

Heteronuclear Unbridged Quadruply Bonded Complexes. Preparation and Characterization of $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$, $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$, and $\text{Mo}^4\text{WCl}_4(\text{PMe}_2\text{Ph})_4$

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The reaction of $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ and $\text{WCl}_4(\text{PPh}_3)_2$ in the presence of PPh_3 yields first $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$ (1), which undergoes partial isomerization to $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (2). These complexes are the first examples of heteronuclear quadruply bonded complexes of the form $\text{Mo}^4\text{WCl}_4\text{L}_3\text{L}'$, where L and L' are tertiary phosphines. The syntheses, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, and a single-crystal X-ray structure of a mixed crystal of these complexes are reported. The complexes 1 and 2 form a solid solution in which ligand positions coincide but metal atoms are reversed. The apparent Mo-W distance is 2.2161 (7) Å. The single-crystal structure of the related complex $\text{Mo}^4\text{WCl}_4(\text{PMe}_2\text{Ph})_4$ (3) is also reported. In addition to a systematic 1:1 disorder of these molecules, there is a 14% contamination by $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$. The apparent Mo-W bond length is 2.207 (3) Å. Crystal data: 1/2, $\text{C}_{42}\text{H}_{48}\text{Cl}_4\text{P}_4\text{MoW}\cdot 0.5\text{C}_6\text{H}_{14}$, monoclinic, space group $P2_1/c$, $a = 23.345$ (7) Å, $b = 13.629$ (3) Å, $c = 15.338$ (2) Å, $\beta = 81.52$ (1)°, $V = 4827$ (7) Å³, $Z = 4$, $R = 0.040$ for 4802 observed reflections; 3, $\text{C}_{32}\text{H}_{44}\text{Cl}_4\text{P}_4[(0.57\text{ Mo})(0.43\text{ W})]_2$, monoclinic, space group $C2/c$, $a = 17.867$ (2) Å, $b = 10.079$ (1) Å, $c = 22.354$ (2) Å, $\beta = 107.73$ (0)°, $V = 3834$ (7) Å³, $Z = 4$, $R = 0.039$ for 2809 observed reflections.

Introduction

The synthetic strategies that may be utilized in the formation of heteronuclear quadruply bonded complexes have recently been reviewed.¹ The reaction between a tetrakis(phosphine)molybdenum(0) complex and $\text{WCl}_4(\text{PPh}_3)_2$ (4) has been shown to provide an easy route to certain compounds containing an unbridged molybdenum-tungsten quadruple bond,^{2,3} although low yields of the homonuclear $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$ complexes are also obtained as byproducts in these reactions. The complex $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ (5) was recently found to be one that affords the desired heteronuclear product in better yield as compared to the complex $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMePh})(\text{PMePh}_2)_3$ (6) which undergoes σ -bonded tertiary phosphine substitution more rapidly.³ Further study of this starting material thus seemed worthwhile.

This report presents the results of an investigation of the reaction between 4 and 5. When this reaction is done in benzene in the presence of PPh_3 , it can lead to at least five products: $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$ (1), $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (2), $\text{Mo}^4\text{WCl}_4(\text{PMe}_2\text{Ph})_4$ (3), $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ (7), and $\text{WOCl}_2(\text{PMe}_2\text{Ph})_3$ (8), all of which are detected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture. Upon dissolution of these products in tetrahydrofuran, the new complexes $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{THF})$ (9) and $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{THF})\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (10) are obtained. The structures of compounds 1-3 have been determined by X-ray crystallography.

Experimental Section

General Data. Oxygen and water were excluded during all operations by using vacuum lines supplied with purified nitrogen. Solvents apart from dichloromethane were dried over and distilled from potassium/sodium benzophenone ketyl under a nitrogen atmosphere. Dichloromethane was dried over phosphorus pentoxide. ^{31}P NMR spectra were recorded on Varian XL-200 and XL-400 (81 and 162 MHz for ^{31}P NMR) spectrometers. The ^{31}P chemical shifts were referenced externally and are reported relative to 85% H_3PO_4 . The microanalysis was performed under an inert atmosphere by Galbraith Laboratories, Inc., Knoxville, TN. The phosphine ligands were used as received from Strem Chemicals. The preparations of $\text{MoWCl}_4(\text{PMe}_2\text{Ph})_4$ (3),³ $\text{WCl}_4(\text{PPh}_3)_2$

(4),⁴ and $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ (5)⁵ have been reported elsewhere.

Preparation of $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$ (1) and $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (2). A solution of $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMe}_2)(\text{PMe}_2\text{Ph})_3$ (5) (200 mg, 0.4 mmol) in 20 mL of C_6H_6 was added to a slurry of complex $\text{WCl}_4(\text{PPh}_3)_2$ (4) (262 mg, 0.4 mmol) and PPh_3 (400 mg, 1.5 mmol) in 20 mL of C_6H_6 . This was stirred for 1.5 h and then filtered to yield a green solution containing the compounds $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$ (1), 25%, $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (2), 15%, $\text{Mo}^4\text{WCl}_4(\text{PMe}_2\text{Ph})_4$ (3), 40%, and $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ (7), 15% (relative yields based on the approximate integration of the ^{31}P NMR spectrum of the solution mixture). This solution was concentrated to 15 mL and layered with 15 mL of isomeric hexanes. After 1 week complexes 1 and 2 had coprecipitated to form green crystals suitable for single-crystal X-ray study. The analysis was carried out on these crystals. Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{Cl}_4\text{P}_4\text{MoW}\cdot 0.5\text{C}_6\text{H}_{14}$: C, 47.35; H, 4.86. Found: C, 47.21; H, 4.80. ^{31}P NMR for $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)$ (1) in C_6H_6 : δ 36.1 (dt, 0.86% P, W-PPh₃ (for W, I = 0), $^2J_{\text{PP}} = 147$ Hz, $^3J_{\text{PP}} = 22$ Hz), 21.3 (dt, 0.86% P, W-PMe₂Ph (for W, I = 0), $^2J_{\text{PP}} = 147$ Hz, $^3J_{\text{PP}} = 25$ Hz), -20.5 (dd, 2 × 0.86% P, Mo-PMe₂Ph (I = 0), $^3J_{\text{PP}} = 22$ Hz, $^3J_{\text{PP}} = 25$ Hz). ^{31}P NMR for $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{PPh}_3)\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (2) in C_6H_6 : δ 18.3 (dd, 2 × 0.86% P, W-PMe₂Ph (for W, I = 0), $^3J_{\text{PP}} = 21$ Hz, $^3J_{\text{PP}} = 25$ Hz), 4.1 (dt, 0.86% P, Mo-PPh₃, $^2J_{\text{PP}} = 141$ Hz, $^3J_{\text{PP}} = 21$ Hz), -15.3 (dt, 0.86% P, Mo-PMe₂Ph, $^2J_{\text{PP}} = 141$ Hz, $^3J_{\text{PP}} = 25$ Hz). The 0.14% P resonances for the isotomers (with ^{183}W abundance 14%) were not clearly defined; see Figure 1.

Reactions of 1 and 2 in THF. Both complexes 1 and 2 undergo displacement of PPh_3 when dissolved in THF to form the new unstable complexes $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{THF})$ (9) and $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{THF})\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (10), respectively. These complexes were identified on the basis of their ^{31}P NMR spectra (supplementary material).

^{31}P NMR for $\text{Cl}_2(\text{PMe}_2\text{Ph})_2\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})(\text{THF})$ (9) in THF: δ 37.4 (t, 0.86% P, W-PMe₂Ph, $^3J_{\text{PP}} = 30$ Hz), -26.9 (d, 2 × 0.86% P, Mo-PMe₂Ph, $^3J_{\text{PP}} = 30$ Hz). ^{31}P NMR for $\text{Cl}_2(\text{PMe}_2\text{Ph})(\text{THF})\text{Mo}^4\text{WCl}_2(\text{PMe}_2\text{Ph})_2$ (10) in THF: δ 15.4 (d, 0.86% P, W-PMe₂Ph, $^3J_{\text{PP}} = 30$ Hz), -6.6 (t, 2 × 0.86% P, Mo-PMe₂Ph, $^3J_{\text{PP}} = 31$ Hz).

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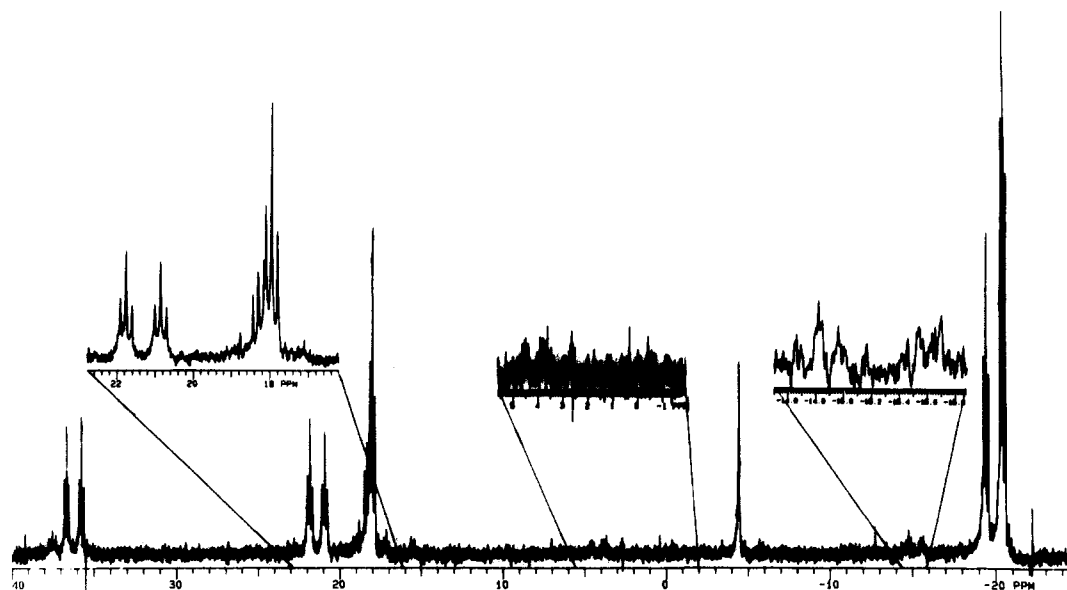


Figure 1. $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum of complexes 1–3 and 7 at 162 MHz in C_6H_6 . The analysis is presented in the Experimental Section and under Results.

Table I. Crystallographic Data for 1/2 and 3

| | 1/2 | 3 ^a |
|---|---|---|
| chem formula | $\text{C}_{45}\text{H}_{55}\text{Cl}_4\text{P}_4\text{MoW}$ | $\text{C}_{32}\text{H}_{44}\text{Cl}_4\text{P}_4\text{W}$ [(0.57 Mo)(0.43 W)] ₂ |
| fw | 1141.44 | 961.3 |
| space group | $P2_1/c$ (No. 14) | $C2/c$ (No. 15) |
| <i>a</i> , Å | 23.345 (7) | 17.867 (2) |
| <i>b</i> , Å | 13.269 (3) | 10.079 (1) |
| <i>c</i> , Å | 15.338 (2) | 22.354 (2) |
| β , deg | 81.52 (1) | 107.73 (0) |
| <i>V</i> , Å ³ | 4827 (7) | 3834 (7) |
| <i>Z</i> | 4 | 4 |
| ρ_{calc} , g/cm ³ | 1.571 | 1.688 |
| μ (Mo $K\alpha$), cm ⁻¹ | 30.706 | 38.502 |
| radiation monochromated in incident beam (λ , Å) | Mo $K\alpha$ (0.71073) | |
| temp, °C | 20 | 20 |
| max, min transm factors, | 99.99, 51.54 | 99.95, 80.68 |
| R^b | 0.040 | 0.039 |
| R_w | 0.053 ^c | 0.060 ^d |

^a This consists of 86% $\text{MoWCl}_4(\text{PMe}_2\text{Ph})_4$ and 14% $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$.
^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|]^2$; $w = 1 / (\sigma^2 + 0.0005|F_o|)$. ^d $w = 1 / (\sigma^2 + 0.001|F_o|)$.

X-ray Structure Determinations. A crystal that turned out to contain a mixture of 1 and 2 was chosen from the reaction described above, covered with epoxy glue, and mounted on the tip of a glass fiber. We shall refer to this crystalline substance as 1/2, and this includes the 0.5 C_6H_{14} molecule of solvation. Suitable crystals of complex 3 were obtained by slow diffusion of isomeric hexanes into a benzene solution of 3 in a Schlenk tube under argon for a period of 2 weeks. A suitable crystal was then transferred into a 0.5-mm Lindemann capillary by using mineral oil.

An abbreviated amount of crystallographic information is given in Table I. The full table is available as supplementary material. The quality of the crystals was first verified by means of rotation photographs, and then reflections suitable for indexing were found by 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). In the case of 3 more accurate unit cell parameters were determined at the end of the data collection by using the program DETH, which resulted in more accurate measurements for θ . Intensity data on each compound were then collected by utilizing the options specified in Table I and the general procedures for data collection as previously described.⁶ All data sets were corrected for Lorentz and polarization effects, and absorption corrections were also applied. The latter were made by using an empirical method based on ψ scans ($\psi = 0\text{--}360^\circ$ every 10°) for χ values near 90° .⁷ The numbers

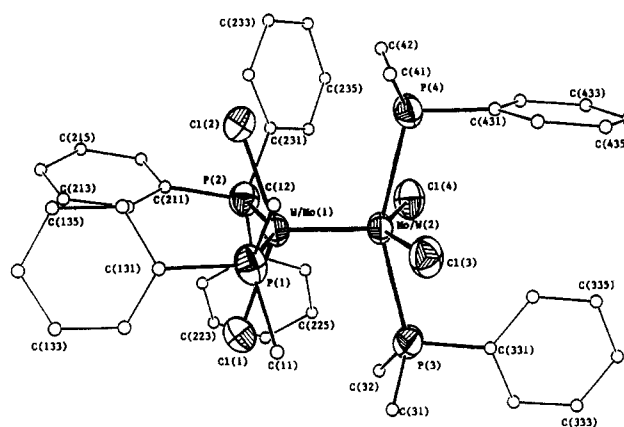


Figure 2. ORTEP view of compounds 1/2 (without the 0.5 C_6H_{14} molecule of solvation), showing the atomic numbering scheme used. The thermal ellipsoids are drawn at the 50% probability level. The carbon atoms are drawn with small open circles for clarity.

of ψ scans used were seven for 1/2 and nine for 3 with maximum, minimum, and average relative transmission factors for 1/2 of 0.9999, 0.5154, and 0.7576 and for 3 of 0.9995, 0.8068, and 0.9032.

The heavy-atom positions of both crystals were obtained from three-dimensional Patterson functions. In the case of 1/2 the two metal atom sites were initially identified and refined as tungsten and molybdenum atoms appropriate to complex 1 but later a fraction of them were reversed as necessary to allow for the presence of 2 at some sites. For 3, a hybrid atom composed of 50% Mo and 50% W was placed at the metal atom position. Subsequently, several full-matrix refinements followed by difference Fourier syntheses revealed the positions of all other non-hydrogen atoms, and the models were then refined anisotropically to convergence. Final refinement was done by employing the SHELX-76 package of programs with variation of occupancy factors used to determine the composition of the metal atom sites. In the case of 1/2 the difference Fourier map showed four peaks ascribable to a disordered hexane molecule near to an inversion center. This molecule was constrained ($d(\text{C}-\text{C}) = 1.51$ Å), and the two disordered carbon atoms were refined with fixed occupancies of 0.5. The isotropic thermal parameters of these carbon atoms were constrained to the same value, and refinement was continued to convergence. The final factors after convergence are listed in Table I. Tables II and III contain positional and thermal parameters for the complexes. Selected bond lengths and angles are listed in Table IV. ORTEP views of the molecules in 1/2 (without the molecule of solvation) and 3 are given in Figures 2 and 3, respectively. Views of the crystal packing in 1/2 (including the disordered hexane molecule) and 3 are presented as supplementary material, and tables of anisotropic

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Table II. Final Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for Complex 1/2^a

| atom | x | y | z | B, ^b Å ² |
|----------------------|-------------|-------------|-------------|--------------------------------|
| W/Mo(1) ^c | 0.22188 (2) | 0.07106 (3) | 0.45427 (3) | 3.05 (1) |
| Mo/W(2) ^d | 0.30423 (2) | 0.09276 (4) | 0.50745 (4) | 2.99 (1) |
| Cl(1) | 0.1593 (1) | -0.0360 (2) | 0.5492 (2) | 4.92 (6) |
| Cl(2) | 0.2250 (1) | 0.1688 (2) | 0.3246 (2) | 4.23 (6) |
| Cl(3) | 0.2954 (1) | 0.2319 (2) | 0.6041 (2) | 4.41 (6) |
| Cl(4) | 0.3731 (1) | -0.0289 (2) | 0.4469 (2) | 4.48 (6) |
| P(1) | 0.1600 (1) | 0.2078 (2) | 0.5283 (2) | 4.15 (6) |
| P(2) | 0.2385 (1) | -0.0773 (2) | 0.3492 (2) | 3.90 (6) |
| P(3) | 0.2915 (1) | -0.0076 (2) | 0.6487 (2) | 4.07 (6) |
| P(4) | 0.3608 (1) | 0.2064 (2) | 0.3968 (2) | 3.56 (6) |
| C(11) | 0.1410 (5) | 0.2084 (9) | 0.6489 (6) | 5.7 (3) |
| C(12) | 0.1810 (5) | 0.3359 (7) | 0.5018 (8) | 5.6 (3) |
| C(31) | 0.2359 (5) | 0.0346 (9) | 0.7378 (7) | 5.8 (3) |
| C(32) | 0.2787 (6) | -0.1422 (7) | 0.6443 (8) | 6.4 (4) |
| C(41) | 0.3327 (4) | 0.3322 (7) | 0.3832 (7) | 4.9 (3) |
| C(42) | 0.3823 (4) | 0.1663 (8) | 0.2824 (6) | 5.1 (3) |
| C(131) | 0.0898 (4) | 0.1948 (7) | 0.4888 (7) | 4.7 (3) |
| C(132) | 0.0447 (5) | 0.143 (1) | 0.5335 (9) | 7.5 (4) |
| C(133) | -0.0074 (6) | 0.131 (1) | 0.501 (1) | 9.5 (5) |
| C(134) | -0.0150 (6) | 0.169 (1) | 0.421 (1) | 7.4 (4) |
| C(135) | 0.0318 (5) | 0.219 (1) | 0.3716 (9) | 7.6 (4) |
| C(136) | 0.0835 (5) | 0.2339 (9) | 0.4056 (8) | 6.2 (3) |
| C(211) | 0.1768 (5) | -0.0849 (8) | 0.2892 (7) | 4.8 (3) |
| C(212) | 0.1271 (5) | -0.0316 (9) | 0.3187 (8) | 6.6 (3) |
| C(213) | 0.0774 (6) | -0.039 (1) | 0.273 (1) | 8.8 (5) |
| C(214) | 0.0794 (7) | -0.096 (1) | 0.198 (1) | 9.9 (6) |
| C(215) | 0.1323 (8) | -0.152 (1) | 0.166 (1) | 10.6 (6) |
| C(216) | 0.1798 (6) | -0.146 (1) | 0.2142 (9) | 8.0 (4) |
| C(221) | 0.2388 (5) | -0.2003 (7) | 0.3980 (6) | 5.0 (3) |
| C(222) | 0.1890 (6) | -0.266 (1) | 0.3954 (9) | 7.9 (4) |
| C(223) | 0.1931 (8) | -0.360 (1) | 0.435 (1) | 8.8 (5) |
| C(224) | 0.2380 (8) | -0.389 (1) | 0.480 (1) | 8.3 (5) |
| C(225) | 0.2838 (7) | -0.325 (1) | 0.4826 (9) | 8.4 (5) |
| C(226) | 0.2835 (6) | -0.2290 (8) | 0.4401 (8) | 6.5 (3) |
| C(231) | 0.2996 (4) | -0.0767 (7) | 0.2571 (6) | 4.2 (2) |
| C(232) | 0.2951 (5) | -0.0091 (8) | 0.1906 (7) | 5.3 (3) |
| C(233) | 0.3416 (6) | -0.004 (1) | 0.1194 (8) | 7.0 (4) |
| C(234) | 0.3899 (6) | -0.067 (1) | 0.1178 (9) | 7.3 (4) |
| C(235) | 0.3906 (6) | -0.137 (1) | 0.1857 (9) | 6.8 (4) |
| C(236) | 0.3470 (5) | -0.1407 (8) | 0.2553 (8) | 5.4 (3) |
| C(331) | 0.3575 (4) | -0.0050 (7) | 0.6983 (6) | 4.1 (2) |
| C(332) | 0.4047 (5) | 0.0592 (7) | 0.6647 (6) | 4.7 (3) |
| C(333) | 0.4550 (5) | 0.0618 (8) | 0.7023 (7) | 5.4 (3) |
| C(334) | 0.4602 (5) | 0.0012 (9) | 0.7741 (8) | 6.0 (3) |
| C(335) | 0.4141 (6) | -0.0607 (9) | 0.8086 (8) | 6.5 (4) |
| C(336) | 0.3626 (5) | -0.0642 (7) | 0.7712 (7) | 5.6 (3) |
| C(431) | 0.4289 (4) | 0.2243 (7) | 0.4401 (6) | 3.8 (2) |
| C(432) | 0.4742 (4) | 0.1590 (8) | 0.4188 (7) | 5.1 (3) |
| C(433) | 0.5250 (5) | 0.1687 (9) | 0.4594 (8) | 6.1 (3) |
| C(434) | 0.5302 (5) | 0.2404 (9) | 0.5195 (8) | 6.1 (3) |
| C(435) | 0.4853 (5) | 0.3068 (9) | 0.5391 (9) | 7.1 (4) |
| C(436) | 0.4352 (4) | 0.2999 (8) | 0.4997 (7) | 5.7 (3) |
| C(51) ^e | 0.019 (1) | 0.531 (2) | 0.446 (2) | 17.1 (6)* |
| C(52) ^e | 0.064 (1) | 0.595 (2) | 0.304 (2) | 17.1 (6)* |
| C(53) ^e | 0.064 (2) | 0.496 (4) | 0.354 (3) | 17.1 (6)* |
| C(54) ^e | 0.030 (2) | 0.634 (4) | 0.385 (4) | 17.1 (6)* |

^a Starred values indicate atoms refined isotropically. ^b Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^c W/Mo(1) represents 67% W and 33% Mo. ^d Mo/W(2) represents 67% Mo and 33% W. These population parameters were obtained by scaling, either up or down, the molybdenum and tungsten scattering curves at the two metal atom sites. ^e Atoms C(51)–C(54) represent the disordered hexane molecule, and atoms C(52) and C(53) were refined at 50% occupancies.

thermal parameters, complete bond lengths and angles, and the structure factors are also available as supplementary material.

Results

Synthesis. The syntheses of complexes 1 and 2 are accomplished by reacting equimolar amounts of 4 and 5 in the presence of an excess of PPh₃ in dry benzene (Scheme I). The complex

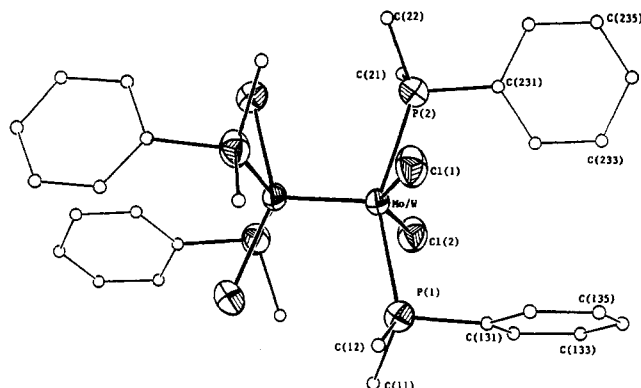
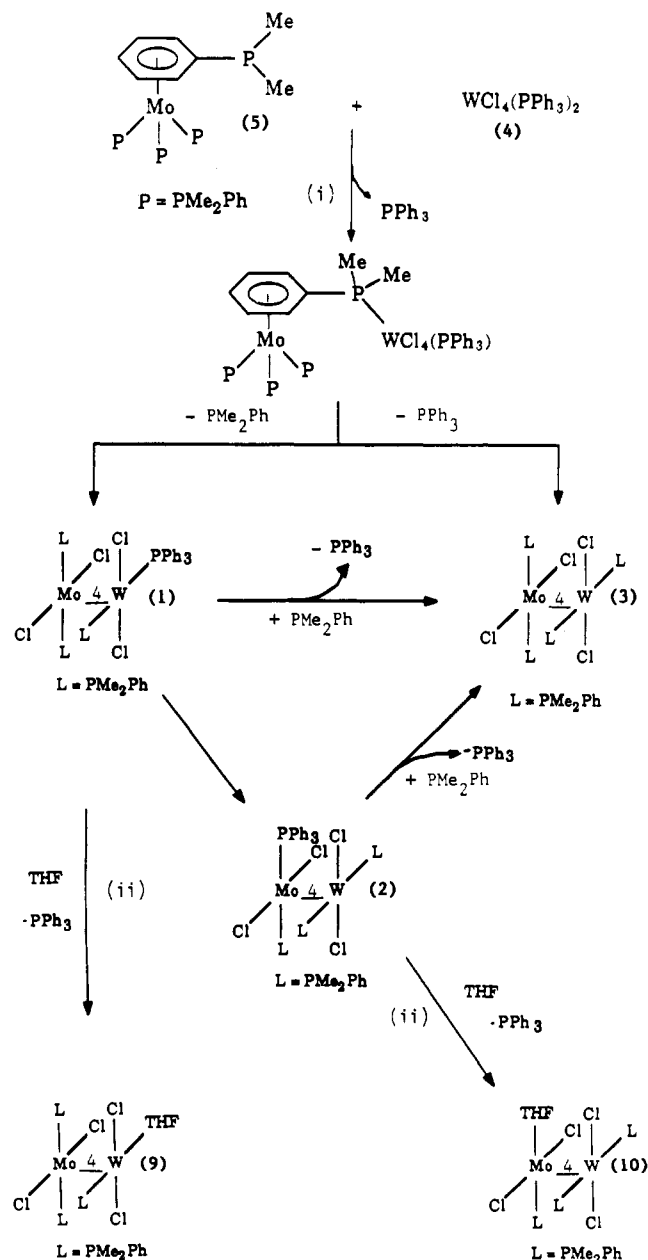


Figure 3. ORTEP view of compound 3, showing the atomic numbering scheme used. The thermal ellipsoids are drawn at the 50% probability level. The carbon atoms are drawn with small open circles for clarity.

Scheme I. Reaction of Mo(η^6 -C₆H₅PMe₂)(PMe₂Ph)₃ (5) and WCl₄(PPh₃)₂ in the Presence of Excess PPh₃^a



^a Reaction conditions: (i) benzene, 3.75 times excess of PPh₃, 1.5 h; (ii) THF, 30 min.

WCl₂(PMe₂Ph)₃ is also formed if the solvent is not thoroughly dried.³ This reaction also produces complexes 3 and 7. The yield

Table III. Final Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for Complex 3

| atom | x | y | z | $B, \text{\AA}^2$ |
|-------------------|--------------|-------------|-------------|-------------------|
| Mo/W ^b | 0.00733 (2) | 0.27405 (4) | 0.20272 (1) | 2.56 (1) |
| Cl(1) | -0.0793 (1) | 0.4395 (2) | 0.14013 (7) | 4.36 (4) |
| Cl(2) | 0.10227 (9) | 0.1042 (2) | 0.20247 (7) | 4.17 (4) |
| P(1) | 0.1158 (1) | 0.4393 (2) | 0.21098 (7) | 3.82 (4) |
| P(2) | -0.09473 (9) | 0.1091 (2) | 0.14060 (7) | 3.59 (4) |
| C(11) | 0.2138 (4) | 0.412 (1) | 0.2673 (3) | 6.4 (2) |
| C(12) | 0.0957 (6) | 0.3839 (8) | 0.7191 (4) | 6.2 (3) |
| C(21) | -0.0810 (5) | -0.0667 (8) | 0.1607 (4) | 5.5 (2) |
| C(22) | -0.1985 (4) | 0.142 (1) | 0.1331 (3) | 5.7 (2) |
| C(131) | 0.1343 (4) | 0.4284 (7) | 0.1351 (3) | 4.0 (2) |
| C(132) | 0.1823 (5) | 0.3246 (9) | 0.1250 (4) | 5.6 (2) |
| C(133) | 0.1914 (6) | 0.688 (1) | 0.5637 (5) | 6.6 (3) |
| C(134) | 0.1522 (5) | 0.601 (1) | 0.5157 (4) | 5.6 (2) |
| C(135) | 0.1052 (4) | 0.4964 (9) | 0.0258 (4) | 5.5 (2) |
| C(136) | 0.0957 (4) | 0.5096 (9) | 0.0849 (3) | 4.6 (2) |
| C(231) | -0.0947 (4) | 0.1121 (7) | 0.0593 (3) | 4.0 (2) |
| C(232) | -0.0308 (5) | 0.1638 (9) | 0.0430 (3) | 5.1 (2) |
| C(233) | -0.0290 (5) | 0.1652 (9) | -0.0191 (3) | 5.5 (2) |
| C(234) | -0.0949 (6) | 0.1143 (9) | -0.0664 (4) | 6.4 (3) |
| C(235) | 0.3428 (6) | 0.435 (1) | 0.4483 (4) | 7.5 (3) |
| C(236) | -0.1605 (5) | 0.0631 (9) | 0.0115 (3) | 6.2 (2) |

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \alpha)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$. ^b Mo/W represents 57% Mo and 43% W, obtained by scaling up the molybdenum scattering curves and scaling down the tungsten scattering curves.

of complexes **1** and **2** was found to be greatest for the experimental conditions reported, and these complexes are isolated by selective precipitation. However, the synthesis of **3** is optimized by reacting 1 equivalent each of **4** and **5** without any added PPh_3 .

This reaction differs from the one reported for **4** and $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{PMePh})(\text{PMePh}_2)_3$ (**6**).^{2,3} In this reaction the best yield of $\text{MoWCl}_4(\text{PMePh}_2)_4$ is obtained by reacting **4** and **6** in a 3:1 ratio. This was found to decrease the amount of the homonuclear $\text{Mo}_2\text{Cl}_4(\text{PMePh}_2)_4$ produced. More importantly, the formation of structures equivalent to **1** and **2** in the reaction of **4** and **6** was never observed.⁸ However, both reactions can involve the η^1, η^6 -bridged phosphine intermediate complex shown in Scheme I, which was postulated to be important for the selectivity of these reactions in producing the heteronuclear complexes.³

The presence of excess PPh_3 suppresses the formation of **3**, which can occur through at least three routes, as shown in Scheme I. One of these routes entails PPh_3 dissociation and PMe_2Ph substitution directly from the η^6 -tertiary phosphine bridged intermediate, while the other two comprise similar reactions whereby PPh_3 is lost from complex **1** or complex **2**. The formation of **2** probably occurs by a three-step process, beginning with loss of PPh_3 , followed by migration of PMe_2Ph from molybdenum to tungsten, and finally by reattachment of a PPh_3 molecule to the molybdenum atom. Direct evidence for the lability of the PPh_3 ligand in **1**, as well as in **2**, is afforded by the observation that it is substituted by THF, when these complexes are dissolved in THF, to produce complexes **9** and **10**, respectively (Scheme I).

³¹P{¹H} NMR Analysis. The ³¹P{¹H} NMR spectrum in C_6H_6 of the heterogeneous precipitate obtained from a typical reaction of **4** and **5** is shown in Figure 1, and the spectrum of the same precipitate dissolved in THF is presented as supplementary material. The resonances for the complexes containing ¹⁸³W ($I = 1/2$) are not clearly observed. The two doublets of triplets, at $\delta = 36.1$ and 21.3, can be attributed to the phosphorus atoms on the PPh_3 and PMe_2Ph ligands, respectively, on the tungsten atom in complex **1**. This assignment is based on the fact that resonances for the phosphorus atom in PPh_3 ($\delta = -5.1$) are found downfield of the one in PMe_2Ph ($\delta = -46.7$). The doublet of doublets at $\delta = -20.5$ can be assigned to the phosphorus atoms on the PMe_2Ph ligands on the molybdenum atom in **1**. Similarly, for complex

2 the doublet of doublets at $\delta = 18.3$ can be assigned to the phosphorus atoms of the PMe_2Ph ligands on the tungsten atom in **2**. The two doublets of triplets at $\delta = 4.1$ and -15.3 are due to the phosphorus atoms on the PPh_3 and PMe_2Ph ligand, respectively, on the molybdenum atom in **2**. Also in Figure 1 are resonances that can be assigned to **3** (two triplets at $\delta = 17.9$ and -19.15) and **7** (a singlet at $\delta = -4.5$).³

The two-bond trans couplings of 147 Hz for **1** and 141 for **2** are similar to that reported for monomeric $\text{Mo}(\text{CO})_2\text{I}_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ (${}^2J_{\text{PP}}(\text{trans}) = 168$ Hz; dppm = bis(diphenylphosphino)methane)⁹ and larger than that for the phosphorus atom in PMe_2Ph trans to the PEt_3 ligand on the quadruply bonded molybdenum dimer $\text{Mo}_2\text{Me}_4(\text{PEt}_3)(\text{PMe}_2\text{Ph})_3$ (${}^2J_{\text{PP}}(\text{trans}) = 106.8$ Hz).¹⁰

The ³¹P NMR spectrum of the heterogenous precipitate in THF (supplementary material) affords further evidence of the lability of the PPh_3 ligand, as postulated in Scheme I. A triplet at $\delta = 35.3$ and a doublet at $\delta = -27.9$ can be attributed to the phosphorus atoms on the tungsten and molybdenum atoms, respectively, on complex **9**. Similarly, a doublet at $\delta = 15.4$ and a triplet at $\delta = -6.6$ can be assigned to the phosphorus atoms on the tungsten and molybdenum atoms, respectively, in complex **10**.

X-ray Structural Results. The shapes of the molecules of **1** and **2** are so similar that they form mixed crystals; that is, they form a uniform solid solution in which the crystallographic sites are randomly occupied by the two isomeric molecules. There is no precedent for this phenomenon in this class of compounds so far as we know. Here we have two different compounds (although they are isomers) sharing the sites in the same crystalline phase. In previous crystalline heteronuclear compounds, the molecules have had a symmetrical array of ligands, and thus all molecules were the same. The disorder arose from the fact that half of them had one orientation of the $\text{Mo-W}^{3,11-13}$ or Cr-Mo^{14} unit, while the other half had the reverse orientation. In the particular crystal of **1/2** that we have studied the refinement lead to the result that 67% of the molecules are **1** and 33% are **2**. In principle it seems possible that crystals of pure **1** or pure **2** could be obtained and that in such crystals each metal atom site would be occupied exclusively by one type of metal atom.

In crystals of **3** we observed the usual type of disorder (i.e., random arrangement) for these heteronuclear systems and the unequal population parameters of the two disordered metal atom sites (ca. 43% W and 57% Mo) indicate that about 14% of the homonuclear species $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ (**7**) is also present.

It must always be kept in mind that in structures such as that of **1/2**, as well as that of **3**, we obtain from the X-ray diffraction data an electron density distribution that is a convolution of those for two different species at each point in space. It does not, therefore, allow us to obtain molecular structure parameters (bond lengths, angles) of the same precision as we would, other things being equal, for a crystal in which all sites are occupied by truly identical chemical entities. The bond lengths and angles obtained are not exactly those of either species in the crystal, and the estimated standard deviations (esd's) given by the least-squares refinements are not strictly applicable.

In view of the remarks made in the preceding paragraph it is necessary to be cautious about comparing differences between structures when one, or both, are derived from crystals displaying the kind of disorder or isomeric mixture shown by **3** and **1/2**, respectively. Thus, the apparent difference, 0.08 (1) Å, between

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Table IV. Selected Bond Lengths and Angles for Complexes 1/2 and 3

| Bond Lengths ^a for Complexes 1/2 and 3 | | | |
|---|------------|---------------------|------------|
| Complexes 1/2 | | | |
| W/Mo(1) ^b -Mo/W(2) ^c | 2.2161 (7) | P(1)-C(131) | 1.84 (1) |
| W/Mo(1)-Cl(1) | 2.399 (3) | P(2)-C(211) | 1.82 (1) |
| W/Mo(1)-Cl(2) | 2.385 (2) | P(2)-C(221) | 1.84 (1) |
| W/Mo(1)-P(1) | 2.522 (3) | P(2)-C(231) | 1.853 (9) |
| W/Mo(1)-P(2) | 2.579 (3) | P(3)-C(31) | 1.83 (1) |
| Mo/W(2)-Cl(3) | 2.397 (2) | P(3)-C(32) | 1.86 (1) |
| Mo/W(2)-Cl(4) | 2.400 (2) | P(3)-C(331) | 1.82 (1) |
| Mo/W(2)-P(3) | 2.543 (3) | P(4)-C(41) | 1.86 (1) |
| Mo/W(2)-P(4) | 2.522 (2) | P(4)-C(42) | 1.836 (9) |
| P(1)-C(11) | 1.84 (1) | P(4)-C(431) | 1.83 (1) |
| P(1)-C(12) | 1.84 (1) | | |
| Complex 3 | | | |
| Mo/W ^d -Mo/W | 2.2077 (4) | Mo/W-Cl(1) | 2.411 (2) |
| Mo/W-Cl(2) | 2.411 (2) | Mo/W-P(1) | 2.519 (2) |
| Mo/W-P(2) | 2.545 (2) | P(1)-C(11) | 1.840 (6) |
| P(1)-C(12) | 1.838 (8) | P(1)-C(131) | 1.827 (7) |
| P(2)-C(21) | 1.826 (8) | P(2)-C(22) | 1.841 (7) |
| P(2)-C(231) | 1.818 (7) | | |
| Bond Angles ^a for Complexes 1/2 and 3 | | | |
| Complexes 1/2 | | | |
| Mo/W(2) ^b -W/Mo(1) ^c -Cl(1) | 109.99 (7) | Cl(3)-Mo/W(2)-P(4) | 85.35 (8) |
| Mo/W(2)-W/Mo(1)-Cl(2) | 108.09 (6) | Cl(4)-Mo/W(2)-P(3) | 86.88 (9) |
| Mo/W(2)-W/Mo(1)-P(1) | 101.87 (7) | Cl(4)-Mo/W(2)-P(4) | 84.78 (8) |
| Mo/W(2)-W/Mo(1)-P(2) | 106.01 (7) | P(3)-Mo/W(2)-P(4) | 152.57 (9) |
| Cl(1)-W/Mo(1)-Cl(2) | 141.85 (9) | W/Mo(1)-P(1)-C(11) | 119.6 (4) |
| Cl(1)-W/Mo(1)-P(1) | 85.36 (8) | W/Mo(1)-P(1)-C(12) | 119.0 (3) |
| Cl(1)-W/Mo(1)-P(2) | 85.66 (8) | W/Mo(1)-P(1)-C(131) | 105.0 (3) |
| Cl(2)-W/Mo(1)-P(1) | 84.72 (8) | W/Mo(1)-P(2)-C(211) | 107.6 (3) |
| Cl(2)-W/Mo(1)-P(2) | 86.20 (8) | W/Mo(1)-P(2)-C(221) | 118.1 (3) |
| P(1)-W/Mo(1)-P(2) | 152.11 (9) | W/Mo(1)-P(2)-C(231) | 120.0 (3) |
| W/Mo(1)-Mo/W(2)-Cl(3) | 109.45 (7) | Mo/W(2)-P(3)-C(31) | 116.6 (4) |
| W/Mo(1)-Mo/W(2)-Cl(4) | 109.48 (7) | Mo/W(2)-P(3)-C(32) | 119.9 (4) |
| W/Mo(1)-Mo/W(2)-P(3) | 104.07 (7) | Mo/W(2)-P(3)-C(331) | 110.3 (3) |
| W/Mo(1)-Mo/W(2)-P(4) | 103.35 (6) | Mo/W(2)-P(4)-C(41) | 118.9 (3) |
| Cl(3)-Mo/W(2)-Cl(4) | 141.05 (9) | Mo/W(2)-P(4)-C(42) | 120.2 (4) |
| Cl(3)-Mo/W(2)-P(3) | 84.86 (8) | Mo/W(2)-P(4)-C(431) | 103.6 (3) |
| Complex 3 | | | |
| Mo/W ^b -Mo/W-Cl(1) | 108.26 (5) | Cl(2)-Mo/W-P(2) | 85.56 (6) |
| Mo/W-Mo/W-Cl(2) | 106.91 (4) | P(1)-Mo/W-P(2) | 151.58 (6) |
| Mo/W-Mo/W-P(1) | 104.05 (4) | Mo/W-P(1)-C(11) | 120.2 (3) |
| Mo/W-Mo/W-P(2) | 104.37 (4) | Mo/W-P(1)-C(12) | 118.7 (3) |
| Cl(1)-Mo/W-Cl(2) | 144.81 (6) | Mo/W-P(1)-C(131) | 104.1 (2) |
| Cl(1)-Mo/W-P(1) | 85.90 (6) | Mo/W-P(2)-C(21) | 118.6 (2) |
| Cl(1)-Mo/W-P(2) | 84.76 (6) | Mo/W-P(2)-C(22) | 117.7 (3) |
| Cl(2)-Mo/W-P(1) | 86.77 (6) | Mo/W-P(2)-C(231) | 108.4 (2) |

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b W/Mo(1) represents 67% W and 33% Mo. ^c Mo/W(2) represents 67% Mo and 33% W. These population parameters were obtained by scaling, either up or down, the molybdenum and tungsten scattering curves at the two metal atom sites. ^d Mo/W represents 57% Mo and 43% W, obtained by scaling up the molybdenum scattering curves and scaling down the tungsten scattering curves.

the Mo-W distances in 1/2 and 3 that would normally be safely regarded as real may not be. On the other hand, the metal to phosphorus atom distance to PPh₃ for complexes 1/2 (2.579 (3) Å), which appears to be substantially larger than the other M-P distances in the same complexes (2.522 (3), 2.543 (3), 2.522 (2) Å), as well as those in complex 3 (2.519 (2), 2.545 (2) Å), may actually be larger. Similar metal to phosphorus distances are found in MoWCl₄(PMePh₂)₄ (average 2.582 Å), a complex that has labile phosphines.³ The larger distance is consistent with the ready substitution of this triphenylphosphine ligand with smaller phosphines such as PMe₂Ph and other sterically smaller ligands such as THF.

Discussion

The importance of the work reported here is that when compared with the previous work on the preparation and properties of MoWCl₄(PMePh₂)₄, it shows how important the steric properties of the phosphine may be in determining the products available. When the starting materials are Mo(η⁶-C₆H₅PMePh)(PMePh₂)₃ and WCl₄(PPh₃)₂, the bulk of PMePh₂

as a ligand in the product is such as to strongly exclude PPh₃, and thus MoWCl₄(PMePh₂)₄ is obtained without significant amounts of either isomer of MoWCl₄(PMePh₂)₃PPh₃. However, with the less sterically demanding PMe₂Ph, simply by making excess PPh₃ available, it is possible to obtain the isomeric mixed-phosphine species, MoWCl₄(PMe₂Ph)₃PPh₃, as the major product.

This result is of more than idle interest because the PPh₃ ligand in the mixed-phosphine species is labile and easily replaceable by other ligands, e.g., THF or another phosphine. This gives convenient synthetic access to a range of mixed-ligand species that we shall make use of in future work.

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Supplementary Material Available: A figure showing the ³¹P{¹H} NMR spectrum of 1/2 in THF, stereoviews of the crystal packing of 1/2 and 3, and tables of full crystallographic information, anisotropic thermal parameters, and complete bond lengths and angles (14 pages); listings of final structure amplitudes for 1/2 and 3 (44 pages). Ordering information is given on any current masthead page.