Inorg. Chem. **1983**, *22*, 2801-2806

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Preparation of $W_2Cl_8^{4-}$ and Several of Its Derivatives

RICHARD R. SCHROCK,* LYNDA G. STURGEOFF, and PAUL R. SHARP

Received December 2, 1982

The sodium amalgam reduction of WCl_4 in tetrahydrofuran in the presence of a tertiary phosphine (L = PMe_3, PBu_3, PMe_2Ph, $PMePh_2$) produces a family of compounds of the type $W_2Cl_4L_4$, which contain a tungsten–tungsten quadruple bond. $W_2Cl_4(dmpe)_2$ and $W_2Cl_4(dppe)_2$ must be prepared by the reaction between $W_2Cl_4(PBu_3)_4$ and dmpe or dppe. In the absence of phosphine, WCl_4 can be reduced to $W_2Cl_6(THF)_4$. $W_2Cl_6(THF)_4$ reacts with phosphine to produce $W_2Cl_6L_4$, and $W_2Cl_6L_4$ can be reduced cleanly to $W_2Cl_4L_4$. In the absence of phosphine $W_2Cl_6(THF)_4$ can be reduced to deep blue $Na_4(THF)_xW_2Cl_8$. Several other derivatives such as $Na_4(TMEDA)_4W_2Cl_8$ have also been prepared. All derivatives that contain the $W_2Cl_8^{4-}$ ion decompose within a few minutes at 25 °C in solvents in which they dissolve. $Na_4(THF)_xW_2Cl_8$ reacts rapidly with phosphine to produce $W_2Cl_4L_4$, with 6-methyl-2-hydroxypyridine in the presence of triethylamine to produce $W_2(mhp)_4$, and with pivalic acid in the presence of triethylamine to produce $W_2(O_2CCMe_3)_4$. We have shown that complexes of the type $W_2Cl_4L_4$ can be oxidized readily to monocations. An attempt to prepare $W_2(O_2CCH_3)_4$ from $W_2Cl_4(PBu_3)_4$ and acetic acid also led to oxidation of the metal to give $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$.

Introduction

Although $Mo_2(O_2CCH_3)_4$,[1] $Mo_2Cl_8^{4-}$,[2] and $Re_2Cl_8^{2-}$,[3] have been known for over 15 years, relatively few compounds containing a tungsten–tungsten quadruple bond[4] have been prepared. Two examples are $W_2Me_8^{4-}$[5] and $W_2(C_8H_8)_3$,[6] the latter necessarily being rather different structurally from the norm for complexes containing a metal–metal quadruple bond. A third example is a compound that contains bridging ligands derived from 6-methyl-2-hydroxypyridine, $W_2(mhp)_4$.[7]

Three years ago we reported[8] in a preliminary communication that reduction of WCl_4 in tetrahydrofuran in the presence of a tertiary phosphine (L) yielded complexes of the type $W_2Cl_4L_4$, analogues of the well-known class of molybdenum complexes.[9] X-ray structural studies[10] showed conclusively that these were authentic examples of complexes containing a tungsten–tungsten quadruple bond. At that time we noticed that $W_2Cl_6(THF)_4$ could be prepared by reducing WCl_4 in tetrahydrofuran and that further reduction of isolated $W_2Cl_6(THF)_4$ produced an intense blue solution.[8] We thought that this thermally unstable blue species might be the long sought $W_2Cl_8^{4-}$ ion, but only relatively recently have we been able to prepare a crystalline TMEDA derivative, a crystal structure of which showed it to be $Na_4(TMEDA)_4W_2Cl_8$.[11] The blue species that we observed initially has now been shown to be $Na_4(THF)_xW_2Cl_8$ ($x \approx 2$). In this paper we report the full details of the preparation of $W_2Cl_4L_4$ and its precursors, $Na_4(THF)_xW_2Cl_8$ and related molecules such as $W_2(O_2CCMe_3)_4$, and several products of oxidation such as $W_2Cl_4L_4^+$ and $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$.

Results

Preparation of $W_2Cl_4L_4$ (L = A Phosphine Ligand). Tertiary phosphines such as PMe_3 react slowly with WCl_4 (a polymer[12]) to give monomeric complexes, WCl_4L_x (x = 3 if L = PMe_3).[8] However, if 2 equiv of sodium amalgam is present, WCl_4 is consumed rapidly, the solution becomes blue-green to green, and complexes with the formula $W_2Cl_4L_4$ can be isolated in good yield (eq 1). $Me_2PCH_2CH_2PMe_2$ (dmpe) or $Ph_2PCH_2CH_2PPh_2$ (dppe) failed to give the analogous complexes $W_2Cl_4(dmpe)_2$ and $W_2Cl_4(dppe)_2$. However, these could be prepared by displacing PBu_3 from $W_2Cl_4(PBu_3)_4$ with dmpe or dppe at 80 °C in toluene. Both crystallize directly from the reaction mixture, $W_2Cl_4(dppe)_2$ as a mixture of green and brown isomers in a ratio that depends on the reaction temperature (see Experimental Section). (Two isomers of $Mo_2Cl_4(dppe)_2$ are also known.[9d])

$$WCl_4 + 2Na/Hg + 2L \xrightarrow{THF} {}^1/_2W_2Cl_4L_4 \qquad (1)$$
$$L = PMe_3,\ PMe_2Ph,\ PMePh_2,\ \text{or}\ PBu_3$$

The dimeric nature of several of the $W_2Cl_4L_4$ complexes has been established by mass spectral, cryoscopic molecular weight, and ^{31}P NMR studies. A typical ^{31}P NMR (Figure 1, top) shows a pattern of satellite peaks due to the magnetically inequivalent phosphine ligands in $L_2Cl_2{}^{183}W\overset{4}{-}WCl_2L_2$. (A similar phenomenon was observed in $[Pt(R_2P(CH_2)_3PR_2)_2]_2$ (R = CMe_3)[13].) A simulated spectrum with the approximate values for $^1J_{PW}$, $^2J_{PW}$, and $^3J_{PP}$ observed for $W_2Cl_4(PBu_3)_4$ is shown in Figure 1, bottom. We cannot tell from these data alone whether the structure of $W_2Cl_4L_4$ contains a *cis*- or a *trans*-WCl_2L_2 unit at each end of the molecule or what the relative orientation of the two ends is.

The structures of several $W_2Cl_4L_4$ complexes have been determined.[10,14] $W_2Cl_4(PMe_3)_4$ has a structure in which the PMe_3 ligands are trans to one another in each $WCl_2(PMe_3)_2$ unit and the two ends are eclipsed. $W_2Cl_4(dmpe)_2$ and green $W_2Cl_4(dppe)_2$ have centrosymmetric eclipsed structures in which the chelating phosphine ligands are each bound to a single metal center. In brown $W_2Cl_4(dppe)_2$, the dppe ligands bridge the two metals and the ends of the molecule are staggered.

---

[1] (a) Stephenson, T. A.; Bannister, E.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2538. (b) Lawton, D.; Mason, R. *J. Am. Chem. Soc.* **1965**, *87*, 921.

[2] Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7.

[3] Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330.

[4] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[5] (a) Cotton, F. A.; Koch, S.; Mertis, K.; Millar, M.; Wilkinson, G. *J. Am. Chem. Soc.* **1977**, *99*, 4989. (b) Collins, D. M.; Cotton, F. A.; Koch, S. A.; Millar, M.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 2017.

[6] Cotton, F. A.; Koch, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 7371.

[7] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[8] Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

[9] (a) San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140. (b) San Filippo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Ibid.* **1974**, *13*, 2121. (c) Glickman, H. P.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Ibid.* **1976**, *15*, 2205. (d) Best, S. A.; Smith, T. J.; Walton, R. A. *Ibid.* **1978**, *17*, 99.

[10] Cotton, F. A.; Felthouse, T. R.; Lay, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 1431.

[11] Cotton, F. A.; Mott, G. N.; Schrock, R. R.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 6781.

[12] Kepert, D. L. "The Early Transition Metals"; Academic Press: New York, 1972; p 26.

[13] Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

[14] (a) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040. (b) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 3880.

0020-1669/83/1322-2801$01.50/0

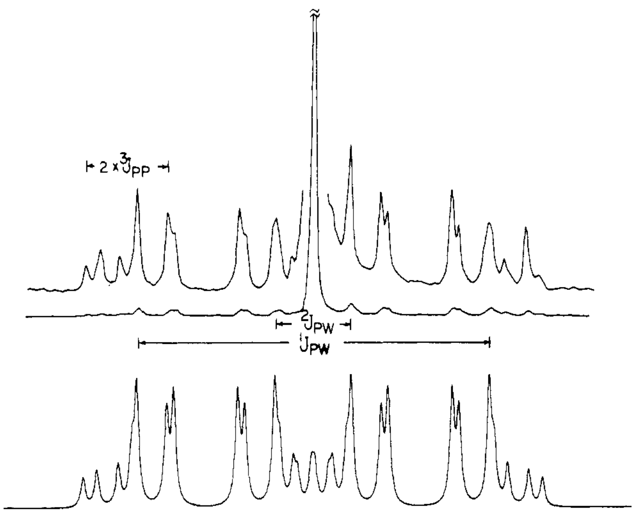
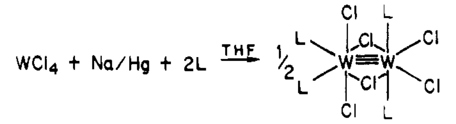


Figure 1. Bottom: Simulated ^{31}P NMR spectrum of $W_2Cl_4(PR_3)_4$ containing one ^{183}W nucleus, with $^1J_{PW} = 230$ Hz, $^2J_{PW} = 49$ Hz, and $^3J_{PP} = 27$ Hz. Top: $^{31}P\{^1H\}$ NMR spectrum of $W_2Cl_4(PBu_3)_4$ in $CDCl_3$.

If only 1 equiv of sodium amalgam is added to a mixture of WCl_4 and PMe_3 in tetrahydrofuran, a red crystalline complex with the formula $W_2Cl_6(PMe_3)_4$ can be isolated in 75% yield (eq 2). The ^1H and ^{31}P NMR spectra of this complex



(2)

suggest that it has a structure that is analogous to that found for $W_2Cl_6(py)_4$[15] (eq 2). Addition of a second equivalent (per W) of sodium amalgam to $W_2Cl_6(PMe_3)_4$ in tetrahydrofuran gives $W_2Cl_4(PMe_4)_4$ in 80% yield.

Reduction of WCl_4 in the Absence of Phosphines. Reduction of WCl_4 in tetrahydrofuran with 1 equiv of sodium amalgam produces a greenish yellow solution, from which green $W_2Cl_6(THF)_4$ can be isolated in good yield. NMR spectra show that two types of THF ligands are present. We propose that $W_2Cl_6(THF)_4$ has a structure analogous to that known for $W_2Cl_6(py)_4$[15] and postulated for $W_2Cl_6(PMe_3)_4$ (eq 2). $W_2Cl_6(THF)_4$ in THF does not react instantly with PMe_3, but after several minutes $W_2Cl_6(PMe_3)_4$ is formed quantitatively.

When $W_2Cl_6(THF)_4$ is treated with 2 equiv of sodium amalgam in tetrahydrofuran, an intense, brilliant blue color develops rapidly. If the solution is kept below 0 °C, a bright blue powder can be isolated by filtering the mixture and removing the solvent in vacuo. This blue powder analyzes as $Na_4(THF)_xW_2Cl_8$ where x is usually on the order of 1–2. Typically, $x \approx 1$ in a sample that has been exposed to a high vacuum for 12–16 h at 25 °C. $Na_4(THF)_xW_2Cl_8$ begins to decompose if heated above ~60 °C in vacuo, and we have not been able to obtain samples that are entirely free of carbon and hydrogen. Since there is not enough chloride ion present to form $Na_4(THF)_xW_2Cl_8$ from $W_2Cl_6(THF)_4$ and since we have never obtained a yield based on tungsten greater than 50%, we propose that the reaction proceeds as in eq 3. Unfortunately, the required chloride ion cannot be added during reduction since the $W_2Cl_9{}^{3-}$ ion is formed and $W_2Cl_9{}^{3-}$ is not reduced to $W_2Cl_8{}^{4-}$ by sodium amalgam in tetrahydrofuran. If $Na_4(THF)_xW_2Cl_8$ is dissolved in tetrahydrofuran at 25 °C, a black powder is deposited within a few minutes, leaving a colorless solution. The black powder analyzes approximately as WCl_2. At 0 °C, a solution of $Na_4(THF)_xW_2Cl_8$ is more stable and we have obtained a visible spectrum that shows a peak at 598 nm with an ϵ of ~1500 characteristic of a $\delta \rightarrow \delta^*$ transition in a complex containing a metal–metal quadruple bond.[4]

$$W_2Cl_6(THF)_4 + 2Na/Hg \xrightarrow[-30\,°C]{THF} {}^1/_2Na_4(THF)_xW_2Cl_8 + \text{“}WCl_2\text{”} \qquad (3)$$

If one attempts to prepare $Na_4(THF)_xW_2Cl_8$ directly from WCl_4 in THF using 2 equiv of sodium amalgam, variable and inevitably low yields are obtained. The problem may be some irreversible reaction of $Na_4(THF)_xW_2Cl_8$ with WCl_4 or with a precursor to $W_2Cl_6(THF)_4$. This hypothesis is supported by the fact that $W_2Cl_6(THF)_4$ can be prepared in situ and then reduced between −20 and 0 °C to give $Na_4(THF)_xW_2Cl_8$ in high yield.

A crystalline TMEDA derivative of $W_2Cl_8{}^{4-}$ can be prepared by adding an excess of TMEDA to a cold, nearly saturated solution of $Na_4(THF)_xW_2Cl_8$ in THF and keeping the solution at −40 °C. Dark blue crystals slowly form along with some green precipitate, which we believe to be approximately the same as that which forms in a few minutes when the dark blue crystals are redissolved in tetrahydrofuran at 25 °C. The dark blue crystals have the composition $Na_4(TMEDA)_4W_2Cl_8$ and do not lose TMEDA readily. At 0 °C a visible spectrum of a THF solution of $Na_4(TMEDA)_4W_2Cl_8$ shows a band at 600 nm with $\epsilon = 1660$. Although crystals of $Na_4(TMEDA)_4W_2Cl_8$ decomposed in an X-ray beam (possibly due to loss of TMEDA), it was possible to solve the structure and show that the complex is indeed a salt of $W_2Cl_8{}^{4-}$ in which four Na(TMEDA) units cap the four equivalent faces of the $W_2Cl_8{}^{4-}$ ion.[11,16]

We now believe that $Na_4(THF)_xW_2Cl_8$ is probably initially (or ideally) $Na_4(THF)_8W_2Cl_8$ with a structure analogous to that of $Na_4(TMEDA)_4W_2Cl_8$. However, THF is simply lost more readily than TMEDA. In fact, it is possible to prepare other complexes that we believe must be analogous to $Na_4(TMEDA)_4W_2Cl_8$. For example, addition of dimethoxyethane to a THF solution of $Na_4(THF)_xW_2Cl_8$ gives a vibrant blue powder that redissolves in tetrahydrofuran and subsequently decomposes to a black powder. Ethylenediamine reacts with $Na_4(THF)_xW_2Cl_8$ to give a dark blue precipitate that is insoluble in all common solvents. Addition of *N,N,N′,N′*-tetrabutylethylenediamine to $Na_4(THF)_xW_2Cl_8$ does not yield a blue precipitate; we believe that $Na_4(TBEDA)_4W_2Cl_8$ is formed but it is soluble and cannot be isolated before it decomposes to green products. Finally, addition of 18-crown-6 to a THF solution of $Na_4(THF)_xW_2Cl_8$ yields a sparingly soluble blue precipitate whose solutions show a band in the visible region at ~600 nm; even this complex decomposes in tetrahydrofuran at 25 °C to a black powder.

Addition of Et_4NCl or (PPN)Cl to THF solutions of $Na_4(THF)_xW_2Cl_8$ does not yield analogous Et_4N^+ or PPN^+ salts of $W_2Cl_8{}^{4-}$, probably because Et_4NCl and (PPN)Cl are not soluble enough to react with $Na_4(THF)_xW_2Cl_8$ before it decomposes. Addition of Bu_4NCl produces a blue to blue-green precipitate that is insoluble in all common solvents.

Reactions of $Na_4(THF)_xW_2Cl_8$. Samples of $Na_4(THF)_xW_2Cl_8$ were shown to react with PMe_3 or PBu_3 to give the $W_2Cl_4(PR_3)_4$ complexes essentially quantitatively (eq 4).

$$Na_4(THF)_xW_2Cl_8 + 4PR_3 \rightarrow 4NaCl + W_2Cl_4(PR_3)_4 \qquad (4)$$

---

(15) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

(16) The original preparation of a few crystals of $Na_4(TMEDA)_4W_2Cl_8$, which we believed at the time to be $W_2Cl_4(TMEDA)_2$, could not be reproduced, and much time was wasted trying to identify the green product to which $Na_4(TMEDA)_4W_2Cl_8$ decomposes in THF. In the meantime, Mott, working for several months with an incomplete set of data, decided the compound could not be $W_2Cl_4(TMEDA)_2$, but $Na_4(TMEDA)_4W_2Cl_8$. At about the same time we managed to reproduce the preparation, provide additional crystals for X-ray study, and obtain an analysis for C, H, N, and Cl.

Table I. Oxidation and Reduction Potentials for $M_2Cl_xL_4$ Complexes (V vs. SCE; x = 4 or 6)[a]

complex	solvent	$E_{1/2}$(ox)	$E_{1/2}$(red)
$W_2Cl_4(PBu_3)_4$	THF	0.04	−2.16
	CH_2Cl_2	−0.24	...
$Mo_2Cl_4(PBu_3)_4$	THF	0.64	−1.92
	CH_2Cl_2	0.38	...
$W_2Cl_6(PMe_3)_4$	CH_2Cl_2	0.29, 0.83	

[a] Scan rate 50 mV s^{-1}; Pt disk working electrode.

In one case ($x \approx 1$, $PR_3 = PMe_3$), the expected amount of sodium chloride was isolated. When the reaction is followed by UV–vis spectroscopy, the absorption due to $W_2Cl_8^{4-}$ disappears in ~10 min to give an intermediate species that absorbs at ~450, 370, and 730 nm. Slowly these absorptions decrease in intensity as those due to $W_2Cl_4(PMe_3)_4$ at 655 and 490 nm appear. The intermediate is likely to be a partially substituted ion, e.g., $W_2Cl_6(PMe_3)_2^{2-}$.

$Na_4(THF)_xW_2Cl_8$ reacts readily with 6-methyl-2-hydroxypyridine in the presence of triethylamine to give the known[7] compound $W_2(mhp)_4$ in ~75% yield. Unfortunately, analogous reactions involving carboxylic acids were not as successful. Yellow $W_2(O_2CCMe_3)_4$ can be prepared in ~50% yield. It can be recrystallized from hot heptane or sublimed at ~170 °C (with considerable decomposition). Its mass spectrum shows a parent ion with the correct isotope pattern for a compound containing two tungsten atoms. Its visible spectrum has one strong absorption at 360 nm (ϵ = 10 300). A reaction between $Na_4(THF)_xW_2Cl_8$, acetic acid, and triethylamine produces a yellow-brown powder, a solution of which also absorbs at 365 nm. A pure yellow product could not be obtained free of triethylammonium chloride by either crystallization or sublimation (with decomposition). Although the as yet unknown $W_2(O_2CCH_3)_4$ is likely to be present, we cannot be certain that other products in which the metal is more oxidized (see below) are not present. Therefore, we cannot yet confirm that we have prepared $W_2(O_2CCH_3)_4$.

Oxidations. Reversible one-electron oxidations of $W_2Cl_4L_4$ complexes have been observed by cyclic voltammetry (Table I). Similar oxidations have been reported for the Mo complexes with other phosphine ligands. The $E_{1/2}$ value (0.38 V vs. SCE) for $Mo_2Cl_4(PBu_3)_4$ in dichloromethane obtained here agrees well with that reported for $Mo_2Cl_4(PBu_3)_4$ (0.38 V vs. SCE).[17] Two trends are observed. First, oxidations are somewhat more difficult in THF than in dichloromethane (0.20 and 0.27 V more positive for W and Mo, respectively). This can be attributed, at least in part, to solvation effects and/or differences in junction potentials since ferrocene shows a similar shift ($E_{1/2}$ = 0.43 V vs. SCE in dichloromethane and 0.54 V vs. SCE in THF). Second, a comparison of the oxidation potentials for the Mo and W complexes shows that the W complexes are considerably easier to oxidize than the Mo complexes (by ~0.6 V in both dichloromethane and THF in each case). If a similar trend is observed for all W quadruply bonded complexes, this relative ease of oxidation could, in large part, explain the difficulty in obtaining W complexes by routes analogous to those used to prepare the more oxidatively robust Mo complexes. Indeed, evidence for such a trend is supported by chemical oxidation reactions of $W_2Cl_8^{4-}$ (vide infra).

One-electron reductions in THF were also observed (Table I), but instability of the anion product was apparent from $i_ci_a^{-1}$ values of less than 1. Reductions were not further investigated.

It is possible to oxidize $W_2Cl_4(PBu_3)_4$ chemically by using $[Ag(MeCN)_4]^+PF_6^-$ to give a brown, paramagnetic monocation (eq 5). The analogous molybdenum complex could be

$$W_2Cl_4(PBu_3)_4 + [Ag(MeCN)_4]^+PF_6^- \xrightarrow{CH_2Cl_2} [W_2Cl_4(PBu_3)_4]^+PF_6^- + Ag \quad (5)$$

prepared at −78 °C in dichloromethane with $[Ag(MeCN)_4]^+PF_6^-$, but at 0 °C the color of $Mo_2Cl_4(PBu_3)_4$ returned and only $Mo_2Cl_4(PBu_3)_4$ could be isolated.

The tungsten(III)–tungsten(III) complex $W_2Cl_6(PMe_3)_4$ is relatively difficult to oxidize, but two reversible oxidation waves were observed. A purple paramagnetic monocation could be prepared (eq 6), but the dication appeared to be unstable. The

$$W_2Cl_6(PMe_3)_4 + FeCp_2^+OTf^- \rightarrow [W_2Cl_6(PMe_3)_4]^+OTf^- + FeCp_2 \quad (6)$$

$$OTf = CF_3SO_3;\ Cp = \eta^5\text{-}C_5H_5$$

monocation could not be prepared cleanly by using $[Ag(MeCN)_4]^+PF_6^-$.

Early in these studies we thought it might be possible to prepare $W_2(O_2CCH_3)_4$ by protonating $W_2Cl_4(PBu_3)_4$ with acetic acid. At room temperature, the reaction between $W_2Cl_4(PBu_3)_4$ and acetic acid is slow and no single product could be obtained. At 160 °C a red complex could be obtained in moderate yield. An X-ray structural determination[10] showed it to be $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$, the tungsten having been oxidized in the process. An intermediate in this reaction is likely to be analogous to $W_2(\mu\text{-H})(\mu\text{-Cl})(PBu_3)_2Cl_2(O_2CPh)_2$, a recently prepared complex that forms on treating $W_2Cl_4(PBu_3)_4$ with 2 equiv of benzoic acid.[18]

Finally, we have shown that solutions containing $W_2Cl_8^{4-}$ react extremely rapidly with HCl to give $W_2Cl_9^{3-}$ quantitatively, even at −78 °C. Presumably an intermediate containing a bridging hydride ligand is formed (cf. $Mo_2Cl_8H^{3-}$ [19]), which reacts with another equivalent of HCl to produce molecular hydrogen and $W_2Cl_9^{3-}$ (eq 7). It is therefore clear why $W_2(mhp)_4$ reacts with HCl to give $W_2Cl_9^{3-}$ instead of $W_2Cl_8^{4-}$.[20]

$$W_2Cl_8^{4-} \xrightarrow{HCl} HW_2Cl_9^{4-} \text{ or } HW_2Cl_8^{3-} \xrightarrow{HCl} H_2 + W_2Cl_9^{3-} + Cl^- \quad (7)$$

Discussion

There has never been any good reason to suspect that the $W_2Cl_8^{4-}$ ion is inherently unstable.[21] However, as one might suspect on the basis of periodicity and the results shown in Table I, and as was shown by SCF–Xα–SW calculations,[21] $W_2Cl_8^{4-}$ should be more easily oxidized than $Mo_2Cl_8^{4-}$, perhaps too easily oxidized to be prepared in the presence of an oxidizing agent such as HCl. Indeed, we find that $W_2Cl_8^{4-}$ reacts with HCl to give $W_2Cl_9^{3-}$, even at −78 °C. Therefore, the synthesis of $W_2Cl_8^{4-}$ that has evolved is necessarily one that does not involve potential oxidizing agents. That is not to say the synthesis is necessarily straightforward. It is possible that the success of the reduction of $W_2Cl_6(THF)_4$ to give $W_2Cl_8^{4-}$ and "WCl_2" rests on some as yet unappreciated, subtle aspects of the reaction mechanism. It is nevertheless interesting to note that the reduction product is not $W_2Cl_4(THF)_4$, an analogue of the isolable phosphine complexes, as we at times, and others,[22] have assumed.

A frustrating problem with $Na_4(THF)_xW_2Cl_8$ as a starting material is its instability in any solvent in which it dissolves. It seems reasonable to propose that in tetrahydrofuran $Na_4(THF)_xW_2Cl_8$ simply loses sodium chloride as shown in eq 8.

$$Na_4(THF)_xW_2Cl_8 \xrightarrow{THF} 4NaCl + 2WCl_2 \quad (8)$$

---

[17] Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

[18] Cotton, F. A.; Mott, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 5978.

[19] Bino, A.; Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1982**, *21*, 3755.

[20] DeMarco, D.; Nimry, T.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 575.

[21] Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1977**, *16*, 2386.

[22] Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880.

We must emphasize that we have have not proven this to be the case; i.e., among other possibilities, tetrahydrofuran could be more intimately involved in the decomposition process.

The $W_2Cl_4L_4$ complexes could form in many ways in the reaction where WCl_4 is reduced in the presence of L, but the two shown in eq 9 and 10 seem most likely. Since WCl_4 reacts

$$WCl_4 \rightarrow W_2Cl_6(THF)_4 \xrightarrow{A} W_2Cl_6L_4 \xrightarrow{B} W_2Cl_4L_4 \qquad (9)$$

$$WCl_4 \rightarrow W_2Cl_6(THF)_4 \xrightarrow{C} W_2Cl_8^{4-} \xrightarrow{D} W_2Cl_4L_4 \qquad (10)$$

fairly slowly with L to give monomeric complexes, reduction of WCl_4 to $W_2Cl_6(THF)_4$ is the postulated first step in each sequence. Qualitatively it appears that the reduction steps B and C are both fast, while the substitution steps A and D are relatively slow but have approximately the same rates. Quantitative rate studies are clearly required in order to determine which sequence is the more likely.

The main problem in forming carboxylate complexes from $Na_4(THF)_xW_2Cl_8$ is probably primarily the competitive decomposition of $Na_4(THF)_xW_2Cl_8$ in tetrahydrofuran under conditions where the chlorides are substituted by carboxylates. Yet the method does appear promising. Besides the pivalate derivative we report here, $W_2(CF_3CO_2)_4\cdot{}^2/_3(\text{diglyme})$[22] and $W_2(C_6H_5CO_2)_4(THF)_2$[23] have been prepared by reactions in which $W_2Cl_8^{4-}$ is likely to be an intermediate. Recently Sattelberger[24] has found that $W_2(O_2CCMe_3)_4$ can be prepared in high yield if the pivalate source is present in excess before WCl_4 is reduced. Under these conditions it is possible that tungsten(III)–tungsten(III) intermediates such as $W_2Cl_4(O_2CCMe_3)_2(THF)_2$ or $W_2Cl_2(O_2CCMe_3)_4$ are formed and that these are then reduced in high yield to tungsten(II)–tungsten(II) compounds. Therefore, future preparations of carboxylate complexes may be more successful if they are designed around reducible tungsten(III)–tungsten(III) complexes rather than $Na_4(THF)_xW_2Cl_8$. It is at least quite clear now that the $W_2(O_2CR)_4$ complexes are not likely to be prepared in the presence of the carboxylic acid. Does $W_2(O_2CCH_3)_4$ exist? There is now no good reason why it should not; we probably have prepared an impure form of it. To find a method of purifying it is now the challenge.

Experimental Section

All operations were performed under a nitrogen atmosphere, in a Vacuum Atmospheres drybox or by Schlenk techniques. Solvents and reagents were dried and purified by standard techniques under nitrogen. WCl_4 was prepared by McCarley's method as detailed below.[25] PMe_3 was prepared by the method of Wolfsberger and Schmidbauer[26] using dibutyl ether instead of diethyl ether.[27] Other phosphines and reagents were purchased from standard sources. Ferricinium triflate was prepared from ferrocene and silver triflate (Aldrich). $[Ag(MeCN)_4]^+PF_6^-$ was prepared by crystallizing $Ag^+PF_6^-$ (Aldrich) from acetonitrile by adding ether.

^{13}C NMR spectra are reported in the proton-gated decoupled mode (unless otherwise noted). If coupling to tungsten can be observed in the proton broad-band decoupled spectrum, then it is reported as part of the data for the ^1H-gated decoupled spectrum even though in this mode long-range C–H coupling usually obscures small C–W couplings.

Mass spectra were run on a Varian Mat 44 Spectrometer. Reported peaks are those containing the ^{184}W isotope. All peaks show the correct single or double tungsten isotope pattern.[28]

Electrochemical measurements were performed with a PAR Model 173 potentiostat, a Model 145 voltage programmer, and a Model 179 digital coulometer. All measurements were made under an atmosphere of Ar. Potentials are referenced to an SCE electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAP). EPR spectra were recorded on a Varian E-9 (9.18 GHz) spectrometer.

The ^{31}P NMR spectrum was simulated as an A_2B_2 system with $\delta << J$ by using a Nicolet spectrosimulation program on a Nicolet 1280 computer. The experimental coupling constants were used ($^1J_{PW} = 230$ Hz, $^2J_{PW} = 49$ Hz, $^3J_{PP} = 27$ Hz), and the line width was 3.6 Hz.

WCl_4.[25] Solid WCl_6 (99 g, 0.25 mol) and $W(CO)_6$ (44 g, 0.125 mol) were combined in a 500-mL flask equipped with a mechanical stirrer. Dry chlorobenzene (300 mL) was then added. Gas evolution started immediately. (*Caution*! The CO should be vented to a hood.) The mixture was heated to reflux while being stirred until no more gas evolved (~12 h). The dark green-gray product was filtered off, washed with chlorobenzene, thoroughly rinsed with dichloromethane or pentane, and dried; the yield was virtually quantitative. It is vitally important to free the product of all traces of chlorobenzene in order to obtain a clean reduction to $W_2Cl_8^{4-}$ in THF.

$W_2Cl_4(PBu_3)_4$. Sodium amalgam (0.41%, 354 g, 80 mmol of Na) and PBu_3 (18 g, 88 mmol) were added to cold (−30 °C) THF (200 mL) followed by WCl_4 (13 g, 40 mmol). The mixture was shaken periodically as it warmed to room temperature. After ~0.5 h, the blue-green solution was decanted from the mercury and filtered through Celite. All solvent was removed from the filtrate in vacuo, and the residue was extracted with pentane. The extract was filtered, and the pentane was removed in vacuo. The resulting oily, dark blue-green, crystalline mass was washed three times with 25 mL of acetonitrile and dried in vacuo (yield 22.4 g, 85%): ^1H NMR (C_6H_6) δ 2.70 (br m, 24, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_2Me}$), 1.60 (br m, 48, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{Me}$), 1.10 (m, 36, $\mathrm{PCH_2CH_2CH_2}\mathit{Me}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 4 (s with complex satellite pattern; $J_{PW} \approx 230$ Hz, $^2J_{PW} \approx 49$ Hz, $^3J_{PP} \approx 27$ Hz; see Figure 1); mol wt (cryoscopic, cyclohexane) calcd 1317, found 1320.

$W_2Cl_4(PMe_3)_4$. The procedure was the same as in the preparation of $W_2Cl_4(PBu_3)_4$ except the first crop of crystals was obtained directly from the reaction mixture as the solvent was being removed in vacuo. The residue was washed with acetonitrile and shown to be pure $W_2Cl_4(PMe_3)_4$ by ^1H and ^{13}C NMR (total yield 66%): ^1H NMR ($CDCl_3$) δ 1.60 (br m, PMe_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −7 (s with complex satellite pattern; $J_{PW} \approx 236$ Hz, $^2J_{PW} \approx 51$ Hz, $^3J_{PP} \approx 28$ Hz); mass spectrum *m/z* 814 (parent), 738 (parent − PMe_3), 662 (parent − $2PMe_3$). Anal. Calcd for $WC_6H_{18}Cl_2P_2$: C, 17.71; H, 4.47. Found: C, 17.82; H, 4.52.

$W_2Cl_4(PMe_2Ph)_4$. The procedure was the same as in the preparation of $W_2Cl_4(PBu_3)_4$ (yield 90%): ^1H NMR ($CDCl_3$) δ 7.41 (br m, 20, $\mathrm{PMe_2}\mathit{Ph}$), 2.22 (m, 24, $\mathrm{P}\mathit{Me}_2\mathrm{Ph}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −1 (s with complex satellite pattern; $J_{PW} \approx 236$ Hz, $^2J_{PW} \approx 49$ Hz, $^3J_{PP} \approx 28$ Hz).

$W_2Cl_4(PMePh_2)_4$. The procedure was the same as in the preparation of $W_2Cl_4(PBu_3)_4$, but the product is only moderately soluble in THF. Therefore, after filtering the reaction mixture, the Celite was extracted exhaustively with dichloromethane. The extract and the filtrate were combined, and the volume was reduced to a minimum in vacuo to give the green microcrystalline product in 88% yield. It dissolves slowly in dichloromethane. Small, metallic green flakes were grown for analysis from a mixture of dichloromethane and ether: ^1H NMR (CH_2Cl_2) δ 7.30 (br m, 40, $\mathrm{PMe}\mathit{Ph}_2$), 1.80 (m, 12, $\mathrm{P}\mathit{Me}\mathrm{Ph_2}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 2 (s with complex satellite pattern; $J_{PW} \approx 234$ Hz, $^2J_{PW} \approx 51$ Hz, $^3J_{PP} \approx 28$ Hz). Anal. Calcd for $WC_{26}H_{26}Cl_2P_2$: C, 47.66; H, 4.00. Found: C, 47.44; H, 4.15.

$W_2Cl_4(dmpe)_2$. $W_2Cl_4(PBu_3)_4$ (3.95 g, 3 mmol) was dissolved in 40 mL of toluene, and dmpe (0.90 g, 6 mmol) was added. The mixture was heated to 60 °C for 16 h and then to 90 °C for 4 h. The green crystals that formed were filtered off, leaving a brown solution (yield 2.18 g, 89% based on $W_2Cl_4(dmpe)_2$). Analysis- and X-ray-quality crystals were grown by cooling a solution of $W_2Cl_4(dmpe)_2$ in a mixture of dichloromethane and toluene and contained one toluene per dimer: $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 31 (s); mass spectrum *m/z* 810 (parent), 795 (parent − Me). Anal. Calcd for $WC_{9.5}H_{20}Cl_2P_2$: C, 25.30; H, 4.48. Found: C, 25.28; H, 4.68.

$W_2Cl_4(dppe)_2$. The procedure was similar to that used to prepare $W_2Cl_4(dmpe)_2$. A mixture of brown and green isomers was obtained. At 90 °C, where the yield was highest (60%), the ratio of the brown to green isomers was 9:1. At lower temperatures, the fraction of the brown isomer increased. Anal. Calcd for $WC_{26}H_{24}Cl_2P_2$: C, 47.81; H, 3.70. Found (9:1 mixture): C, 48.25; H, 4.01.

---

(23) Cotton, F. A.; Wang, W. *Inorg. Chem.* **1982**, *21*, 3859.

(24) Sattelberger, A. P., personal communication.

(25) Schaefer-King, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

(26) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

(27) Sharp, P. R. Ph.D. Thesis, Massachusetts Institute of Technology, 1980.

(28) Chisholm, M. H.; Haitko, D. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046.

$W_2Cl_6(THF)_4$. WCl_4 (13 g, 40 mmol) was added to 200 mL of THF containing sodium amalgam (80 mmol), and the mixture was stirred for 1 h. The resulting yellow-green mixture was filtered through Celite. The solvent was removed in vacuo, and the resulting oil was triturated with pentane to give a yellow-green powder. This powder was dissolved in a minimum volume of THF, and 3 volumes of pentane were added. After the solution stood at −30 °C for 1 day, green needles (86%) were isolated by filtration: ^{1}H NMR (CH_2Cl_2) δ 4.33 (m, 8, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}}$), 3.80 (m, 8, $\overline{\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{O}'}$), 2.80 (m, 16, $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}}$ and $\overline{\mathrm{CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2O}'}$). Anal. Calcd for $WC_8H_{16}Cl_3O_2$: C, 22.12; H, 3.71. Found: C, 22.30; H, 3.83.

$W_2Cl_6(PMe_3)_4$. A solution of $W_2Cl_6(THF)_4$ in THF slowly turned dark red on addition of 4 equiv of PMe_3. After 0.5 h the THF was removed in vacuo to leave 0.65 g of dark red crystals (74%). Red needles could be grown from a mixture of dichloromethane and ether: ^{1}H NMR (CH_2Cl_2) δ 1.40 (s, 9, PMe_3), 0.75 (s, 9, PMe_3'); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 200 (vbr s, PMe_3), −150 (br s, PMe_3'); mass spectrum *m/z* 733 (parent − $2PMe_3$), 581 (parent − $4PMe_3$). Anal. Calcd for $WC_6H_{18}Cl_3P_2$: C, 16.29; H, 4.10. Found: C, 16.37; H, 4.14.

$W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3$. $W_2Cl_4(PBu_3)_4$ (5 g, 3.80 mmol) was dissolved in 5 mL of glyme, and glacial acetic acid (1.9 mL, 34.2 mmol) was added. The tube was sealed and heated to 160 °C for 4 h. The contents were flushed down a column (1 in. × 6 in.) of grade I alumina with ether. The solvents were removed in vacuo, and the residue was dissolved in a minimum volume of toluene. The solution was cooled to −30 °C to give a first crop of 1.30 g. Pentane was added to the mother liquor to give a second crop of 0.2 g (total yield 1.5 g, 40%): ^{1}H NMR ($CDCl_3$) δ 2.15–1.20 (m, 54, $P(C\mathit{H}_2)_3Me$), 2.03 (s, 3, $MeCO_2$), 0.91 (t, $^2J_{HP}$ = 7 Hz, 27, $P(CH_2)_3\mathit{Me}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 185 (s, $Me\mathit{C}O_2$), 25–21 ($P(\mathit{C}H_2)_3Me$), 24 (s, $MeCO_2$), 14 (s, $P(CH_2)_3\mathit{Me}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 7 (s with ^{183}W satellites, J_{PW} = 370 Hz, 2 PBu_3), 5 (s with ^{183}W satellites, J_{PW} = 358 Hz, PBu_3'). Anal. Calcd for $W_3C_{38}H_{84}Cl_5O_4P_3\cdot{}^1/_2C_7H_8$: C, 32.82; H, 5.84. Found: C, 33.13; H, 6.05.

$[W_2Cl_4(PBu_3)_4]^+PF_6^-$. $[Ag(MeCN)_4]^+PF_6^-$ (0.33 g, 0.83 mmole was slowly added to a stirred solution of $W_2Cl_4(PBu_3)_4$ (1.10 g, 0.83 mmol) in 3 mL of dichloromethane. The resulting brown solution was filtered to remove silver, and the dichloromethane was removed in vacuo. The oily residue was washed with pentane and dissolved in a minimum volume of ether. The solution was cooled to −30 °C for 16 h to give 0.85 g (70%) of brown crystals that are soluble in toluene, THF, acetonitrile, and chlorobenzene: EPR (CH_2Cl_2, −196 °C) $g_\parallel$ = 1.97, $g_\perp$ = 1.82. Anal. Calcd for $W_2C_{48}H_{108}Cl_4F_6P_5$: C, 39.39; H, 7.44. Found: C, 38.87; H, 7.41.

Observation of $[Mo_2Cl_4(PBu_3)_4]^+PF_6^-$. $Mo_2Cl_4(PBu_3)_4$ (0.14 g, 0.13 mmol) was dissolved in 10 mL of dichloromethane. The solution was cooled to −78 °C, and $[Ag(MeCN)_4]^+PF_6^-$ (0.05 g, 0.14 mmol) in 3 mL of dichloromethane was added with stirring to give an emerald green solution. An aliquot was removed for an EPR spectrum. The remaining solution was warmed to room temperature. At 0 °C the solution began to turn blue. Workup of the mixture gave only $Mo_2Cl_4(PBu_3)_4$: EPR (CH_2Cl_2, −196 °C) $g_\parallel$ = 2.00, $g_\perp$ = 1.96. This agrees well with the values for the PPr_3 analogue.[17]

$[W_2Cl_6(PMe_3)_4]^+[CF_3SO_3]^-$. Ferricenium triflate (0.17 g, 0.5 mmol) was added to a solution of $W_2Cl_6(PMe_3)_4$ (0.44 g, 0.5 mmol) in 5 mL of dichloromethane. Ether (3 mL) was added, and the solution was cooled to −30 °C for 16 h. Dark purple crystals (0.40 g) were removed by filtration. The solvent was removed from the filtrate in vacuo, and the resulting residue washed with toluene. The residue was dissolved in a minimum volume of dichloromethane, and 3 volumes of ether were added to give 0.11 g of crystals (total yield 0.51 g, 98%). Anal. Calcd for $W_2C_{13}H_{26}Cl_6P_4F_3O_3S$: C, 15.10; H, 3.51. Found: C, 15.33; H, 3.55.

$Na_4(THF)_xW_2Cl_8$. Sodium amalgam (70 g, 0.46%, 14 mmol) was added to a solution of $W_2Cl_6(THF)_4$ (4.34 g, 5 mmol) in THF (60 mL) that had been cooled to −40 °C, and the mixture was shaken vigorously for 15 min. The royal blue solution was decanted away from the mercury and filtered through Celite to remove residual mercury, sodium chloride, and a black precipitate. The Celite was washed with a total of ~20 mL of THF. The THF was removed in vacuo from the combined filtrates. The resulting royal blue powder was redissolved in minimum amount of THF (~60 mL), and the solution was filtered through Celite again to remove a small amount of the black precipitate. The THF was removed in vacuo to give a royal blue microcrystalline powder. All operations were performed as rapidly as possible in an attempt to keep the temperature of any solution below 0 C. Typical yields are ~3.4 g. If $Na_4(THF)_xW_2Cl_8$ is prepared without isolating the $W_2Cl_6(THF)_4$, the yield is ~3.0 g: UV–vis (THF, 0 °C) λ_{max} 598 nm (ϵ ~1500). For a sample left at 0.1 μm for ~1 h: Anal. Calcd for $W_2C_8H_{16}O_2Cl_8N_4$: C, 10.83; H, 1.82; Cl, 31.96. Found: C, 9.03; H, 1.57; Cl, 31.06. For a sample left at 0.1 μm at room temperature overnight: Anal. Calcd for $W_2C_4H_8OCl_8N_4$: C, 5.89; H, 0.98; Cl, 34.78; Na, 11.28. Found: C, 4.96; H, 0.84; Cl, 33.83; Na, 11.80.

$Na_4(DME)_4W_2Cl_8$. 1,2-dimethoxyethane (30 mL) was added to a solution of $Na_4(THF)_xW_2Cl_8$ (2.5 mmol) in THF (80 mL) (which had been prepared as above not not isolated) to give shiny blue microcrystals (yield 2.72 g). This material can also be prepared directly from WCl_4 in a manner analogous to that used to prepare $Na_4(THF)_xW_2Cl_8$ except using DME as the solvent instead of THF. However, $Na_4(DME)_4W_2Cl_8$ is insoluble in DME and must be extracted from the Celite with THF.

$Na_4(DME)_4W_2Cl_8$ is more stable thermally than $Na_4(THF)_xW_2Cl_8$ and can be recrystallized, with care, from a 5:1 mixture of THF and DME at −78 °C: UV–vis (THF) λ_{max} 595 nm (ϵ 1640).

$Na_4(TMEDA)_4W_2Cl_8$. TMEDA (0.7 mL, 4.64 mmol) was added to a solution of $Na_4(THF)_xW_2Cl_8$ (0.8 g) in THF (20 mL), which had been cooled to −40 °C. The solution was immediately placed in a refrigerator (−40 °C). After 18 h the first crop of blue crystals was isolated by decanting off the mother liquor along with some green precipitate. The dark blue crystals were washed three times with pentane (3 mL) and dried in vacuo. The mother liquor from above was filtered and quickly placed back in the refrigerator. A second crop of crystals was isolated in the same way. By this time, the mother liquor was olive green due to decomposition of $Na_4(TMEDA)_4W_2Cl_8$ and was discarded (total yield 0.61 g): UV–vis (THF, 0 °C) λ_{max} 600 nm (ϵ 1657), 480 (sh), 385 (ϵ 769). Anal. Calcd for $W_2C_{12}H_{32}N_4Cl_4Na_2$: C, 23.86; H, 5.34; N, 9.28; Cl, 23.48. Found: C, 23.77; H, 5.30; N, 8.96; Cl, 23.09.

Reaction of $Na_4(THF)_xW_2Cl_8$ with Phosphines. Trimethylphosphine (3 mL, 31.5 mmol) was added to a solution of $Na_4(THF)_xW_2Cl_8$ ($x \approx 1$, 0.60 g, 0.74 mmol) in THF (30 mL) that had been cooled to −30 °C. After 5 h at 25 °C the solvent and excess PMe_3 were removed from the green solution in vacuo, and the solid, dark green residue was extracted with dichloromethane (35 mL). The extract mixture was filtered to remove NaCl (0.168 g, 98%). The dichloromethane was removed in vacuo to give 0.58 g of $W_2Cl_4(PMe_3)_4$ (97%). $W_2Cl_4(PMe_3)_4$ was identified by ^{31}P NMR (−7 ppm) and by its UV–vis spectrum [λ_{max} 657 nm (ϵ 4100), 490 (ϵ 350)].

A similar reaction involving PBu_3 gave high yields of $W_2Cl_4(PBu_3)_4$.

$W_2(mhp)_4$. To a solution of $Na_4(THF)_xW_2Cl_8$ (0.798 g) in THF (30 mL) at −30 °C was added a THF (5 mL) solution of methylhydroxypyridine (Hmhp) (0.437 g, 4 mmol) and triethylamine (0.56 mL, 4 mmol) that had been cooled to −30 °C. The mixture was warmed to room temperature, and after 1 h the THF was removed in vacuo. The residue was extracted with toluene, and the extract was filtered. Toluene was removed in vacuo to give 0.453 g of bright red $W_2(mhp)_4$, which was identical with a sample prepared by Cotton's method.[7]

Preparation of $W_2(O_2CCMe_3)_4$. To a solution of $Na_4(THF)_xW_2Cl_8$ (1.5 mmol) in THF (70 mL) at −30 °C was added (dropwise) a −30 °C solution of pivalic acid (1.35 mL, 12 mmol) and triethylamine (1.67 mL, 12 mmol) in THF (10 mL). The resulting solution was allowed to warm to room temperature over 20 min during which time it turned yellow-brown. The THF was removed in vacuo, and the semisolid mass was extracted with ether. The extract was filtered, and the ether was removed in vacuo. The residue was washed with pentane to give 0.65 g (56%) of a yellow powder, which could be recrystallized from hot heptane or sublimed (with considerable decomposition) at 170 °C and <0.001 μm: ^{1}H NMR (C_6H_6) δ 1.4 (s, $(CH_3)_3CCO_2$); ^{13}C NMR (toluene-d_8) δ 184.0 (s, $Me_3C\mathit{C}O_2$), 38.7 (s, $Me_3\mathit{C}CO_2$), 27.4 (q, $^1J_{CH}$ = 126 Hz, $(\mathit{C}H_3)_3CCO_2$); mass spectrum *m/z* 772 (parent), 757 (parent − CH_3); UV–vis (toluene) λ_{max} 360 nm (ϵ 10400).

Acknowledgment. We thank the National Science Foundation for supporting this research. L.G.S. acknowledges a postgraduate scholarship from the Natural Sciences and Engineering Research Council of Canada. We thank M. S. Wrighton and W. E. Geiger for helpful discussions and use

of electrochemical equipment.

Registry No. $W_2Cl_4(PBu_3)_4$, 73133-23-0; $W_2Cl_4(PMe_3)_4$, 73495-54-2; $W_2Cl_4(PMe_2Ph)_4$, 73133-21-8; $W_2Cl_4(PMePh_2)_4$, 73133-22-9; $W_2Cl_4(dmpe)_2$, 73133-09-2; $W_2Cl_4(dppe)_2$, brown isomer, 73133-24-1; $W_2Cl_4(dppe)_2$, green isomer, 86782-93-6; $W_2Cl_6(THF)_4$, 77479-88-0; $W_2Cl_6(PMe_3)_4$, 73146-59-5; $W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3$, 73470-14-1; $[W_2Cl_4(PBu_3)_4]^+PF_6^-$, 86728-81-6; $[W_2Cl_6(PMe_3)_4]^+[CF_3SO_3]^-$, 86747-51-5; $Na_4(DME)_4W_2Cl_8$, 86747-52-6; $Na_4(TMEDA)_4W_2Cl_8$, 83232-09-1; $W_2(mhp)_4$, 67634-84-8; $W_2(O_2CCMe_3)_4$, 86728-84-9; $Mo_2Cl_4(PBu_3)_4$, 39306-31-5; WCl_4, 13470-13-8; $FeCp_2^+OTf^-$, 86728-83-8; $[Ag(MeCN)_4]^+PF_6^-$, 86728-82-7; W, 7440-33-7.

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Synthesis and Reactivity of $[Ir(\eta^2\text{-}E_2R)(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$ (E = S, Se; R = H, CH_3)

JOHN E. HOOTS and THOMAS B. RAUCHFUSS*

Received October 19, 1982

The stereochemistry and reactivity of $[Ir(E_2R)(dppe)_2]^{2+}$ (dppe = $Ph_2P(CH_2)_2PPh_2$; E = S, Se; R = H, CH_3) have been examined. In solution, $[Ir(E_2CH_3)(dppe)_2]^{2+}$ exists as a mixture of two diastereomers in the ratio of 20:1 (E = S) and 6:1 (E = Se). Protonation of $[Ir(E_2)(dppe)_2]^+$ with strong acids gave $[Ir(E_2H)(dppe)_2]^{2+}$ complexes, which are spectroscopically and stereochemically similar to the η^2-E_2CH_3 derivatives. In contrast to $[Ir(S_2)(dppe)_2]^+$, the $[Ir(S_2CH_3)(dppe)_2]^{2+}$ (**1**) complex can act as both a potent sulfur atom and CH_3S^+ transfer reagent. The nature of the S-transfer reaction depends on the substrate (X) used and the stability of the corresponding S–X and $[X\text{–}SCH_3]^+$ products. **1** reacts rapidly with PPh_3 (2 equiv) to give $[Ir(dppe)_2]^+$, Ph_3PS, and $[Ph_3PSCH_3]^+$. With CH_3NC (2 equiv) and **1**, sulfur atom transfer occurs, and *cis*-$[Ir(SCH_3)(CH_3NC)(dppe)_2]^{2+}$ and CH_3NCS are produced. Reaction of CN^- with **1** gave *cis*-$[Ir(SCH_3)(SCN)(dppe)_2]^+$. Oxidative addition of CH_3SH and CH_3SCl to $[Ir(dppe)_2]^+$ gave $[Ir(SCH_3)H(dppe)_2]^+$ and $[Ir(SCH_3)Cl(dppe)_2]^+$, respectively. ^1H NMR species confirmed the utility of the high-field ortho phenyl, the S_2CH_3, and the SCH_3 resonances in structure elucidation. Also described is the applicability of gel-permeation chromatography and field-desorption mass spectrometry for the purification and characterization of these ionic, high molecular weight complexes.

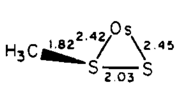
Introduction

In recent years, considerable attention has been directed toward the synthetic and catalytic chemistry of metal sulfides. Within the realm of sulfur-rich metal complexes, the reactivities of disulfur and pentasulfido ligands have been particularly fruitful areas of research.[1,2] A second class of sulfur-rich metal complexes, the perthiocarboxylates, has also received considerable attention.[3]

In this report, we describe reactivity studies on the simplest organic perthio ligand, S_2CH_3, as found in $[Ir(\eta^2\text{-}S_2CH_3)(dppe)_2]^{2+}$ (dppe = $Ph_2PCH_2CH_2PPh_2$). Salts of this ion were first prepared in 1979 via the alkylation of $[Ir(S_2)(dppe)_2]^+$:[4]

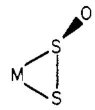
$$[Ir(S_2)(dppe)_2]^+ \xrightarrow[25°C]{CH_3OSO_2F} [Ir(\eta^2\text{-}S_2CH_3)(dppe)_2]^{2+} \qquad (1)$$

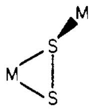
The geometry about the perthio ligand in this iridium complex is presumed to resemble that found crystallographically in $[Os(\eta^2\text{-}S_2CH_3)(CO)_2(PPh_3)_2]ClO_4$:[5]



$\angle SOsS = 49.1°$
$\angle OsSS = 65.9°, 65.0°$
$\angle SSC = 105.4°$
$\angle OsSC = 117.4°$

As such, the η^2-S_2CH_3 ligand is structurally and electronically related to other derivatives of the S_2 ligand such as





which can be found, inter alia, in $[Ir(S_2O)(dppe)_2]Cl$[6] and $[Mo_4(NO)_4S_{13}]^{4-}$,[7] respectively. Therefore, characterization of the reactivity of the η^2-S_2CH_3 ligand is relevant to the chemistry of other sulfur-rich metal complexes.

Cysteine perthiolate ligation has been considered in the context of two enzymatic processes. Arguments have been advanced that both rhodanese[8] and xanthine oxidase[9] contain perthiolates at their active sites. Characteristic reactions of each enzyme involve the formation of thiocyanate upon treatment with cyanide (eq 2). In the case of xanthine oxidase, this process deactivates the enzyme,[10] while eq 2 is but one of the many manifestations of the catalytic sulfur-transfer properties of rhodanese.[8]

$$E{\cdot}S + CN^- \rightarrow E + SCN^- \qquad (2)$$

Reactivity studies on η^2-S_2CH_3 complexes bear on the chemistry of the η^2-O_2R ligand, which is presumed to be a

---

(1) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245. Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551 and references therein.

(2) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947 and references therein.

(3) Fackler, J. P., Jr.; Fetchin, J. A.; Fries, D. C. *J. Am. Chem. Soc.* **1973**, *94*, 7323 and references therein.

(4) Plute, K. L. K.; Haltiwanger, R. C.; Rakowski DuBois, M. *Inorg. Chem.* **1979**, *18*, 3246.

(5) Clark, G. R.; Russell, D. R. *J. Organomet. Chem.* **1979**, *173*, 377.

(6) Schmid, G.; Ritter, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 645.

(7) Müller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 168.

(8) Sörbo, B. In "Metabolic Pathways"; Greenberg, D. M., Ed.; Academic Press: New York, 1975; pp 433–453. Westley, J. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1973**, *39*, 327.

(9) Massey, V.; Edmondson, D. *J. Biol. Chem.* **1970**, *245*, 6595. Coughlan, M. P. "Molybdenum and Molybdenum-Containing Enzymes"; Pergamon Press: New York, 1980; pp 148–149. Stiefel, E. I. *Ibid.*, pp 73–74, 88–90.

(10) Gutteridge, S.; Tanner, S. J.; Bray, R. C. *Biochem. J.* **1978**, *175*, 887.