nuclei bonded to molybdenum in the isotopomer containing ^{183}W.

Table V. Electronic Absorption and Electrochemical Data

complex	$E_{1/2}(\mathrm{ox})^a$	$E_{1/2}(\mathrm{red})^a$	$\lambda(\delta^2 \rightarrow \delta\delta^*)$,[b] nm
$Mo_2Cl_4(PMePh_2)_4$ (**1**)			
green	0.28^c	−0.95	602
blue	0.88^c	−1.54	601
$Mo_2Cl_4(PMe_2Ph)_4$ (**2**)	0.80^d	−1.63	592
$Mo_2Cl_4(PMe_3)_4$ (**3**)	0.78^d	−1.64	586
$MoWCl_4(PMe_2Ph)_4$ (**4**)	0.43^c	−1.73	647
$MoWCl_4(PMePh_2)_4$ (**5**)	0.47	-1.72^e	650^f
$Cl_2(PMe_3)_2MoWCl_2(PMePh_2)_2$ (**6**)	0.43^e	−1.73	643
$MoWCl_4(PMe_3)_4$ (**7**)	0.42^e	-1.86^e	635

[a] Vs. SCE. Conditions: 22 °C; solvent, THF; electrolyte, $(n\text{-}Bu)_4NBF_4$; scan rate, 50 mV/s. [b] C_6H_6 solution. [c] $E_p(\mathrm{ox})$, (irreversible potential). [d] Quasi-reversible only at scan rates > 500 mV/s. [e] Quasi-reversible. [f] In other solvents: THF, 648 nm; pyridine, 648 nm; acetonitrile, 654 nm.

3.2 ppm, respectively. A possible explanation for this is that electron density is transferred from tungsten to molybdenum in the heteronuclear species.[9] This would result in a difference in effective charge between the two metal atoms, an effect that would be constant regardless of the phosphine substituents. The chemical shifts of the phosphorus atoms would then be attributed to either the resulting paramagnetic effects or simple diamagnetic screening considerations, or a combination of these two effects.

Electronic Absorption and Electrochemical Data. The visible absorption and cyclic voltammetric data for these complexes are listed in Table V. The energies of the $\delta^2 \rightarrow \delta\delta^*$ transitions[30] increase along the series **1** < **2** < **3**, probably because the electron-donating abilities of their phosphine ligands also increase.

The $\delta^2 \rightarrow \delta\delta^*$ transitions of the complexes $MoWCl_4(PR_3)_4$ (PR_3 = PMe_3, $PMePh_2$) fall between the energies of their Mo_2 and W_2 congeners[19] but are closer to the W_2 values. There is a shift in this transition to higher energy as the $PMePh_2$ ligands are replaced by PMe_3 in the homonuclear $Mo_2Cl_4(PR_3)_4$ and heteronuclear series. This can be attributed to an increase in electron density at the metals and in the $\mathrm{Mo}\overset{4}{-}\mathrm{M}$ bond due to the presence of the smaller and more basic PMe_3 ligands (see Table V). This shift observed for the heteronuclear complexes is paralleled by a decrease in the energies of both reversible redox couples $MoW^+ \leftrightarrow MoW$ ($E_{1/2}(\mathrm{ox})$) and $MoW \leftrightarrow MoW^-$ ($E_{1/2}(\mathrm{red})$), which again indicates that the complexes with more PMe_3 ligands are more reducing.

There is not a significant change in the position of the visible absorption for **5** with a change in the polarity of the solvent. This suggests that solvent coordination along the $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ bond is weak or nonexistent for this crowded heteronuclear complex. The $\delta^2 \rightarrow \delta\delta^*$ transition of less sterically hindered $Mo_2(O_2CCF_3)_4$ does show a solvent dependence.[31]

Previous electrochemical studies on related unbridged quadruple bonds have revealed that $Mo_2Cl_4(PR_3)_4$ (PR_3 = PEt_3 or P-*n*-Pr_3)[32] and $Mo_2Cl_4(AsEt_3)_4$[33] can be reversibly oxidized. Schrock et al. have reported both one-electron oxidations and reductions for $Mo_2Cl_4(PBu_3)_4$ and $W_2Cl_4(PBu_3)_4$.[34] We have found that **1**–**7** undergo one-electron oxidations and reductions though in some cases the oxidized or reduced species is not stable, see Table V.

Assuming a transfer of electron density from tungsten to molybdenum as discussed earlier, then in the oxidation of **5** the electron would be lost from a molecular orbital that has more atomic molybdenum contribution than tungsten. The substitution of two $PMePh_2$ ligands on **5** by two equivalents of PMe_3 would then result in a greater change in the $E_{1/2}(\mathrm{ox})$ value compared to the $E_{1/2}(\mathrm{red})$ value, as only the phosphines on the molybdenum end of **5** are substituted to give **6**. Also for complexes **6** and **7**, the difference between $E_{1/2}(\mathrm{red})$ values should be greater than that between $E_{1/2}(\mathrm{ox})$ values because it is the phosphines on the tungsten end of **6** that are substituted. These effects are indeed observed (Table V). Suitable monooxidizing and monoreducing agents, which would lead to the isolation of $\mathrm{Mo}\overset{4}{-}\mathrm{W}^+$ and $\mathrm{Mo}\overset{4}{-}\mathrm{W}^-$ species, have not yet been discovered. It becomes easier to oxidize and more difficult to reduce the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ compounds as the $PMePh_2$ ligands in **1** (blue isomer) are replaced with more electron-rich phosphines as in complexes **2** and **3**.

Complex **1** when initially formed has a green color. Subsequent recrystallizations on this complex result in a color change to a blue isomeric form. There was no observable difference in the ^{31}P NMR of these two isomeric forms, and even their visible absorption spectra were almost identical. However, there is a difference in the cyclic voltammograms of these isomers. The green isomer or the kinetic product of the synthesis is both more easy to oxidize and reduce than the blue isomer, the thermodynamic product (Table V). Wilkinson et al. were the first to observe the green to blue color change of **1**.[17] They speculated that this might be due to a D_{2h} arrangement of phosphine and chloride ligands over the quadruple bond (green isomer) as opposed to the more stable D_{2d} arrangement (blue isomer).

The Raman active $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ stretch of **1** at 349 cm^{-1} was readily observable.[17] However no mode for $\nu(\mathrm{Mo}\overset{4}{-}\mathrm{W})$ for **5** could be located in the region 400–200 cm^{-1} by Raman or IR spectroscopy. There was no vibrational progression in the absorption due to the $\delta^2 \rightarrow \delta\delta^*$ transition of **6** at 45 K. $\nu(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})$ modes have been observed on the $\delta^2 \rightarrow \delta\delta^*$ absorption and emissions of $Mo_2X_4(PMe_3)_4$ compounds, X = Cl, Br or I.[35] The photoelectron spectrum of $MoWCl_4(PMe_3)_4$ which has recently been reported showed a δ ionization at 6.11 eV.[20] No vibrational progressions were resolved here either.

X-ray Diffraction Studies of 5–7.[7-9] Complex **6** was found to be ordered with respect to the arrangement of the metal atoms and to have crystallographic 2-fold symmetry. This permits the accurate determination of the $\mathrm{Mo}\overset{4}{-}\mathrm{W}$ and the metal to ligand distances: $d(\mathrm{Mo}\overset{4}{-}\mathrm{W})$ = 2.207 (1), d(Mo—P) = 2.532 (2), d(W—P) = 2.539 (2), d(Mo—Cl) = 2.424 (2), d(W—Cl) = 2.378 (2) Å.

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Cotton et al. have previously noted a significant shortening of *d*(W–L) over the corresponding d(Mo–L) distances in related complexes (≤0.038 Å).[19] In **6** this effect is even more pronounced for the M–Cl distances (0.046 (4) Å) and must also be occurring for the W–P and Mo–P distances, which have virtually the same lengths despite a significant difference in the Tolman cone angles for the two phosphine ligands. The W–Cl distances are also significantly shorter than the corresponding distances in the homonuclear complex $W_2Cl_4(PMe_3)_4$ (Table III) and the $W_2Cl_8^{4-}$ anion (2.412–2.450 (4) Å).[36] The only shorter W–Cl bonds in this type of complex are observed for some of the bonds in the bridged dppe compound $W_2Cl_4(dppe)_2$, which, significantly, has a 31° twist of the ligands about the W$\overset{4}{-}$W bond.[37] With the short W–Cl distances in **6** it is notable that the ClWCl angle is significantly enlarged (141.5 (1)°) over the ClMoCl angle in **6** (133.6 (1)°) and the other ClWCl angles in the compounds mentioned above.

Complexes **5** and **7** have a disordered arrangement for the metal atoms, which, to our knowledge, is found for all other heteronuclear quadruply bonded species where crystal structures have been determined. In **5** each of the metal sites is within the measured esd's essentially $^1/_2$(Mo + W) with only a slight preference in the orientations of the Mo$\overset{4}{-}$W vector in the two molecules (Table II). Complex **7** also has crystallographic 2-fold symmetry, and the population parameters of the two disordered sites (both with average compositions of ca. 44% W and 56% Mo) would indicate that there may be up to 6% of the Mo$\overset{4}{-}$Mo species present in addition to the statistical arrangement of the Mo$\overset{4}{-}$W compounds, (Table II).

Disorder in **5** and **7** has lead to some averaging of bond lengths and bond angles. For **7** it is notable that the average M–P and M–Cl distances and PMP and ClMCl angles are close to values obtained by averaging corresponding distances and angles in the homonuclear species $M_2Cl_4(PMe_3)_4$ (M = Mo, W). However the metal–phosphorus distances found for the bulky phosphine ligands on **5** (average 2.582 Å) are substantially longer than similar distances for other quadruple-bonded complexes (Table III) and are some of the longest known for Mo(II) complexes. These ligands are indeed easily substituted, as shown in Scheme I. Notably the average M–Cl distance in **5** (2.384 Å) shows some shortening over the average values in **6** (2.401 Å) and **7** (2.400 Å) and values from averaging the distances in the $M_2Cl_4(PMe_3)_4$ compounds (2.403 Å).

Complexes **5**–**7** all have similar geometries with the ligand arrangement over the metal–metal bond defining an eclipsed geometry with chlorine and phosphine ligands next to each other across the Mo$\overset{4}{-}$W bond. Changing a phosphine substituent on the Mo$\overset{4}{-}$W core had little effect on the length of this bond (Table III). Furthermore there was no significant difference between these species in the torsional angles that relate the two pseudo-square-planar ML_2Cl_2 fragments. Therefore the change in visible transition to higher energies from complex **5** to **7** (Table V) has to be attributed to inductive effects of the phosphine substituents, and not to a twist around the Mo$\overset{4}{-}$W bond, which has been observed for some Mo$\overset{4}{-}$Mo complexes.[38]

A feature in common with $M_2X_4L_4$ complexes is that the chlorine and phosphine ligands are staggered across the Mo$\overset{4}{-}$W bond. Another similarity with homonuclear $M_2X_4L_4$ complexes[19] is the magnitude of the ClMCl and PMP angles. These are 133–141° and 153–158°, respectively. This could result in blocking of the sites trans to the Mo$\overset{4}{-}$W bond and could explain why no significant shift in visible absorption is found for complex **5** as one changes the polarity of the solvent (Table V). Such effects were noted primarily for bridged quadruple-bond complexes[31] where the equivalent angles are much closer to 180°.

An interesting structural feature of bridged MoW complexes is that the Mo$\overset{4}{-}$W bond is shorter than expected, an indication of special stability. The covalent bond radii for bridged quadruple bonds with small or no axial interactions range from 1.03 to 1.05 Å for Mo[4,39] and 1.08 to 1.09 Å for W,[4] and so the Mo–W distances in $MoW(O_2CCMe_3)_4$,[3] 2.080 (1) Å, and $MoW(mhp)_4$,[4] 2.091 (1) Å, fall short of the sum of these radii (2.11–2.14 Å). However the data for the unbridged complexes reveal a different answer. Approximate covalent bond radii for unbridged quadruple bonds can be derived from the structures of the homonuclear complexes $M_2Cl_4(PMe_3)_4$ (M = Mo, W):[19] $r\overset{4}{-}$(Mo) = 1.065 Å; $r\overset{4}{-}$(W) = 1.131 Å. Therefore the observed Mo–W distances in **5**–**7** (~2.207 (1) Å (Table III)) are slightly longer than the sum of these radii (2.196 (1) Å), and thus there is no evidence for an extra shortening of the bond with respect to bond distances of the homonuclear complexes. It is interesting that even in an oxidized form of a bridged heteronuclear quadruple bond, $MoW(O_2CCMe_3)_4(I)(CH_3CN)$,[2] the Mo$\overset{3.5}{-}$W distance is 2.194 (2) Å. The bridging ligands must be responsible for the unexpectedly large shortening of the metal–metal bond in $MoW(O_2CCMe_3)_4$ and $MoW(mhp)_4$.

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Supplementary Material Available: Figure 2 (a stereoview of the crystal packing of **6**) and Table II-S (positional and thermal parameters for phenyl ring carbon atoms of complex **5**), Table A (anisotropic thermal parameters for **5**–**7**), and Table B (bond lengths and bond angles in the phosphine ligands for **5**–**7**) (9 pages); Table C (final structure amplitudes for **5**–**7**) (45 pages). Ordering information is given on any current masthead page.

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