reaction observed, an α-hydrogen abstraction is presumed to be occurring in at least this case. As expected, once the *tert*-butyl alcohol radical is consumed, the optical signals for $\mathbf{1}^{+}\cdot$ and $\mathbf{2}^{+}\cdot$ are completely stable for over 10 s (nonflowing conditions, the slowest time scale that could be employed using the pulse radiolysis equipment). In contrast, the $\mathbf{3}^{+}\cdot$ optical signal decreases by a relatively slow first-order process after the initial fast reaction with $\cdot CH_2CMe_2OH$ is completed. The observed rate constant for $\mathbf{3}^{+}\cdot$ disappearance is $135 \pm 15\ s^{-1}$ at 25 °C, pH independent between 2.7 and 5.3 (the lower limit is imposed by the decreased yield of $\mathbf{3}^{+}\cdot$ when the $e_{aq}^{-} + H^{+}$ reaction consumes too great a fraction of the electrons produced, and the upper limit by decomposition of $\mathbf{3}^{2+}$). We suggest that this uncatalyzed first-order decomposition of $\mathbf{3}^{+}\cdot$ is caused by thermal cleavage of the three-electron σ bond. This cleavage allows the nitrogens to move apart until they no longer interact significantly, and the acidic amine radical cation[6] and basic free amino group produced will undergo very rapid, irreversible net proton transfer at the pH employed; cleavage of the $R_3N\cdots NR_3^{+}$ bond should be irreversible. The 5-ms observed half-life corresponds to $\Delta G^{\ddagger}$ of 14.5 kcal/mol using the Erying equation, which we suggest is an experimental measure of the strength of the three-electron σ bond of $\mathbf{3}^{+}\cdot$. The tricyclic radical cations $\mathbf{1}^{+}\cdot$ and $\mathbf{2}^{+}\cdot$ are structurally prevented from cleaving the N–N bond and have solution lifetimes of hours and months, respectively.[1,2]

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Received October 29, 1979

Synthesis of a Class of Complexes Containing Tungsten–Tungsten Quadruple Bonds

Sir:

Despite the large number of complexes of Mo containing quadruple metal–metal bonds, few are known for W.[1] This probably is due largely to the fact that a W analogue of $Mo_2(OAc)_4$ (the major starting material for preparing complexes containing quadruple bonds) has not yet been prepared.[2] We have been attempting to systematize the chemistry of tungsten halides and have found that a class of complexes with the formula $W_2Cl_4L_4$ (L = a phosphine ligand) can be prepared readily, either by reducing $[WCl_4]_x$ with sodium amalgam in the presence of L or by pyrolyzing monomeric W(II) complexes. The former demonstrates that, once a metal–metal bond of order greater than one is present, it will quite likely survive upon reducing the metal to give a bond of higher order.[3]

Phosphines react fairly slowly with WCl_4 suspended in THF to yield WCl_4L_x (x = 2 or 3) complexes. However, when 2 equiv of sodium amalgam (0.4%) is added to a stirred mixture of WCl_4 and PBu_3 in THF at −20 °C and the mixture is warmed to room temperature, WCl_4 is consumed and the solution turns blue-green. $W_2Cl_4(PBu_3)_4$ can be isolated in high yield after filtering the mixture through Celite. Analogous green to blue-green complexes (**1**) containing PMe_3, PMe_2Ph, or $PMePh_2$ can be obtained similarly in 60–80% yield (eq 1). We have also used this method to prepare more simply and directly one member [blue $Mo_2Cl_4(PBu_3)_4$] of the well-known class of analogous molybdenum complexes.[4]

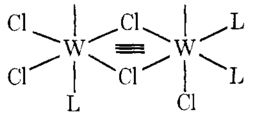
$$WCl_4 + 2Na/Hg + 2L \xrightarrow{THF} W_2Cl_4L_4\ (\mathbf{1}) \qquad (1)$$

$$L = PMe_3,\ PMe_2Ph,\ PMePh_2,\ \text{or}\ PBu_3$$

The reaction fails to give $W_2Cl_4(L\text{-}L)_2$ (**2**, L-L = dmpe or diphos) directly. These must be prepared by displacing PBu_3 from $W_2Cl_4(PBu_3)_4$ in toluene at 80 °C. Sparingly soluble, brown $W_2Cl_4(diphos)_2$ or green $W_2Cl_4(dmpe)_2$ crystallize from the reaction mixture in 60 and 95% yields, respectively. Actually brown $W_2Cl_4(diphos)_2$ contains ~10% green crystalline form. (Two forms of $Mo_2Cl_4(diphos)_2$ were also isolated.[5])

The formulations of **1** and **2** are based on elemental analyses[6] and the following data (cf. the analogous Mo complexes[4,5]). All are air stable in the solid state and only moderately sensitive in solution. A cryoscopic molecular weight determination for $W_2Cl_4(PBu_3)_4$ (calcd 1317; found 1320) and parent peaks in the mass spectra of $W_2Cl_4(PMe_3)_4$ and $W_2Cl_4(dmpe)_2$ show that they are dimers. The ^{31}P and ^{1}H NMR spectra are virtually identical with those reported for the $Mo_2Cl_4L_4$ complexes except for the presence of ^{183}W satellites in the ^{31}P spectra.[7] A Raman spectrum[8] of $W_2Cl_4(PBu_3)_4$ revealed an intense peak at $260 \pm 10\ cm^{-1}$ which we tentatively assign as the tungsten–tungsten stretch.

If only 1 equiv of sodium amalgam is used, a mixture of WCl_4 and PMe_3 yields a red solution from which red, crystalline $W_2Cl_6(PMe_3)_4$ (**3a**) can be isolated in 75% yield. We believe that **3a** has a structure analogous to the known $W_2Cl_6Py_4$ (**3b**)[9] based on the fact that its ^{1}H NMR spectrum shows two types of phosphine ligands. The reduction of **3a** with 1 more equiv of sodium amalgam/W yields $W_2Cl_4(PMe_3)_4$ in 80% yield.



3a, L = PMe_3
b, L = Py
c, L = THF

If phosphine is absent, 1 equiv of sodium amalgam reduces WCl_4 to give a greenish yellow solution in which greenish yellow crystals form on addition of pentane. Since the ^{1}H NMR spectrum of this complex shows two types of THF ligands 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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(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.

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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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Received October 15, 1979

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**, $W_2Cl_4(dmpe)_2$•C_7H_8; **3**, green $W_2Cl_4(dppe)_2$•$0.5H_2O$; **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.

0002-7863/80/1502-1431$01.00/0