but in the formation of **16**, the carbene carbon moves toward the *o*-methyl group. Products **13** and **19** show that the first few steps of the mechanism in Scheme I are reversible and that carbene **14** can close to **13** or undergo a hydrogen transfer to give the *o*-quinodimethane **20** and that some of **13** or **20** can rearrange to **19**.

Thus the results of our labeling experiments are consistent with the conclusion that the major pathway for the rearrangement of **1** to **2** involves a series of arylcarbene–cycloheptatetraene interconversions.

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Use of η^6-Arylphosphine Complexes of Molybdenum(0) for the Synthesis of Complexes Containing $\text{Mo}\overset{4}{-}\text{Mo}$ and $\text{Mo}\overset{4}{-}\text{W}$ Bonds

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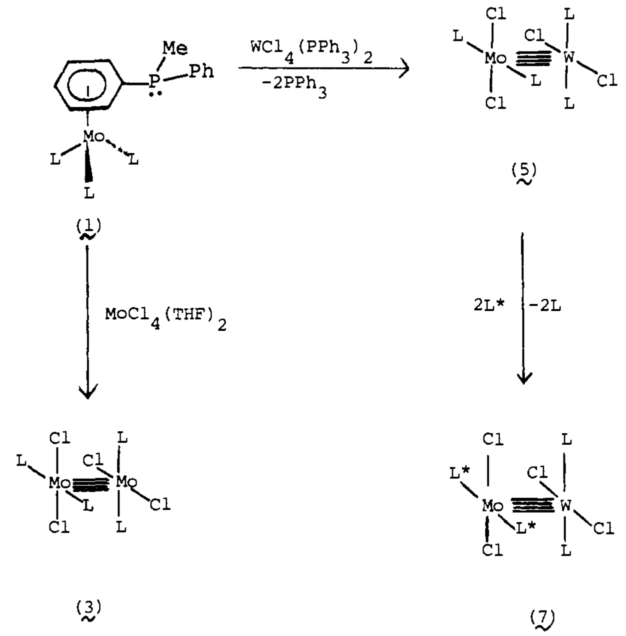
The three heterobimetallic complexes known to have quadruple metal–metal bonds are $\mathrm{CrMo(O_2CMe)_4}$,[1] $\mathrm{MoW(O_2CCMe_3)_4}$,[2] and $\mathrm{MoW(mhp)_4}$.[3] In each case the quadruple bonds are bridged by bidentate ligands: acetate, pivolate, or 2-hydroxy-6-methylpyridine anion, respectively. Complexes containing the homonuclear quadruple bonds $\text{Mo}\overset{4}{-}\text{Mo}$ or $\text{W}\overset{4}{-}\text{W}$ with and without bridging ligands have been well studied,[4] including complexes $\mathrm{Mo_2Cl_4(PR_3)_4}$[5-9] and $\mathrm{W_2Cl_4(PR_3)_4}$[5,10,11] where $\mathrm{PR_3}$ is a tertiary phosphine ligand. We report here the very efficient synthesis of $\mathrm{MoWCl_4(PMePh_2)_4}$, which contains the first heterobimetallic quadruple bond that is not supported by bridging ligands. The properties of this bond can be compared for the first time with $\text{Mo}\overset{4}{-}\text{Mo}$ and $\text{W}\overset{4}{-}\text{W}$ bonds that are free of bridging ligands. Our synthesis of $\mathrm{MoWCl_4(PMePh_2)_4}$ involves two novel features: first, the reaction of a mononuclear complex of Mo(0) with chloride compounds of Mo(IV) or W(IV) to give $\text{Mo}\overset{4}{-}\text{M}$ dimers (eq 1);

$$\text{Mo(0)} + \text{M(IV)} \rightarrow \text{Mo}\overset{4}{-}\text{M} \qquad \text{M = Mo, W} \qquad (1)$$

Scheme I



$\mathrm{L = PMePh_2}$, $\mathrm{L^* = PMe_3}$

Table I. ^{31}P NMR Data for **5** (in $\mathrm{C_6H_6}$ vs. 85% $\mathrm{H_3PO_4}$) and $\mathrm{W_2Cl_4P_4}$ (**6**),[10] $\mathrm{P = PMePh_2}$

isotopomer	$\delta(^{31}\text{P})$, ppm	$J_{\text{PP}}{}^3$, Hz	$J_{\text{PW}}{}^2$, Hz	$J_{\text{PW}}{}^1$, Hz
$\text{W}\overset{4}{-}\text{Mo—P}$	−13.1 t	23.5		
$^{183}\text{W}\overset{4}{-}\text{Mo—P}$	−13.1 dt	23.5	43	
$\text{P–W}\overset{4}{-}\text{Mo}$	21.9 t	23.5		
$\text{P–}^{183}\text{W}\overset{4}{-}\text{Mo}$	21.9 dt	23.5		266
$^{183}\text{W}\overset{4}{-}\text{W}$ (**6**)	2.0 m	28	51	234

second, the use of a Mo(0) complex containing an η^6-PhPMePh ligand to give a $\text{Mo}\overset{4}{-}\text{M}$ compound in a regiospecific reaction.

During our study of the use of derivatives of $\mathrm{Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3}$ (**1**) as phosphine-like ligands,[12] we discovered that complex **1** reacted with $\mathrm{MoCl_4(THF)_2}$[13] (**2**) after stirring for 10 h in degassed tetrahydrofuran (THF) at 22 °C to give the known complex $\mathrm{Mo_2Cl_4(PMePh_2)_4}$[7,14] (**3**) in its green form[14] (Scheme I). Precipitation with hexanes and recrystallization from benzene/hexanes gave **3** as its blue isomer[14] in 75% yield. The dinitrogen complex *trans*-$\mathrm{Mo(N_2)_2(PMePh_2)_4}$ also reacted with **2** to give **3**. Complex **3** was identified by C, H analysis and ^{31}P NMR.[14] The blue isomer in benzene had a visible absorption ($\delta \rightarrow \delta^*$) at 596 nm and a Raman active mode, $\nu(\text{Mo}\overset{4}{-}\text{Mo})$, at 349 cm^{-1} in agreement with literature values.[14]

The new complex $\mathrm{MoWCl_4(PMePh_2)_4}$ (**5**)[15] is prepared according to Scheme I by adding a benzene solution of **1** dropwise to a 3-fold excess of $\mathrm{WCl_4(PPh_3)_2}$ (**4**)[16] suspended in dry benzene under $\mathrm{N_2}$. The reaction is instantaneous at 22 °C; excess **4** is filtered off after 5 min and green complex **5**, contaminated with approximately 5% **3**, is crystallized with hexanes. Complex **3** is the only detectable side product; however, if traces of water are present then side reactions give $\mathrm{WOCl_2(PMePh_2)_3}$[17] as well as complex **3**. Complex **3** cannot be separated from **5** by chromatography, but **3** can be fairly selectively converted by reaction with

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PMe_3 at 20 °C to soluble derivatives which then remain in solution when pure **5** (60% yield) is precipitated with hexanes.

Significantly if $Mo(N_2)_2(PMePh_2)_4$ is used in place of **1** in the reaction then a mixture of **3** (35% based on the starting Mo complex **1**), **5**(20%), and $WOCl_2(PMePh_2)_3$ (30%) is formed. Thus the regiospecificity of the reaction could be attributed to the ability of **1** to coordinate via the η^6-ligand to the tungsten and hence favor heterobimetallic bonding.[12] The complex $W_2Cl_4(PMePh_2)_4$ (**6**)[10] is not produced in any of these reactions. Preliminary work shows that $MoWCl_4(PMe_2Ph)_4$[18] is produced when $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$[19] is used in place of **1** in Scheme I.

Complex **5** is most readily identified by the coupling constants of the inequivalent phosphorus atoms on the $^{183}W\overset{4}{-}Mo$ isotopomer in the ^{31}P NMR spectrum. The J values are similar to those observed for the $^{183}W\overset{4}{-}W$ isotopomer of complex **6** (Table I). The ^1H NMR spectrum of **5** in C_6D_6 shows two methyl resonances as virtual triplets at 1.90 and 2.07 ppm and two sets of ortho phenyl proton multiplets at 7.56 and 7.73 ppm consistent with two types of phosphines, whereas **3** gives only one methyl peak at 1.98 ppm and one ortho proton multiplet at 7.65 ppm. The λ_{max}(visible) of **5** in benzene at 650 nm falls in the range of $\delta \rightarrow \delta^*$ transitions of homonuclear complexes,[5,8,14,20] including $Mo_2Cl_4(PMe_3)_4$ at 582 nm[5] and $W_2Cl_4(PMe_3)_4$ at 657 nm.[5] It is interesting that the $Mo\overset{4}{—}W$ complex with bridging carboxylates[2] has a yellow color; perhaps a $\delta \rightarrow \pi^*$ (ligand) transition, recently observed in the 500–600 nm region for $W_2(O_2CR)_4$ complexes,[21] complicates the visible spectrum when these bridging ligands are present. No frequency (IR or Raman) assignable to $\nu(Mo\overset{4}{-}W)$ is observed in the range 250–400 cm.$^{-1}$ Solutions of **5** are sensitive to water and oxygen. Complex **5** decomposes when refluxed in degassed toluene; it does not disproportionate to **3** and **6**.

The substitution reactions of **5** are proving to be fascinating. For example, **5** reacts with excess PMe_3 at 20 °C for 3 h to give $(Me_3P)_2Cl_2Mo\overset{4}{-}WCl_2(PMePh_2)_2$ (**7**)[22] where only the phosphines on the molybdenum have been substituted. Further reaction (45 °C, 19 h) gives $MoWCl_4(PMe_3)_4$.[23] The course of reaction differs from that reported for $Mo_2Me_4(PEt_3)_4$.[24]

The structure of **5** (Scheme I) is proposed on the basis of the D_{2d} geometry of the homonuclear complexes.[5] Work is under way to obtain crystals of **5** or its derivatives suitable for X-ray diffraction in order to verify the structure and obtain further data on this unique heteronuclear bond.

Note Added in Proof. Preliminary X-ray crystallographic analysis of complex **7** confirms the geometry shown in Scheme I. The structure has refined to R = 3.8% in the space group $I_2/_a$. The molybdenum–tungsten distance is 2.209 (1) Å. (Personal communication from Jeffrey F. Sawyer.)

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Supplementary Material Available: Preparation of **3** and **5** and ^1H and ^{31}P NMR spectra of **5** (4 pages). Ordering information is given on any current masthead page.

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(17) Identified by ^{31}P NMR (C_6H_6) δ −16.7 (1 P, J_{PW} = 416, J_{PP} < 5 Hz), 0.0 (2 P, J_{PW} = 339, J_{PP} < 5 Hz).[16]

(18) ^{31}P NMR (C_6H_6) δ −20.1 (2 PMo, $J_{PP}{}^3$ = 24.0, $J_{PW}{}^2$ = 50 ± 5 Hz), 17.4 (2PW, $J_{PP}{}^3$ = 24.0, $J_{PW}{}^1$ = 280 Hz).

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(22) ^{31}P NMR (C_6H_6) δ −28.9 (2 PMe_3Mo, $J_{PP}{}^3$ = 24.4 Hz), +21.7 (2 $PMePh_2W$, $J_{PP}{}^3$ = 24.4, $J_{PW}{}^1$ = 273 Hz).

(23) ^{31}P NMR (C_6H_6) δ −28.9 (2 PMe_3Mo, $J_{PP}{}^3$ = 25.6 Hz), +9.5 (2 PMe_3W, $J_{PP}{}^3$ = 25.6 Hz, $PMe_3{}^{183}W$, $J_{PW}{}^1$ = 271, $J_{PP}{}^3$ = 24.4 Hz).

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Synthesis of Anatoxin-*a*: Very Fast Death Factor

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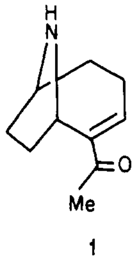
A class of microalgae, the cyanophytes, contains several toxic strains, including *Anabaena flos-aquae*.[1] Graphic descriptions of the death of animals induced by such blue-green algae have been recorded.[2,3] An alkaloidal toxin identified from these sources was shown[4] to be 2-acetyl-9-azabicyclo[4.2.1]non-2-ene (anatoxin-*a*, **1**), also designated "Very Fast Death Factor" (VFDF).[3]



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This structural assignment was confirmed by X-ray crystallography.[5] Anatoxin-*a* has been shown to be a potent muscarinic[1] and nicotinic agonist[6] and has engendered synthetic interest.[7–9]

We report herein an efficient, nitrone-based entry to this interesting natural product. It was anticipated[10,11] that the addition of 1-pyrroline 1-oxide (**2**) to *trans*-3,5-hexadien-2-ol (**3**)[12–14] would exhibit the desired site selectivity and regioselectivity (cf., Scheme I) to afford the isoxazolidine **4a**.[15] The latter, formed in 70% yield, upon oxidation with manganese dioxide (Celite, methylene chloride), produces the ketone **6a**, which exhibits a clean quartet at δ 4.71 (J = 6.71 Hz), assignable to the C-5 proton (isoxazolidine numbering).

Oxidative cleavage[16,17] of the isoxazolidine ring with *m*-chloroperbenzoic acid gives the nitrone **5** as the sole identifiable product in 79% yield. The product is a single regioisomer exhibiting a broad singlet in its ^1H NMR spectrum ($CDCl_3$) 7.0 ppm (1 H) characteristic of the proton at C-2 of the nitrone function. Warming of a solution containing the nitrone to 45 °C leads to the formation of a single cycloadduct, **6a** in 71% overall

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