gands and since it is slowly converted into **3a** by PMe_3, we formulate it as $W_2Cl_6(THF)_4$ (**3c**).[10] Further reduction of **3c** in THF yields an intense blue solution which contains an as yet unidentified thermally unstable species.

From these data alone we are not able to choose between several possible pathways to **1.** Both **3a** and **3c** are plausbile intermediates. At present we believe the intermediate would more likely be **3a** since **3c** (as noted above) does not appear to react rapidly enough with PMe_3 to give **1**.

If WCl_4 is allowed to react with PMe_3 to yield $WCl_4(PMe_3)_3$ before any sodium amalgam is added, then subsequent reduction yields only monomeric species. $WCl_4(PMe_3)_3$ is reduced first to orange, crystalline *mer*-$WCl_3(PMe_3)_3$[11] and then to orange, crystalline *trans*-$WCl_2(PMe_3)_4$[12] with 1 and 2 equiv of sodium amalgam (respectively) in THF at 25 °C in the presence of 1 equiv of PMe_3. Interestingly, however, dimeric $W_2Cl_4(PMe_3)_4$ *can* be prepared from $WCl_2(PMe_3)_4$ in 60% yield in refluxing dibutyl ether (eq 2); loss of volatile PMe_3 must yield fragments such as $WCl_2(PMe_3)_3$ which can then dimerize, ultimately to give $W_2Cl_4(PMe_3)_4$. Note that a similar attempt to make **3a** from $WCl_3(PMe_3)_3$ gave a 2:1 mixture of $WCl_4(PMe_3)_3$ and $W_2Cl_4(PMe_3)_4$; presumably $WCl_3(PMe_3)_3$ first disproportionates to $WCl_2(PMe_3)_x$ and $WCl_4(PMe_3)_y$ (eq 3).

$$WCl_2(PMe_3)_4 \xrightarrow[Bu_2O]{\text{refluxing}} 0.5W_2Cl_4(PMe_3)_4 + 2PMe_3 \quad (2)$$

$$WCl_3(PMe_3)_3 \xrightarrow[Bu_2O]{\text{refluxing}} 0.25W_2Cl_4(PMe_3)_4 + 0.5WCl_4(PMe_3)_3 + 0.5PMe_3 \quad (3)$$

It is quite likely that these $W_2Cl_4L_4$ compounds are isostructural with the analogous Mo species. This is largely true, although there still are some surprises, as shown by X-ray studies of several of these species.[13]

We had hoped that the $W_2L_4Cl_4$ species would provide a route to $W_2(OAc)_4$ (a facile reaction when the metal is Mo[14]). Unfortunately, it appears that the tungsten complexes are more resistant to simple reactions under mild conditions than the Mo species. For example, heating $W_2Cl_4(PBu_3)_4$ with 4–9 equiv of acetic acid in glyme at 160 °C for 4 h gives a moderate yield of a soluble red complex which contains two types of uncoupled phosphorus nuclei (2:1 by ^{31}P NMR), Cl, and what appears to be an acetate ligand by ^{13}C NMR. We are still attempting to characterize this "W acetate".[13]

Acknowledgments. We thank the National Science Foundation for support (CHE79-05307) and the Dow Chemical Company for a fellowship to P.R.S. We also thank Mr. Luke Schoeniger of Professor E. Solomon's group for obtaining the Raman data.

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(6) Calcd for $W_2Cl_4(PMe_3)_4(W_2C_{12}H_{36}Cl_4P_4)$: C, 17.71; H, 4.47. Found: C, 17.82; H, 4.52. Calcd for $W_2Cl_4(PMePh_2)_4(W_2C_{52}H_{52}Cl_4P_4)$: C. 47.66; H, 4.00. Found: C, 47.44; H, 4.15. Calcd for $W_2Cl_4(diphos)_2(W_2C_{52}H_{48}Cl_4P_4)$: C, 47.81; H, 3.70. Found: C, 48.25; H, 4.01. Calcd for $W_2Cl_4(dmpe)_2$·toluene($W_2C_{19}H_{40}Cl_4P_4$): C; 25.30; H; 4.48. Found: C, 25.28; H, 4.68.
(7) (a) Reasonable values for $^1J_{PW}$, $^2J_{PW}$, and $^3J_{pp}$ (230, 49, and 27 Hz, respectively, for L = PBu_3) can be obtained by a procedure similar to that employed by Yoshida et al.[7b] However, in the present case, the spectra are not first order and computer fitting will be necessary for a proper analysis. (b) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.
(8) Rotating KBr pellet with argon laser 5145-nm light (scanning rate 0.5 cm^{-1} s^{-1}).
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(11) (a) Calcd for $WCl_3(PMe_3)_3(WC_9H_{27}Cl_3P_3)$: C, 20.85; H, 5.25. Found: C, 20.51; H, 5.19. The compound shows two very broad peaks for the PMe_3 protons in the ^1H NMR spectrum at δ −11 and −15 in a 1:2 ratio. We therefore assign the mer geometry to it. An analogous *mer*-$MoCl_3py_3$ complex is known.[11b] (b) Brencic, J. V. *Z. Anorg. Allgem. Chem.* **1974,** *403*, 218–224.
(12) Calcd for $WCl_2(PMe_3)_4(WC_{12}H_{36}Cl_2P_4)$: C, 25.78; H, 6.49. Found: C, 26.20; H, 6.48. A trans geometry was tentatively assigned based on a single broad peak observed for the PMe_3 protons at δ 3.8 in the ^1H NMR spectrum.
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Structural Characterization of Four Quadruply Bonded Ditungsten Compounds and a New Trinuclear Tungsten Cluster

Sir:

In contrast to the ease with which quadruply bonded dimolybdenum compounds may be obtained in enormous numbers and variety,[1] the attempted preparation of similar tungsten compounds has been a relatively unproductive exercise.[2–6] Thus, the recent success of Sharp and Schrock[7] in preparing a whole class of mixed halogeno-phosphine complexes of the general type $W_2X_4(PR_3)_4$, which are stable in air at room temperature, constitutes a very significant contribution to the field of metal–metal multiple bonds.[8]

Structural characterization of representative members of this new group of compounds has been carried out and the results present an interesting mixture of the expected and the unexpected. We report here the structures of five compounds, all supplied to us in crystalline form by Sharp and Schrock: **1,** $W_2Cl_4(PMe_3)_4$; **2,** $W_2Cl_4(dmpe)_2{\cdot}C_7H_8$; **3,** green $W_2Cl_4(dppe)_2{\cdot}0.5H_2O$; **4,** brown $W_2Cl_4(dppe)_2$; **5,** $W_3O_3Cl_5(CH_3CO_2)(PBu^n{}_3)_3$·solvate. In these formulas dmpe = $Me_2PCH_2CH_2PMe_2$ and dppe = $Ph_2PCH_2CH_2PPh_2$. Full descriptions of all these structures will be published elsewhere.[9,10]

$W_2Cl_4(PMe_3)_4$, 1, has the structure shown in Figure 1. Unlike the stoichiometrically and conformationally similar $Re_2Cl_4(PEt_3)_4$[11] this compound does *not* pack in a disordered manner and the structure was solved simply and straightforwardly. The structure is that anticipated from our knowledge of dimolybdenum and dirhenium compounds. There should be a W–W quadruple bond and the overall eclipsed conformation is consistent with this; the PMe_3 groups are staggered among themselves. A few important bond distances and angles, for this and for compounds **2–4,** are given in Table I.

Table I. Some Key Bond Distances and Angles in **1–4**[a,b]

	distances, Å			angles, deg	
compd	W–W	W–Cl	W–P	W–W–Cl	W–W–P
1	2.262 (1)	2.393 (2)	2.506 (2)	111.73 (6)	101.13 (6)
2	2.287 (1)	2.426 (2)	2.451 (2)	116.1 (1)	96.2 (1)
3	2.280 (1)	2.409 (1)	2.502 (1)	111.0 (1)	98.1 (1)
4	2.314 (1)	2.371 (4)	2.530 (4)	112.3 (1)	97.0 (1)

[a] Figures in parentheses are esd's occurring in the least significant digit. [b] Values given reflect averages of chemically equivalent distances and angles.

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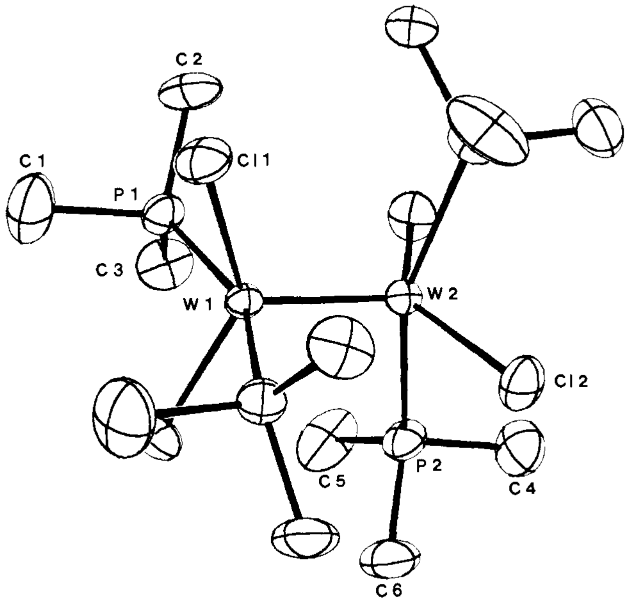

Figure 1. The structure of $W_2Cl_4(PMe_3)_4$, **1**, with thermal ellipsoids at the 50% probability level. A twofold rotation axis passes through the W-W bond.

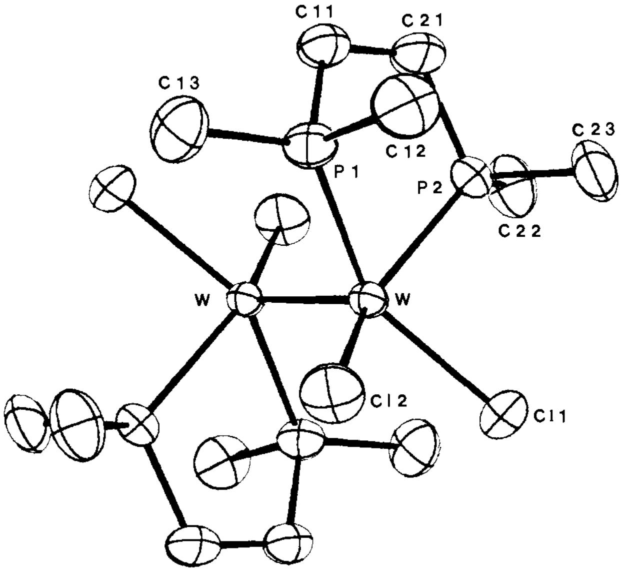

Figure 2. The structure of the $W_2Cl_4(dmpe)_2$ unit in $W_2Cl_4(dmpe)_2{\cdot}C_7H_8$, **2**. Vibrational ellipsoids are scaled so as to enclose 50% of their electron density. A crystallographic center of inversion is located at the midpoint of the W-W bond.

$W_2Cl_4(dmpe)_2{\cdot}C_7H_8$, 2, has a structure which is fundamentally unsurprising but in detail highly novel; it is shown in Figure 2. The remarkable feature, of course, is the presence of the dmpe ligands as chelating rather than bridging groups; the chelate ring has a chair conformation. The molecule resides on a crystallographic center of symmetry which ensures an eclipsed arrangement of the eight ligand atoms with overall C_{2h} symmetry.

Green **$W_2Cl_4(dppe)_2{\cdot}0.5H_2O$, 3,** is found as an "impurity" (about mol 10%) in the reported[7] brown compound **4**. It has a structure analogous to that of **2** and its bond distances and angles (Table I) are very similar.

In brown **$W_2Cl_4(dppe)_2$, 4,** we find the dppe ligands in the bridging posture already familiar from $Mo_2X_4(dppm)_2$ with dppm = $Ph_2PCH_2PPh_2$ and X = Cl and -NCS,[12] $Mo_2Br_4(arphos)_2$ with arphos = $Ph_2PCH_2CH_2AsPh_2$,[13] and $Re_2Cl_4(dppe)_2$,[14] as shown in Figure 3. The Mo_2 species just mentioned are expected to have quadruple bonds and hence small internal torsion angles. The first two have angles of 0° and 13.3° while the arphos compound has a mean angle of 30°; this last angle is not, however, incompatible with the retention of considerable δ bonding.[13] The rhenium compound, in which only a triple bond is expected, has a mean torsion angle of 45°, i.e., the conformation is staggered. It is to be noted that $Mo_2Br_4(arphos)_2$ and $Re_2Cl_4(dppe)_2$ are "isomorphous" in the usual loose usage of that term; brown $W_2Cl_4(dppe)_2$ is similarly "isomorphous" with both of them. Since $W_2Cl_4(dppe)_2$ has the proper number of electrons to contain a $\sigma^2\pi^4\delta^2$ quadruple bond, a torsion angle comparable with that in $Mo_2Br_4(arphos)_2$ might have been anticipated, but, in fact, **4** has an essentially staggered conformation like that of $Re_2Cl_4(dppe)_2$.[15]

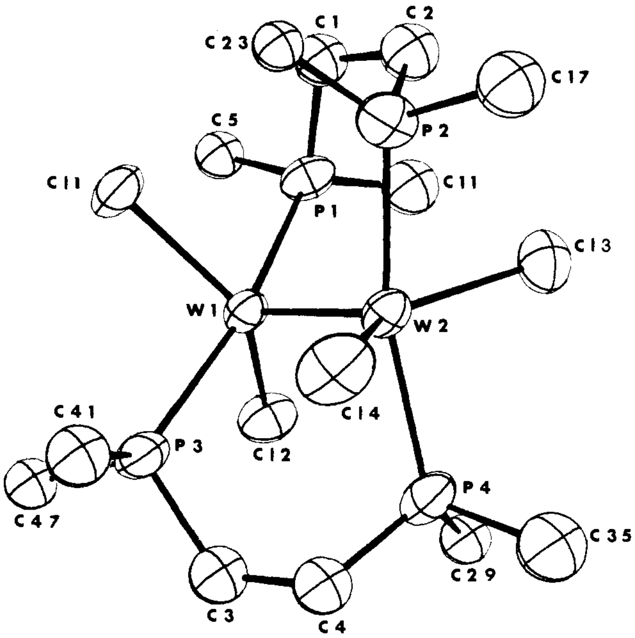

Figure 3. An ORTEP drawing of brown $W_2Cl_4(dppe)_2$, **4**, showing only the α-carbon atoms of the phenyl rings in the dppe ligands. Thermal ellipsoids are drawn at the 50% probability level.

In compounds **1, 2,** and **3** the mean W-W distance, 2.276 (1) Å, is much longer than those found in $W_2(mhp)_4$ (mhp = the anion of 2-hydroxo-6-methylpyridine), 2.161 (1) Å, and closely related molecules,[16] very similar to those typical of triply bonded $L_3W{\equiv}WL_3$ species,[8b] 2.25-2.30 Å, and only slightly longer than those (~2.26 Å) in the $[W_2Me_8]^{4-}$ and $[W_2Me_{8-n}Cl_n]^{4-}$ ions.[3]

$W_2O_3Cl_5(CH_3CO_2)(PBu^n{}_3)_3{\cdot}$solvate, 5, is the "uncharacterized W acetate" obtained by Sharp and Schrock[7] upon treatment of $W_2Cl_4(PBu^n{}_3)_4$ with excess acetic acid in a glyme-type solvent at 160 °C. Its structure is shown in Figure 4. It is clearly a new example of the "M_3X_{13}" type of trinuclear cluster which has been observed in several variations when M = Mo[17,18] but so far only known in the form of the $[W_3O_4F_9]^{5-}$ ion reported by Mattes[19] for tungsten. As in other "M_3X_{13}" species a set of W-W single bonds between the W(IV) atoms can be postulated and the mean W-W distance, 2.609 Å, is consistent with this.[20] Each tungsten atom has the usual coordination geometry for the "M_3X_{13}" structure, although the ligands cause a somewhat unequal distribution of formal charge. Note that we have for the first time a μ_3-Cl in a trinuclear Mo or W cluster; also, each $PBu^n{}_3$ ligand is trans to μ_3-Cl.

Acknowledgment. We are grateful to the National Science Foundation for financial support. We thank Dr. M. W. Extine of the Molecular Structure Corporation for his participation in the solution and refinement of structure **1**.

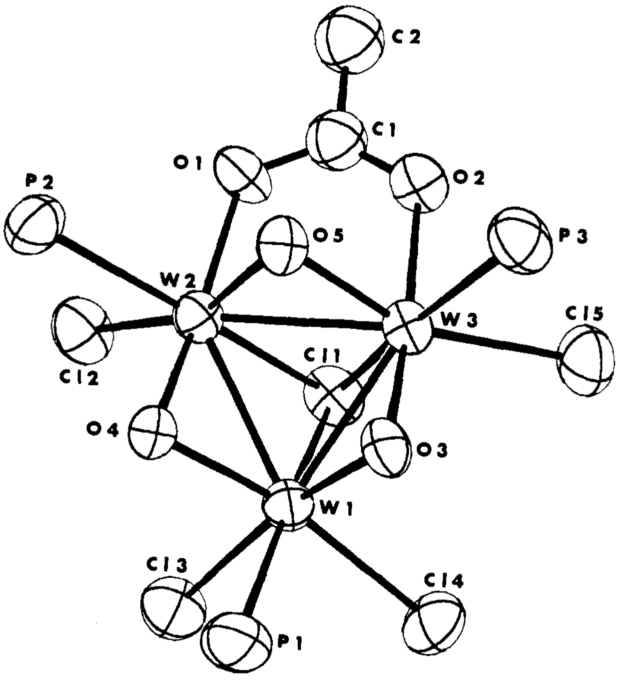

Figure 4. The $W_3O_3Cl_5(CH_3CO_2)(PBu^n{}_3)_3$ unit in compound **5**, omitting the *n*-Bu groups. Ellipsoids are shown at the 50% probability level.

Supplementary Material Available: Tables (II–VI) of atomic positional parameters for compounds **1–5** (4 pages). Ordering information is given on any current masthead page.

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(10) Tables of atomic positional parameters are available as supplementary material. All structures are now refined to very low *R* values and the few additional modifications in the refinement procedures are not expected to affect any bond distances or angles significantly. Crystallographic data are as follows. **1:** space group $C2/c$; a = 18.297 (3), b = 9.192 (2), c = 19.042 (2) Å; β = 124.93 (1)°; Z = 4; R_F = 0.031, R_{wF} = 0.045 for 1741 reflections with $I > 3\sigma(I)$. **2:** space group $P2_1/n$; a = 9.150 (2), b = 12.029 (1), c = 14.245 (2) Å; β = 105.88 (2)°; Z = 2; R_F = 0.033, R_{wF} = 0.047 for 2082 reflections with $I > 3\sigma(I)$. **3:** space group $C2/c$; a = 24.702 (5), b = 10.024 (1), c = 22.822 (4) Å; β = 118.81 (2)°; Z = 4; R_F = 0.028, R_{wF} = 0.039 for 3261 reflections with $I > 3\sigma(I)$. **4:** space group $P2_1/n$; a = 23.103 (3), b = 13.254 (2), c = 16.781 (3) Å; β = 107.53 (1)°; Z = 4; R_F = 0.054, R_{wF} = 0.061 for 3517 reflections with $I > 3\sigma(I)$. **5:** space group $P2_1/n$; a = 12.056 (3), b = 20.248 (4), c = 23.977 (7) Å; β = 92.17 (2)°; Z = 4; R_F = 0.049, R_{wF} = 0.063 for 5729 reflections with $I > 3\sigma(I)$.

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(15) The staggered configuration rules out the existence of a δ bond and the W–W distance in this case is ~0.038 Å longer than those in **1, 2,** and **3.** Whether **4** is paramagnetic with two unpaired electrons, as a simple analysis would suggest, remains to be determined. In any case, it appears that **4** provides a clear example of the strength of the conformational preference of the fused six-membered rings, which met no resistance in $Re_2Cl_4(dppe)_2$ but here apparently overcomes the resistance offered by the tendency toward δ bonding.

(16) In keeping with this, Sharp and Schrock[7] found ν_{W-W} of 260 cm^{-1} whereas, for $W_2(mhp)_4{\cdot}CH_2Cl_2$, a ν_{W-W} of 295 cm^{-1} was found.[5]

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(20) See, for example, the W—W single bonds in W_3O_2-type clusters[21] that have distances of ~2.75 Å, the W—W bond in $[W_3O_3F_9]^{5-}$ (2.515 Å),[19] and the W—W (2.791 Å) and W═W (2.530 Å) bonds in disulfur bridged species.[22]

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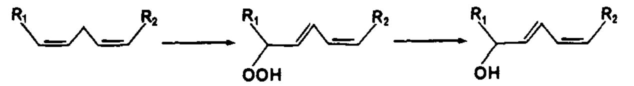
Controlled Chemical Synthesis of the Enzymatically Produced Eicosanoids 11-, 12-, and 15-HETE from Arachidonic Acid and Conversion into the Corresponding Hydroperoxides (HPETE)

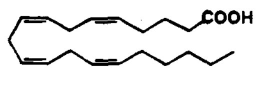
Sir:

Arachidonic acid (**1**) serves as the biological precursor of a growing family of physiologically active eicosanoids[1,2] which includes not only the prostaglandins and their further transformation products (thromboxanes, prostacyclines, etc.) but also lipoxygenase-derived hydroperoxides and alcohols (HPETE's and HETE's, respectively).[3–7] Although the lipoxygenase type of oxidation of *cis,cis*-1,4-dienes (Scheme I) can in principle be effected by singlet oxygen ($^1\Delta g$ state), the reaction of this reagent with polyunsaturated acids is so nonselective (leading to mixtures of all of the expected "ene" oxidation products)[8] as to be preparatively useless. In this communication we describe an approach to the synthesis of three biologically interesting HETE's by methods which are suitable for multigram laboratory preparation and which illustrate useful new synthetic methodology as well.

Scheme I



The one-step conversion of arachidonic acid into the 14,15-epoxide (**2**) in 98% yield by internal oxygen transfer has recently been described.[9] Reaction of **2** with 5 equiv of the reagent prepared from isopropylcyclohexylamine and methylmagnesium bromide (1:1) in tetrahydrofuran (THF) at 0 °C for 10 min and then 0–23 °C for 2 h and 23 °C for 3.5 h was very clean and afforded, after quenching with saturated aqueous sodium dihydrogen phosphate, extractive isolation with ether, concentration, and simple chromatographic sepa-



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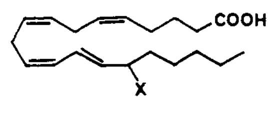
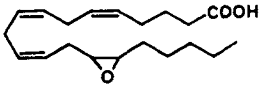


3 X=OH
11 X=OOH



2