

Triangular Trinuclear Cluster Compounds: Molybdenum and Tungsten Complexes of the Type $[M_3S_4(\text{diphos})_3X_3]^+$ with $X = \text{Cl}$ and H

F. Albert Cotton,* Rosa Llusar, and Cassandra T. Eagle

Contribution from Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. Received November 9, 1988

Abstract: New synthetic methods of an essentially nonaqueous nature are reported for the preparation of compounds containing the $\text{Mo}_3\text{S}_4^{4+}$ and $\text{W}_3\text{S}_4^{4+}$ cluster cores surrounded by a combination of diphosphine ligands and either Cl^- or H^- ligands. The synthetic methods entail reactions of $\text{MoCl}_3(\text{THF})_3$ or WCl_4 with NaHS and dmpe (or depe) in THF to obtain the chloro species and treatment of tungsten chloro compounds with LiBH_4 to obtain the hydrido compounds. The new compounds described in detail (including crystal structures for those marked*) are as follows: $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3][\text{PF}_6]\cdot\text{CH}_3\text{OH}^*$ (**1**), $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3][\text{PF}_6]\cdot\text{H}_2\text{O}^*$ (**2**), $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3][\text{PF}_6]^*$ (**3**), $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]^*$ (**4**), and $[\text{W}_3\text{S}_4\text{H}_3(\text{depe})_3][\text{BPh}_4]^*$ (**5**). Compounds **1** and **2** form isomorphous crystals in space group $R\bar{3}c$ with $Z = 6$; for **1**, $a = 15.310$ (7) Å and $c = 30.640$ (3) Å; for **2**, $a = 15.269$ (2) Å and $c = 30.620$ (6) Å. The two cations have almost identical dimensions, with $\text{Mo}-\text{Mo} = 2.766$ (4) Å, $\text{W}-\text{W} = 2.755$ (1) Å, and all other distances (e.g., $\text{M}-\text{S}$, $\text{M}-\text{Cl}$, $\text{M}-\text{P}$) equal within ± 0.01 Å. In each case, the dmpe ligands span positions such that one P is trans to $\mu_3\text{-S}$ and the other trans to a $\mu_2\text{-S}$ atom within the approximately octahedral coordination sphere, MS_3ClP_2 , about each metal atom. The cations are therefore chiral. The $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3]^+$ ion in compound **3** is very similar to the $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ ion in **2**. Compound **3** crystallizes in space group $P\bar{1}$ with $Z = 2$, $a = 15.552$ (6) Å, $b = 17.768$ (7) Å, $c = 10.572$ (3) Å, $\alpha = 106.54$ (3)°, $\beta = 98.25$ (3)°, $\gamma = 95.70$ (3)°. Compound **4** has a cation nearly isostructural with that in **2** except that each Cl atom is replaced by an (X-ray-invisible) H atom. The $\text{W}-\text{W}$ distances are equal in the two cations. Compound **4** crystallizes in space group $P2_1/c$ with $Z = 4$, $a = 14.947$ (2) Å, $b = 11.237$ (2) Å, $c = 32.942$ (5) Å, $\beta = 97.90$ (1)°. The two hydrido compounds, **4** and **5**, react smoothly with PhCOCl to regenerate the chloro compounds. The $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ ion undergoes two quasireversible one-electron reductions (-0.64 and -0.85 V vs Ag/AgCl electrode). The $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ and $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3]^+$ ions showed reductions at -1.11 and -1.12 V that appear to produce unstable products. NMR studies of the cation in **2**, **4**, and **5** support the formulation of **4** and **5** as hydride complexes. **4** and **5** show ^1H resonances at -0.914 and -0.80 ppm, respectively, which appear as doublets of doublets with $^2J_{\text{HP}}$ values of 30 and 45 Hz and satellites with $^1J_{\text{HW}}$ of ca. 30 Hz.

The earliest reports of what we now recognize as metal atom cluster compounds of molybdenum and tungsten were made in the period 1857-1861 by C. W. Bloomstrand.¹ Although his compounds were long thought to be trinuclear, crystallographic studies by Brosset² in the 1940s showed them to be hexanuclear, and it was not until the late 1970s that the first authentic discrete trinuclear triangular cluster species of molybdenum and tungsten were unequivocally identified.³⁻⁵ The past decade has seen a phenomenal rate of growth in the chemistry of these substances,⁶ and structurally similar compounds of niobium and tantalum have also recently been discovered.⁷

One of the most interesting and important subsets of these compounds are those containing the $\text{M}_3\text{S}_4^{4+}$ core, with C_{3v} symmetry and a set of $\text{Mo}-\text{Mo}$ or $\text{W}-\text{W}$ single bonds. In this paper we report entirely new synthetic entries into derivatives of these cores in which the additional ligands are bidentate diphosphines and chlorine atoms, as well as the conversion of the chloro species to hydrido species. The latter are the first hydrido compounds of this type of so-called "electron-poor" metal atom clusters.⁸ A

few of the results described here have been the subject of preliminary communications.⁹

Experimental Section

Materials and Methods. While all of the new compounds reported here are stable in air, both as solids and in solution, the preparative reactions were carried out under nitrogen or argon using Schlenk techniques in case any of the reaction intermediates might be unstable toward the laboratory atmosphere. 1,2-Bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), as well as most other reagents were obtained from commercial suppliers. The compounds MoCl_3 ,¹⁰ $\text{MoCl}_3(\text{THF})_3$,¹¹ WCl_4 ,¹² and NaHS ¹³ were prepared according to literature methods.

Solvents were of best commercial grade. Tetrahydrofuran (THF) and hexane were distilled from benzophenone ketyl, methanol from Mg, and CH_2Cl_2 from P_4O_{10} prior to use. Chromatography was performed on silica gel (American Scientific Products, 60 Å).

Spectroscopic measurements were made on a Cary 17D (UV-vis) and a Varian XL-200 spectrometer at 200 (^1H NMR) or 81 MHz (^{31}P NMR). Electrochemical measurements were performed on a Bioanalytical Systems, Inc., Model BAS 100 electrochemical analyzer in conjunction with a Houston Instruments Model DMP 40 digital plotter. $E_{1/2}$ values, determined as $(E_{\text{pa}} + E_{\text{pc}})/2$, were referenced to a Ag/AgCl electrode at ca. 22 °C.

X-ray crystallography was done in an essentially routine manner.^{14,15}

(1) Bloomstrand, C. W. *J. Prakt. Chem.* **1857**, 71, 449; **1859**, 77, 88; **1861**, 82, 433.

(2) Brosset, C. *Ark. Kemi* **1949**, Band 1, No. 43, and earlier papers summarized therein.

(3) Mennemann, K.; Mattes, R. *Z. Anorg. Allg. Chem.* **1977**, 437, 175.

(4) Müller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M. *Angew. Chem.* **1978**, 90, 564.

(5) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, 100, 5252.

(6) For some representative recent papers giving earlier references, see: (a) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *Inorg. Chem.* **1986**, 25, 3654. (b) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, 5, 357. (c) Huang, J.; Shang, M.; Huang, J.; Zhuang, H.; Lu, S.; Lu, J. *J. Struct. Chem.* **1982**, 1, 1 (in Chinese). (d) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *Chem. Lett.* **1987**, 2025. (e) Shibahara, T.; Takeuchi, A.; Kunimoto, T.; Kuroya, H. *Chem. Lett.* **1987**, 867.

(7) Cotton, F. A.; Diebold, M. P.; Feng, X.; Roth, W. *J. Inorg. Chem.* **1988**, 27, 3413.

(8) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 875.

(9) (a) Cotton, F. A.; Llusar, R. *Polyhedron* **1987**, 6, 1741. (b) Cotton, F. A.; Llusar, R. *Inorg. Chem.* **1988**, 27, 1303.

(10) Mallock, A. G. *Inorg. Nucl. Chem. Lett.* **1967**, 3, 441.

(11) Dilworth, J. R.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1983**, 397.

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

(13) Eibeck, R. E. *Inorg. Synth.* **1963**, 7, 128.

(14) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, 18, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, 50, 227.

(15) Calculations were done on the VAX 11/780 computer at the Department of Chemistry and on the local area VAX CLUSTER (VMS 4.6) at the Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX, with the SHELX-76, SHELX-86, and SDP software packages.

Table I. Crystal Data for $[W_3S_4Cl_3(depe)_3][PF_6]$ (3) and $[W_3S_4H_3(dmpe)_3][BPh_4]$ (4)

| formula | $W_3S_4Cl_3P_7F_6C_{30}H_{72}$ | $W_3S_4P_6C_{42}B_1H_{71}$ |
|---|--|--|
| fw | 1549.88 | 1452.5 |
| space group | $P\bar{1}$ | $P2_1/c$ |
| systematic absences | none | ($h0l$): $l = 2n + 1$; ($0k0$): $k = 2n + 1$ |
| a , Å | 15.552 (6) | 14.947 (2) |
| b , Å | 17.768 (7) | 11.237 (2) |
| c , Å | 10.572 (3) | 32.942 (5) |
| α , deg | 106.54 (3) | |
| β , deg | 98.25 (3) | 97.90 (1) |
| γ , deg | 95.70 (3) | |
| V , Å ³ | 2741 (4) | 5480 (2) |
| Z | 2 | 4 |
| d_{calc} , g/cm ³ | 1.878 | 1.76 |
| cryst size, mm | $0.3 \times 0.2 \times 0.2$; $0.3 \times 0.2 \times 0.1$ | $0.3 \times 0.2 \times 0.2$ |
| μ (Mo $K\alpha$), cm ⁻¹ | 69.56 | 67.65 |
| data col instrument | Rigaku AFC5R | Syntex P3 |
| radiation (monochromated in incident beam) | Mo $K\alpha$ ($\lambda_{\alpha} = 0.71073$ Å) | |
| orientation reflns: | 25, 20–30 | 15, 20–30 |
| no., range (2θ), deg | | |
| temp, °C | 21 | 20 |
| scan method | ω - 2θ | ω |
| data col range, 2θ , deg | 4–45 | 4–45 |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 5940, 4451 | 5785, 3848 |
| no. of params refined | 551 | 505 |
| trans factors: max, min | 1.35, 0.60; 1.334, 0.70 | 0.999, 0.521 |
| R^a | 0.0906 | 0.045 |
| R_w^b | 0.0762 | 0.050 |
| quality-of-fit indicator ^c | 1.525 | 1.058 |
| largest shift/esd, final cycle | 0.01 | 0.21 |
| largest peak, e/Å ³ | 1.8 | 1.071 |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^cQuality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Because the clusters of molybdenum and tungsten previously reported are air stable, no special precautions are required when mounting crystals of these complexes. The crystals typically were mounted on the tip of a thin glass fiber with the use of epoxy cement. X-ray data were collected on an automated four-circle diffractometer using monochromated Mo $K\alpha$ radiation (Enraf-Nonius CAD-4 or CAD-4S, Syntex P1 or P3, Rigaku AFC5R).

Crystallographic Details. For the four compounds characterized by X-ray crystallography, the procedural details and basic crystallographic characteristics have either already been published⁹ or are collected in Table I. For compounds 1, 3, and 4 the final atomic positional parameters and equivalent isotropic displacement parameters are available as supplementary material. The following additional comments may be made.

For 1. Intensity standards monitored every hour showed no decay during 47.5 h of exposure to X-rays. The Laue class ($3m$) and the observed systematic absences limited the possible space groups to $R3c$ and $R\bar{3}c$. With a cell volume indicative of $Z = 6$, the expected type of molecule could be accommodated in an ordered way only in $R3c$ and this choice was confirmed by the smooth refinement. Friedel pairs were collected and used to chose the correct enantiomorph. After the entire cluster cation and the PF_6 anion had been located and refined, two peaks, one on the 3-fold axis and the other on a general position, remained in the difference Fourier map. These were interpreted as the C and O atoms of methanol and refined as such with isotropic thermal parameters. A table of crystallographic data has already been published.^{9a}

For 2. Again, no crystal decay during data collection was observed. This compound was clearly seen to be isotopic with compound 1 and all of the positional parameters from 1 (except for the C and O atoms) were used to begin refinement. The remaining carbon atoms of the cluster cation were then located routinely from difference maps. Finally, only one nontrivial peak remained, on a special position. This was treated as the oxygen atom of H_2O (originating from the wet methanol used). Again both enantiomers were fully refined, and the one giving the lower residuals is reported. See ref 9b for crystallographic data in detail.

For 3. In this case crystal decay occurred and data were collected on two separate crystals and merged. The positions of W and S atoms were derived from a Patterson map employing the program SHELXS-86 and the remaining atoms found by alternating least-squares refinements and difference maps. Carbon atoms generally seemed to have large thermal motions and were refined with restrained C-P (1.81 Å) and C-C (1.51

Å) distances. Even so, four carbon atoms gave non-positive-definite thermal ellipsoids and were thus refined with isotropic temperature factors.

For 4. This structure posed no problems. No crystal decay was observed and the structure was solved by direct methods (SHELXS-86).

Synthesis of $[Mo_3S_4Cl_3(dmpe)_3][PF_6] \cdot CH_3OH$ (1). NaHS (40 mg, 0.72 mmol) was added to a solution of $MoCl_3(THF)_3$ (300 mg, 0.72 mmol) in 15 mL of THF under argon. This mixture was cooled to -78 °C and then dmpe (120 μ L, ca. 0.72 mmol) was introduced. Addition of 3 mL of MeOH (to dissolve the NaHS) followed by slow warming to room temperature produced a mixture consisting of a dark precipitate and a green solution. This green solution was filtered under argon and it seemed to be air stable at least for several days. It was taken to dryness in vacuum, the residue redissolved in CH_2Cl_2 , and the solute adsorbed on a silica gel column. After the column was washed with acetone, the green band that remained on the top was eluted with MeOH. The UV-visible spectrum of this green solution showed a band at 625 nm. Addition of NH_4PF_6 to the above solution followed by slow evaporation in air afforded green crystals suitable for X-ray diffraction studies. Yield: 40%. These crystals were characterized as $[Mo_3S_4Cl_3(dmpe)_3][PF_6] \cdot CH_3OH$.

This compound can also be prepared by reaction of $MoCl_3$ and NaHS with dmpe in MeOH at -78 °C followed by a workup of the solution similar to the one described previously.

Preparation of $[W_3S_4Cl_3(dmpe)_3][PF_6] \cdot H_2O$ (2). NaHS (86 mg, 1.54 mmol) was added to a suspension of WCl_4 (374 mg, 1.15 mmol) in 15 mL of THF. Addition of 10 mL of methanol (to dissolve the NaHS) produced an instantaneous color change to green. Dmpe (190 μ L, 1.15 mmol) was introduced and the reaction mixture refluxed for 2 h. After the mixture was cooled to room temperature, a brown precipitate was separated from a dark blue solution by filtration under argon. This blue solution is air stable and was adsorbed on a silica gel column. After the column was washed with acetone, the blue band that remained on the top was eluted with methanol. The resulting blue ion in solution was precipitated with $NaBPh_4$ and the precipitate washed with ether and dried under vacuum. This precipitate has been characterized as $[W_3S_4Cl_3(dmpe)_3][BPh_4]$. Yield: ca. 20%. The UV-visible spectrum of this compound in acetone shows two bands at 560 and 300 nm, respectively. While this BPh_4^- salt is satisfactory for bulk isolation of the $[W_3S_4Cl_3(dmpe)_3]^+$ ion, it failed to meet the requirements for X-ray crystallography.

Growth of crystals suitable for diffraction work was attempted by adding different counterions such as Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and ClO_4^- to the blue methanol solution eluted from the silica gel column and allowing the solvent to evaporate slowly. Well-shaped dark crystals grew within 1 day from the solution containing NH_4PF_6 to which one drop of water was previously added.

Preparation of $[W_3S_4Cl_3(depe)_3][PF_6]$ (3). NaHS (74.6 mg, 1.33 mmol) was added to a suspension of WCl_4 (332 mg, 1 mmol) in 15 mL of THF. Addition of 10 mL of methanol (to dissolve the NaHS) produced an instantaneous color change to green. Depe (233 μ L, 1 mmol) was introduced and the reaction mixture refluxed for 2 h. After the mixture was cooled to room temperature a green precipitate was separated from a dark brown-green solution by filtration under argon. The solution, which seemed to be air stable at least for several days, was adsorbed on a silica gel column and an orange band eluted with acetone-hexane (1:1 mixtures). A blue band remained on the top and was eluted with MeOH. This resulting blue solution was treated with NH_4PF_6 and then allowed to evaporate slowly in air to give black crystals suitable for X-ray diffraction studies. Yield: ca. 15%. These crystals were characterized as $[W_3S_4Cl_3(depe)_3][PF_6]$. The BPh_4^- salt could also be obtained by addition of $NaBPh_4$ to the blue eluate. The UV-visible spectrum of this compound shows one band at 565 nm and one shoulder at 340 nm.

Synthesis of $[W_3S_4H_3(dmpe)_3][BPh_4]$ (4). $[W_3S_4Cl_3(dmpe)_3][BPh_4]$ (56 mg, 0.036 mmol) was reacted under argon with $LiBH_4$ (8 mg, 0.36 mmol) in 5 mL of THF. The solution color changed from blue to pink within 30 min. The pink solution was filtered to remove any undissolved material. The filtrate was combined with ether (10 mL) and was cooled to -10 °C. After several hours a red microcrystalline solid was formed. The red solid was separated from the solution by filtration, washed with ether, and dried under vacuum. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of ether into a THF solution of the red microcrystalline solid. These crystals were characterized by X-ray diffraction and NMR studies as $[W_3S_4H_3(dmpe)_3][BPh_4]$. UV-visible (THF): $\lambda_1 = 490$ nm (band), $\lambda_2 = 350$ (sh), $\lambda_3 = 295$ (sh). Yield: ca. 70%.

Synthesis of the $[W_3S_4H_3(depe)_3]^+$ and Its $[BPh_4]$ Salt (5). Method A. $[W_3S_4Cl_3(depe)_3][PF_6]$ (25 mg, 0.016 mmol) was reacted with a 20 M excess of $NaBH_4$ in MeOH (10 mL). The solution color changed

from blue to pink within 5 min. The pink solution was filtered to remove any insoluble material. The filtrate was taken to dryness and redissolved in THF. The resulting ion in solution was characterized by its UV-visible spectrum, having features identical with those of the $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3]^+$ cluster ion. UV-visible (THF): $\lambda_1 = 500$ nm (band), $\lambda_2 = 360$ (sh), $\lambda_3 = 300$ (sh).

Method B. This procedure is analogous to the synthetic route followed for the synthesis of the compound $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]$ (4). In this case, $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3][\text{BPh}_4]$ (34 mg, 0.02 mmol) was reacted under argon with LiBH_4 (8 mg, 0.36 mmol) in 5 mL of THF. A workup of the reaction mixture, analogous to the one described for compound 4, allowed the isolation of $[\text{W}_3\text{S}_4\text{H}_3(\text{depe})_3][\text{BPh}_4]$. The compound was characterized, as in method A, by its UV-visible spectrum.

Reaction of $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]$ with Benzoyl Chloride. A dilute solution of $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]$ (ca. 3 mg in 5 mL of THF) was reacted with an excess of PhCOCl (two drops). The solution was stirred for 3 h. This resulted in a color change of the solution from pink to blue. The blue ion in solution has been characterized by its UV-visible spectrum as the $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ trinuclear ion ($\lambda_1 = 560$ nm, $\lambda_2 = 300$ nm).

Reaction of $[\text{W}_3\text{S}_4\text{H}_3(\text{depe})_3][\text{BPh}_4]$ with Benzoyl Chloride. A dilute solution of $[\text{W}_3\text{S}_4\text{H}_3(\text{depe})_3][\text{BPh}_4]$ (ca. 5 mg in 5 mL of THF) was reacted with an excess of PhCOCl (two drops). Stirring for 3 h resulted in a color change of the solution from pink to blue. The blue ion in solution was characterized by its UV-visible spectrum as the $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3]^+$ trinuclear cation ($\lambda_1 = 565$ nm, $\lambda_2 = 340$ nm).

Reactions of MoCl_3 with Monodentate Phosphines (L) in the Presence of Na_2S . **L = PMe_3 .** NaHS (84 mg, 1.5 mmol) was added to a suspension of MoCl_3 (300 mg, 1.5 mmol) in 15 mL of THF. PMe_3 (285 μL , 3 mmol) was introduced and 5 mL of MeOH added to the solution. The reaction mixture was allowed to stand overnight at room temperature under an inert atmosphere. A dichroic purple solution was separated from a dark precipitate by filtration under argon. The UV-visible spectrum of this solution showed a band at 575 nm. The solvent was removed under vacuum and the residue redissolved in a minimum amount of toluene. Single crystals suitable for crystallographic study were obtained by slow cooling of the toluene solution at -10 °C. The unit cell parameters, monoclinic C-centered $a = 18.369$ (2) Å, $b = 9.172$ (2) Å, $c = 17.274$ (2) Å, $\beta = 115.33$ (1)°, $V = 2639$ (2) Å³, correspond to the quadruply-bonded dimolybdenum compound $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$. Analogous results are obtained with $\text{MoCl}_3(\text{THF})_3$ instead of MoCl_3 as starting material.

L = PMe_2Ph . NaHS (300 mg, 0.72 mmol) was added to a solution of $\text{MoCl}_3(\text{THF})_3$ (300 mg, 0.72 mmol) in 10 mL of THF. PMe_2Ph (250 μL , 1.44 mmol) was introduced. After adding 20 mL of MeOH , the reaction mixture was allowed to stand overnight. Part of the solvent (ca. 15 mL) was filtered under argon giving a brown-green solution and a blue precipitate. The blue precipitate was washed with MeOH and redissolved in toluene. The UV-visible spectrum of the dichroic blue solution shows a band at 585 nm. ³¹P NMR: $\delta = 1.78$ (s). The spectroscopic measurements are consistent with the presence of the quadruply-bonded dinuclear cluster $\text{Mo}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$ in solution.

Results

We have developed a new type of synthetic entry to $\text{Mo}_3\text{S}_4^{4+}$ and $\text{W}_3\text{S}_4^{4+}$ cluster compounds and have also, for the first time, obtained and characterized compounds of this general class in which some of the ligands are hydride ions. Four crystalline compounds have been structurally characterized by X-ray crystallography, and we shall present these results first. We shall then present NMR data that are especially important for the hydrido species and finally present other spectroscopic and electrochemical data.

Structural Data. The $[\text{M}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ Ions. These ions, with $M = \text{Mo}$ and W , are structurally characterized in the isotopic PF_6^- salts, namely, compounds 1 and 2. Figure 1 shows a drawing of the principal bond lengths and angles in both cations. There are small but real deviations from C_{3v} symmetry in the M_3S_4 core, attributable to the arrangement of the two P and one Cl atom in the external sites on each metal atom. The M-M and M-(μ_2 -S) distances are, of course, all equal, but there are two kinds of M-(μ_2 -S) distances and some attendant slight differences in the two sorts of M-M-(μ_2 -S) angles. The M-(μ_2 -S) distance that is roughly trans to an M-P bond is significantly longer, by 0.046 (10) and 0.039 (7) Å for compounds 1 and 2, respectively, than the one that is roughly trans to an M-Cl bond. The two types of M-P distances also differ, by 0.071 (11) Å for compound 1

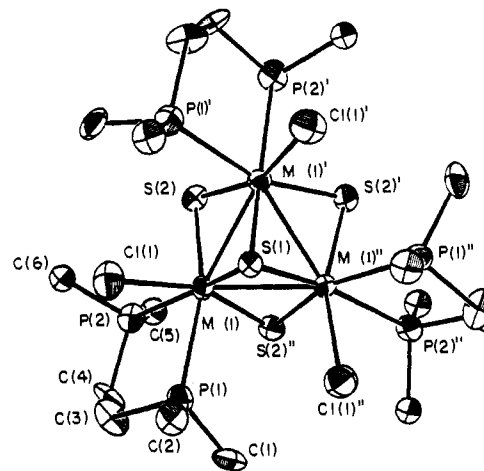


Figure 1. ORTEP representation of the $[\text{M}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ ions ($M = \text{Mo}, \text{W}$), viewed approximately along the 3-fold axis.

Table II. Selected Bond Lengths (Å) and Angles (deg) in the $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ and $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ Cluster Cations

| | M = Mo | M = W |
|--------------------|-----------|------------|
| Distances | | |
| M(1)-M(1)' | 2.766 (4) | 2.755 (1) |
| M(1)-Cl(1) | 2.473 (7) | 2.488 (4) |
| M(1)-S(1) | 2.360 (9) | 2.382 (5) |
| M(1)-S(2) | 2.336 (7) | 2.327 (3) |
| M(1)-S(2)'' | 2.290 (7) | 2.288 (5) |
| M(1)-P(1) | 2.605 (8) | 2.595 (3) |
| M(1)-P(2) | 2.534 (8) | 2.520 (4) |
| Angles | | |
| M(1)''-M(1)''-M(1) | 60.00 (0) | 60.00 (2) |
| M(1)''-M(1)-Cl(1) | 136.7 (2) | 136.9 (1) |
| M(1)''-M(1)-S(1) | 54.1 (2) | 54.66 (8) |
| M(1)''-M(1)-S(2) | 98.4 (2) | 98.6 (1) |
| M(1)''-M(1)-S(2)'' | 54.0 (2) | 54.00 (8) |
| M(1)''-M(1)-P(1) | 99.1 (2) | 98.99 (9) |
| M(1)''-M(1)-P(2) | 140.9 (2) | 141.15 (9) |
| M(1)'-M(1)-Cl(1) | 101.2 (2) | 101.25 (8) |
| M(1)'-M(1)-S(1) | 54.1 (2) | 54.67 (8) |
| M(1)'-M(1)-S(2) | 52.5 (2) | 52.7 (1) |
| M(1)'-M(1)-S(2)'' | 99.5 (2) | 99.58 (8) |
| M(1)'-M(1)-P(1) | 146.6 (2) | 146.4 (1) |
| M(1)'-M(1)-P(2) | 134.7 (2) | 135.07 (7) |
| Cl(1)-M(1)-S(1) | 82.9 (2) | 82.5 (1) |
| Cl(1)-M(1)-S(2) | 97.9 (3) | 97.4 (1) |
| Cl(1)-M(1)-S(2)'' | 158.8 (3) | 158.9 (1) |
| Cl(1)-M(1)-P(1) | 75.4 (3) | 75.7 (1) |
| Cl(1)-M(1)-P(2) | 81.0 (2) | 80.6 (1) |
| S(1)-M(1)-S(2) | 105.1 (2) | 105.7 (1) |
| S(1)-M(1)-S(2)'' | 106.6 (3) | 107.0 (1) |
| S(1)-M(1)-P(1) | 92.7 (3) | 92.1 (1) |
| S(1)-M(1)-P(2) | 163.1 (3) | 162.1 (1) |
| S(2)-M(1)-S(2)'' | 97.8 (4) | 98.1 (2) |
| S(2)-M(1)-P(1) | 160.2 (3) | 160.1 (2) |
| S(2)-M(1)-P(2) | 82.2 (3) | 82.4 (1) |
| S(2)''-M(1)-P(1) | 85.0 (3) | 84.9 (1) |
| S(2)''-M(1)-P(2) | 87.0 (2) | 87.3 (1) |
| P(1)-M(1)-P(2) | 78.3 (3) | 78.1 (1) |
| M(1)-S(1)-M(1)'' | 71.8 (3) | 70.7 (2) |
| M(1)-S(2)-M(1)' | 73.4 (2) | 73.3 (1) |

and 0.075 (7) Å for compound 2, with the one trans to the capping sulfur atom being shorter. We may also note that in this early transition metal cluster the M-Cl distance is appreciably shorter than the M-P distances, a quite common situation in early transition metal phosphine complexes generally.

$[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3][\text{PF}_6]$ (3). The structure of the cation in this compound is depicted in Figure 2, and its dimensions are listed in Table III. It is, not surprisingly, generally similar to the cations in compounds 1 and 2, but in this case there is no statistically significant difference between the two types of W-(μ_2 -S) distances. Although there is no crystallographically imposed symmetry and

Table III. Selected Bond Distances and Angles for $[W_3S_4Cl_3(depe)_3][PF_6]^-$ (3)^a

| (a) Bond Distances, Å | | | | | |
|-----------------------|--------|-----------|--------|--------|-----------|
| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
| W(1) | W(2) | 2.774 (1) | W(2) | S(2) | 2.322 (6) |
| W(1) | W(3) | 2.774 (1) | W(2) | S(3) | 2.316 (5) |
| W(1) | Cl(1) | 2.476 (9) | W(2) | P(21) | 2.532 (5) |
| W(1) | S(1) | 2.367 (5) | W(2) | P(22) | 2.611 (8) |
| W(1) | S(3) | 2.316 (5) | W(3) | Cl(3) | 2.463 (5) |
| W(1) | S(4) | 2.280 (8) | W(3) | S(1) | 2.383 (6) |
| W(1) | P(11) | 2.618 (7) | W(3) | S(2) | 2.306 (5) |
| W(1) | P(12) | 2.531 (8) | W(3) | S(4) | 2.290 (7) |
| W(2) | W(3) | 2.779 (1) | W(3) | P(31) | 2.521 (8) |
| W(2) | Cl(2) | 2.466 (6) | W(3) | P(32) | 2.622 (6) |
| W(2) | S(1) | 2.353 (4) | | | |

| (b) Bond Angles, deg | | | | | | | |
|----------------------|--------|--------|-----------|--------|--------|--------|-----------|
| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
| W(2) | W(1) | W(3) | 60.13 (3) | W(2) | W(3) | P(31) | 138.2 (1) |
| W(2) | W(1) | Cl(1) | 102.3 (2) | W(2) | W(3) | P(32) | 99.1 (2) |
| W(2) | W(1) | S(1) | 53.8 (1) | Cl(3) | W(3) | S(1) | 84.8 (2) |
| W(2) | W(1) | S(3) | 53.2 (1) | Cl(3) | W(3) | S(2) | 158.1 (2) |
| W(2) | W(1) | S(4) | 99.2 (2) | Cl(3) | W(3) | S(4) | 98.7 (2) |
| W(2) | W(1) | P(11) | 146.8 (2) | Cl(3) | W(3) | P(31) | 82.7 (2) |
| W(2) | W(1) | P(12) | 135.6 (2) | Cl(3) | W(3) | P(32) | 76.5 (2) |
| W(3) | W(1) | Cl(1) | 140.4 (2) | S(1) | W(3) | S(2) | 105.7 (2) |
| W(3) | W(1) | S(1) | 54.5 (1) | S(1) | W(3) | S(4) | 104.9 (2) |
| W(3) | W(1) | S(3) | 98.8 (2) | S(1) | W(3) | P(31) | 167.0 (2) |
| W(3) | W(1) | S(4) | 52.8 (2) | S(1) | W(3) | P(32) | 96.5 (2) |
| W(3) | W(1) | P(11) | 100.1 (2) | S(2) | W(3) | S(4) | 97.0 (2) |
| W(3) | W(1) | P(12) | 135.6 (2) | S(1) | W(1) | S(4) | 105.7 (2) |
| Cl(1) | W(1) | S(1) | 86.1 (2) | S(1) | W(1) | P(11) | 93.2 (2) |
| Cl(1) | W(1) | S(3) | 95.6 (2) | S(1) | W(1) | P(12) | 166.9 (2) |
| Cl(1) | W(1) | S(4) | 158.5 (3) | S(3) | W(1) | S(4) | 98.3 (2) |
| Cl(1) | W(1) | P(11) | 75.5 (3) | S(3) | W(1) | P(11) | 159.0 (2) |
| Cl(1) | W(1) | P(12) | 82.7 (3) | S(3) | W(1) | P(12) | 82.5 (2) |
| S(1) | W(1) | S(3) | 105.4 (2) | S(4) | W(1) | P(11) | 85.7 (3) |
| W(1) | W(2) | S(1) | 54.2 (1) | S(4) | W(1) | P(12) | 83.0 (3) |
| W(1) | W(2) | S(2) | 97.5 (2) | P(11) | W(1) | P(12) | 77.5 (2) |
| W(1) | W(2) | S(3) | 53.2 (1) | W(1) | W(2) | W(3) | 59.93 (3) |
| W(1) | W(2) | P(21) | 138.5 (1) | W(1) | W(2) | Cl(2) | 137.9 (1) |
| W(1) | W(2) | P(22) | 100.3 (2) | S(1) | W(2) | P(22) | 93.5 (2) |
| W(3) | W(2) | Cl(2) | 100.8 (2) | S(2) | W(2) | S(3) | 95.9 (2) |
| W(3) | W(2) | S(1) | 54.6 (1) | S(2) | W(2) | P(21) | 82.6 (2) |
| W(3) | W(2) | S(2) | 52.8 (1) | S(2) | W(2) | P(22) | 158.9 (2) |
| W(3) | W(2) | S(3) | 98.6 (2) | S(3) | W(2) | P(21) | 85.4 (2) |
| W(3) | W(2) | P(21) | 135.5 (2) | S(3) | W(2) | P(22) | 85.8 (2) |
| W(3) | W(2) | P(22) | 147.9 (1) | P(21) | W(2) | P(22) | 76.5 (2) |
| Cl(2) | W(2) | S(1) | 83.8 (2) | W(1) | W(3) | W(2) | 59.94 (3) |
| Cl(2) | W(2) | S(2) | 97.6 (2) | W(1) | W(3) | Cl(3) | 103.8 (2) |
| Cl(2) | W(2) | S(3) | 160.5 (2) | W(1) | W(3) | S(1) | 54.0 (1) |
| Cl(2) | W(2) | P(21) | 82.4 (2) | W(1) | W(3) | S(2) | 97.9 (2) |
| Cl(2) | W(2) | P(22) | 76.6 (2) | S(2) | W(3) | P(31) | 85.0 (2) |
| S(1) | W(2) | S(2) | 106.2 (2) | S(2) | W(3) | P(32) | 83.1 (2) |
| S(1) | W(2) | S(3) | 105.9 (2) | S(4) | W(3) | P(31) | 80.4 (3) |
| S(1) | W(2) | P(21) | 164.5 (2) | S(4) | W(3) | P(32) | 157.6 (3) |
| W(1) | W(3) | S(4) | 52.5 (2) | P(31) | W(3) | P(32) | 77.3 (3) |
| W(1) | W(3) | P(31) | 132.9 (2) | W(1) | S(1) | W(2) | 72.0 (1) |
| W(1) | W(3) | P(32) | 149.8 (2) | W(1) | S(1) | W(3) | 71.4 (2) |
| W(2) | W(3) | Cl(3) | 137.8 (2) | W(2) | S(1) | W(3) | 71.9 (2) |
| W(2) | W(3) | S(1) | 53.6 (1) | W(2) | S(2) | W(3) | 73.8 (2) |
| W(2) | W(3) | S(2) | 53.4 (2) | W(1) | S(3) | W(2) | 73.6 (1) |
| W(2) | W(3) | S(4) | 98.8 (2) | W(1) | S(4) | W(3) | 74.7 (2) |

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

the highest possible symmetry for the cation as a whole is C_3 , the central W_3S_4 unit has, effectively, C_{3v} symmetry.

$[W_3S_4H_3(dmpe)_3][BPh_4]^-$ (4). The structure of the trinuclear cluster cation $[W_3S_4H_3(dmpe)_3]^+$ is shown in Figure 3. Important bond lengths and angles are given in Table IV. With space group $P2_1/c$ and one entire formula unit per asymmetric unit, there is no crystallographic symmetry imposed on this cation. However, it has effectively C_3 symmetry. The average intermetallic distance in the cluster, 2.751 (4) Å, is statistically identical with the one found in the starting material, $[W_3S_4Cl_3(dmpe)_3]^+$ (2), 2.755 (1) Å. This is consistent with the presence of a single metal-to-metal bond between adjacent W atoms and an oxidation state of IV for

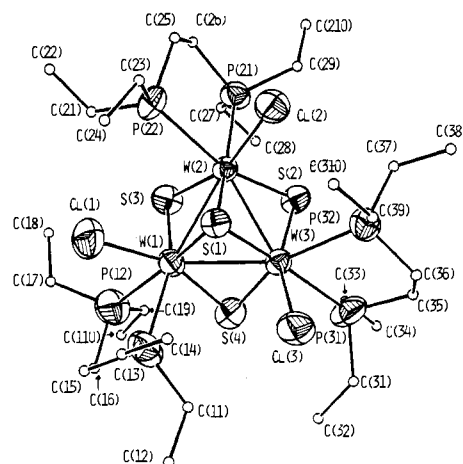


Figure 2. Perspective (ORTEP) drawing of the $[W_3S_4Cl_3(depe)_3]^+$ ion. Carbon atoms are drawn with arbitrarily small radii for clarity.

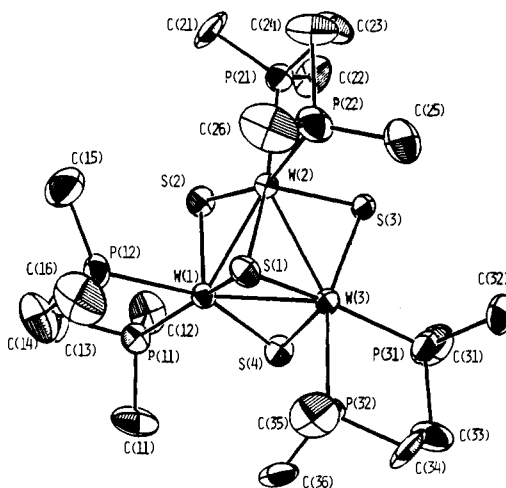


Figure 3. ORTEP drawing of the $[W_3S_4H_3(dmpe)_3]^+$ ion, with atoms represented by their thermal ellipsoids at the 40% probability level.

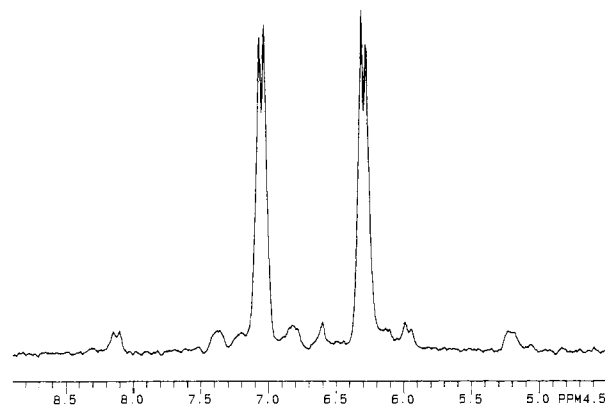


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $[W_3S_4Cl_3(dmpe)_3][PPh_4]$.

the metals in both compounds, 3 and 4. In order to balance the charge in this cluster, 4, three hydride ligands must be present even though they are not detectable in the crystal structure.

NMR Spectra. Because the presence of hydride ligands in 4 could not be confirmed by direct observation in the crystal structure, we carried out NMR studies on this compound, on the other hydride complex, $[W_3S_4H_3(depe)_3]^+$ and, for comparison on the $[W_3S_4Cl_3(dmpe)_3]^+$ ion. The $^{31}P\{^1H\}$ spectrum of the latter ion is shown in Figure 4. It is fundamentally an AA' spectrum indicative of two nonequivalent phosphorus nuclei ($\delta = 7.045$ and 6.291 ppm) very weakly coupled to each other ($^2J_{PP} = 2.7$ Hz). In addition, however, a complex pattern of satellite peaks caused by ^{183}W nuclei is seen. The 1:12:1 intensity ratio is as expected

Table IV. Bond Distances and Angles for $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]^-$ (4)^a

| (a) Bond Distances, Å | | | | | |
|-----------------------|--------|-----------|--------|--------|-----------|
| atom 1 | atom 2 | distance | atom 1 | atom 2 | distance |
| W(1) | W(2) | 2.748 (0) | W(2) | S(2) | 2.320 (5) |
| W(1) | W(3) | 2.755 (0) | W(2) | S(3) | 2.339 (5) |
| W(1) | S(1) | 2.354 (5) | W(2) | P(21) | 2.472 (5) |
| W(1) | S(2) | 2.338 (5) | W(2) | P(22) | 2.512 (5) |
| W(1) | S(4) | 2.331 (5) | W(3) | S(1) | 2.351 (5) |
| W(1) | P(11) | 2.486 (5) | W(3) | S(3) | 2.335 (5) |
| W(1) | P(12) | 2.522 (6) | W(3) | S(4) | 2.346 (4) |
| W(2) | W(3) | 2.749 (0) | W(3) | P(31) | 2.470 (6) |
| W(2) | S(1) | 2.356 (5) | W(3) | P(32) | 2.513 (5) |

| (b) Bond Angles, deg | | | | | | | |
|----------------------|--------|--------|-----------|--------|--------|--------|-----------|
| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
| W(2) | W(1) | W(3) | 59.95 (3) | S(1) | W(3) | S(3) | 105.6 (2) |
| W(2) | W(1) | S(1) | 54.3 (1) | S(1) | W(3) | S(4) | 105.5 (2) |
| W(2) | W(1) | S(2) | 53.6 (1) | S(1) | W(3) | P(31) | 159.2 (2) |
| W(2) | W(1) | S(4) | 101.5 (1) | S(4) | W(1) | P(12) | 159.2 (2) |
| W(2) | W(1) | P(11) | 142.5 (1) | P(11) | W(1) | P(12) | 79.3 (2) |
| W(2) | W(1) | P(12) | 99.2 (1) | W(1) | W(2) | W(3) | 60.15 (3) |
| W(3) | W(1) | S(1) | 54.1 (1) | W(1) | W(2) | S(1) | 54.3 (1) |
| W(3) | W(1) | S(2) | 101.4 (1) | W(1) | W(2) | S(2) | 54.1 (1) |
| W(3) | W(1) | S(4) | 54.2 (1) | W(1) | W(2) | S(3) | 102.3 (1) |
| W(3) | W(1) | P(11) | 139.8 (1) | W(1) | W(2) | P(21) | 139.9 (2) |
| W(3) | W(1) | P(12) | 138.6 (1) | W(1) | W(2) | P(22) | 138.5 (2) |
| S(1) | W(1) | S(2) | 105.4 (2) | W(3) | W(2) | S(1) | 54.2 (1) |
| S(1) | W(1) | S(4) | 105.9 (2) | W(3) | W(2) | S(2) | 102.0 (1) |
| S(1) | W(1) | P(11) | 158.4 (2) | W(3) | W(2) | S(3) | 53.9 (1) |
| S(1) | W(1) | P(12) | 84.5 (2) | W(3) | W(2) | P(21) | 140.6 (1) |
| S(2) | W(1) | S(4) | 104.1 (2) | W(3) | W(2) | P(22) | 101.1 (2) |
| S(2) | W(1) | P(11) | 88.9 (2) | S(1) | W(2) | S(2) | 105.9 (2) |
| S(2) | W(1) | P(12) | 89.9 (2) | S(1) | W(2) | S(3) | 105.3 (2) |
| S(4) | W(1) | P(11) | 85.6 (2) | S(1) | W(2) | P(21) | 159.8 (2) |
| S(2) | W(2) | P(21) | 85.8 (2) | S(1) | W(2) | P(22) | 84.5 (2) |
| S(2) | W(2) | P(22) | 156.5 (2) | S(2) | W(2) | S(3) | 105.6 (2) |
| S(3) | W(2) | P(21) | 86.7 (2) | S(1) | W(3) | P(32) | 85.5 (2) |
| S(3) | W(2) | P(22) | 91.4 (2) | S(3) | W(3) | S(4) | 104.9 (2) |
| P(21) | W(2) | P(22) | 79.0 (2) | S(3) | W(3) | P(31) | 85.3 (2) |
| W(1) | W(3) | W(2) | 59.89 (3) | S(3) | W(3) | P(32) | 159.7 (2) |
| W(1) | W(3) | S(1) | 54.2 (1) | S(4) | W(3) | P(31) | 88.2 (2) |
| W(1) | W(3) | S(3) | 102.2 (1) | S(4) | W(3) | P(32) | 87.8 (2) |
| W(1) | W(3) | S(4) | 53.7 (1) | P(31) | W(3) | P(32) | 79.3 (2) |
| W(1) | W(3) | P(31) | 141.9 (2) | W(1) | S(1) | W(2) | 71.4 (1) |
| W(1) | W(3) | P(32) | 98.0 (1) | W(1) | S(1) | W(3) | 71.7 (2) |
| W(2) | W(3) | S(1) | 54.3 (1) | W(2) | S(1) | W(3) | 71.5 (2) |
| W(2) | W(3) | S(3) | 54.0 (1) | W(1) | S(2) | W(2) | 72.3 (1) |
| W(2) | W(3) | S(4) | 101.0 (1) | W(2) | S(3) | W(3) | 72.1 (1) |
| W(2) | W(3) | P(31) | 139.3 (1) | W(1) | S(4) | W(3) | 72.2 (2) |
| W(2) | W(3) | P(32) | 139.8 (2) | | | | |

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

for the natural abundance (ca. 14%) for ¹⁸³W. The ¹J_{PW} values are 171.66 and 174.48 Hz, but in addition, ²J_{PW} couplings of 41.6 and 49.1 Hz are also observed.

For the $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3]^+$ cation, the ³¹P spectrum without ¹H decoupling was too complicated to be useful in gaining information on the hydride ligands. On the other hand, because the chemical shift of the hydride ligands signal (ca. -0.9 ppm) places it so close to the other ¹H signals, it was not possible to obtain a cleanly selective decoupling of all but the hydridic hydrogen nuclei. Figure 5 shows the principal results obtained. With normal, full-power ¹H decoupling, each type of phosphorus nucleus gives a separate signal showing no fine structure, with a pair of ¹⁸³W satellites: $\delta_{\text{P}(1)} = -6.22$ ppm (¹J_{PW} = 113.9 Hz) and $\delta_{\text{P}(2)} = 14.08$ ppm (¹J_{PW} = 184.2 Hz). There are grounds to proposing an assignment of these signals to the two structurally different type of phosphorus atoms (see Figure 3). The phosphorus atoms that are essentially trans to the μ_3 -S atom are closer to the positive direction of the W_3S_4 dipole and should thus be more deshielded. Moreover, these W-P bonds are shorter than the other type and this should lead^{16,17} to a larger value of ¹J_{PW}. On this basis these

(16) Pregosin, P. S.; Kung, R. W. *³¹P and ¹³C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979; Part B, Vol. 1.

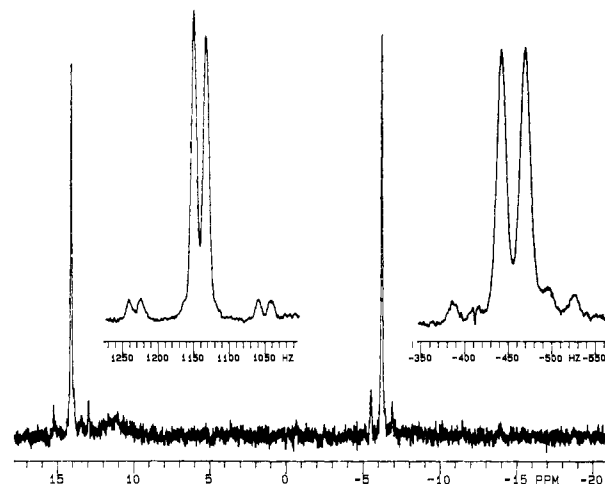


Figure 5. ³¹P NMR spectra of $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]$. The lower trace is the ³¹P{¹H} spectrum. The insets are the two resonances observed when the ¹H decoupling was adjusted to cover all alkyl protons completely but the hydride protons only partly.

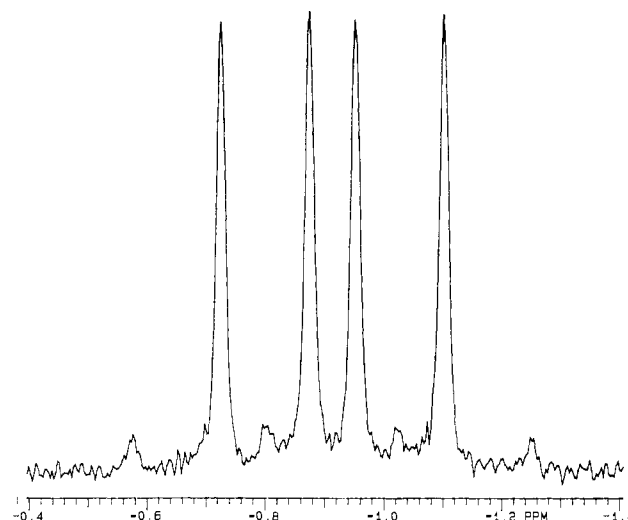


Figure 6. ¹H NMR spectrum in the region of the hydride ligand for $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3][\text{BPh}_4]$.

phosphorus atoms are assigned to the P(2) signal and the others to the P(1) signal. The absence of any detectable P(1)-P(2) coupling is by no means unprecedented.^{18,19} We may recall that the value of ²J_{PP} in the chloro cation was very small (2.7 Hz) although detected. In this case, the line widths in the ³¹P{¹H} spectrum are broader (ca. 2 Hz), thus making the detection of a coupling of only ≤ 2 Hz impossible.

Also shown in Figure 5 are the best results we were able to obtain in attempting to decouple all but the hydridic hydrogen atoms. With sufficient decoupler power to decouple the protons in the dmpe ligands completely, γB_2 (γ is the magnetogyric ratio divided by 2π and B_2 the RF field amplitude) was comparable to the difference in the chemical shifts. Thus, by a relationship between chemical shift difference and the observed coupling constant known as the reduced Ernst equation,²⁰ we expect the values of ²J_{PH} seen in the ³¹P spectrum to be smaller than the true ones, which should be (and were, vide infra) measurable in the ¹H spectrum.

Finally, we turn to the piece de resistance among the NMR spectra, namely, the ¹H spectrum in the region of the hydridic

(17) Mather, G. G.; Rapsey, G. J. N.; Pidcock, A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 567.

(18) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(19) Grim, S. O.; Barth, R. C.; Mitchell, J. D.; DelGaudio, J. *Inorg. Chem.* **1977**, *16*, 1776.

(20) Martin, M. L.; Delpuch, J. J.; Martin, G. J. *Practical NMR Spectroscopy*; Heyden: London, 1980; Chapter 6.

Table V. Comparison of Bond Lengths (deg)^a

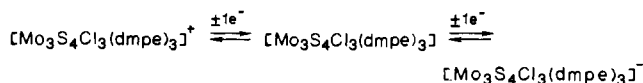
| distance | $[Mo_3S_4Cl_3(dmpe)_3]^+$ | $[W_3S_4Cl_3(dmpe)_3]^+$ | $[W_3S_4Cl_3(depe)_3]^+$ | $[W_3S_4H_3(dmpe)_3]^+$ |
|--------------------|---------------------------|--------------------------|--------------------------|-------------------------|
| M-M | 2.766 (4) | 2.755 (1) | 2.776 [3] | 2.751 [4] |
| M-(μ_3 -S) | 2.360 (9) | 2.382 (5) | 2.368 [15] | 2.354 [2] |
| M-(μ_2 -S) | 2.336 (7) | 2.327 (3) | 2.309 [17] | 2.329 [6] |
| | 2.290 (7) | 2.288 (5) | 2.301 [19] | 2.341 [4] |
| M-(μ_2 -S) av | 2.313 [15] | 2.308 [14] | 2.305 [17] | 2.335 [9] |
| M-Cl | 2.473 (7) | 2.488 (4) | 2.468 [7] | |
| M-P(1) | 2.605 (8) | 2.595 (3) | 2.617 [6] | 2.516 [6] |
| M-P(2) | 2.534 (8) | 2.520 (4) | 2.528 [6] | 2.476 [9] |

^a Average values for the last two compounds, P(2) is the phosphorus atom roughly trans to the capping sulfur.

ligand hydrogen atoms. As seen in Figure 6, this is principally a 1:1:1:1 quartet centered at $\delta = -0.914$ ppm, with associated satellites due to ^{183}W couplings. The main quartet is attributed to the splitting of the 1H resonance by the two nonequivalent phosphorus atoms bonded to the same metal atom, with $^2J_{HP}$ values of 30.0 and 45.3 Hz. The ^{183}W satellites can be attributed to a $^1J_{HW}$ value of ca. 30 Hz.

For the analogous $[W_3S_4H_3(depe)_3]^+$ ion, a similar resonance was found at ca. -0.80 ppm and displayed by $^1J_{HW} = 28$ Hz, $^2J_{HP} = 30, 45$ Hz.

Cyclic Voltammetry.²¹ For $[Mo_3S_4Cl_3(dmpe)_3]^+$, the cyclic voltammogram shows two waves which correspond to two reductions at -0.64 and -0.85 V (scan speed, 300 mV/s). These processes are coupled with oxidations on the reverse sweep. The peak separations of 85 and 84 mV and the virtually equal peak current values suggest that we are observing two quasireversible one-electron reductions, which can presumably be represented as follows:



This indicates the existence of 7-electron and 8-electron clusters as predicted by the theoretical calculations.²² The same kind of electrochemical behavior has been observed for the anionic complex $[Mo_3S_4(ida)_3]^{2-}$.^{6b} However, a different redox chemistry has been found for the $[Mo_3S_4(CN)_9]^{5-}$ cluster anion. Instead of two mono-electronic reduction waves, one oxidation and one reduction mono-electronic process have been observed between $+0.5$ and -1.9 V.²³ For the compound $[Mo_3S_4Cl_3(dmpe)_3]^+$, we have not seen any oxidation wave within the potential studied (interval $+0.8$ and -1.2 V). In the case of the trinuclear $Mo_3O_4^{4+}$ cluster no such oxidation state as $[Mo^{IV}]_2Mo^{III}$ has been found in the reduction process.²⁴⁻²⁶

The cyclic voltammogram of the tungsten cations $[W_3S_4Cl_3(dmpe)_3]^+ 2$ and $[W_3S_4Cl_3(depe)_3]^+ 3$ showed in each case the presence of a quasireversible couple that corresponds to a reduction, $E_{1/2} = -1.11$ V for compound **2** and $E_{1/2} = -1.12$ for compound **3**. The separation between the "coupled" anodic and cathodic peaks (ΔE_p) was 100 and 75 mV for compounds **2** and **3**, respectively, at 300 mV/S. The i_{pa}/i_{pc} ratios were in the range 0.5-0.55 for compound **2** and 0.7-0.75 for compound **3**. The ratio approached 1 as the scan speed increased. This is indicative of a reversible reaction at fast scan speed with some chemical event that follows the electrochemical process. In the absence of any more information, it is impossible to assess whether the electron transfer is mono- or bielectronic.

Discussion

The results presented here are novel in three aspects. (1) The preparative approach to the M_3S_4 cores is different from any previously reported. (2) The number of W_3S_4 compounds de-

scribed here (three) is greater than the entire number (two) of such species previously reported. (3) The hydrido species are the first hydrido compounds of early transition metal clusters to be made. Table V summarizes the main structural results for the four compounds studied by X-ray crystallography.

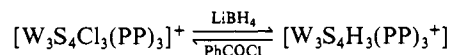
Many compounds containing the $Mo_3S_4^{4+}$ core are already known, but most of them have been obtained by procedures carried out in aqueous media. In several of these procedures the starting material is the Müller complex,²⁷ $[Mo_3(\mu_3-S)(\mu_2-S)_2(S_2)_3]^{2-}$, which undergoes desulfurization to afford such products as $[Mo_3S_4(CN)_9]^{5-}$,²⁸ $[Mo_3S_4(SCH_2CH_2S)_3]^{2-}$,²⁹ $[Mo_3S_4(NTA)-(HNTA)_2]^{2-}$,³⁰ and $[Mo_3S_4(C_2O_4)(HC_2O_4)_2(H_2O)_3]$.³⁰ Degradation of the $Mo_4S_4^{7+}$ unit can produce, for example, $[Mo_3S_4-(9)aneN_3]^{4+}$ ³¹ or others.³² One exception to this, which was reported about the same time as our preliminary communication,^{9a} is the method of Saito et al.,^{6d} who employed $Mo_3S_7Cl_4$. This was treated with excess PEt_3 in THF and afforded either of two similar products, depending on workup procedure, in 20-50% yields, namely, $Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$ and $Mo_3S_4Cl_4(PEt_3)_4(MeOH)$.

Our method entails the use of $MoCl_3$ or, better, $MoCl_3(THF)_3$ along with $NaHS$ as a source of sulfur. The $[Mo_3S_4Cl_3(dmpe)_3]^+$ cation was most conveniently isolated as its BPh_4^- salt, but the yield is only about 20%. Moreover, in numerous attempts to use the method to prepare analogous or related species with monodentate phosphines, we have never been able to isolate any $Mo_3S_4^{4+}$ products. Instead, we obtained $Mo_2Cl_4(PR_3)_4$ compounds containing Mo-Mo quadruple bonds.

At the present time, there are many preparative methods leading to $Mo_3S_4^{4+}$ -containing products, but none that has generality or gives high yields. There is clearly a need for improvement in one or both of these respects, and we are working on this aspect of the chemistry.

Turning now to the tungsten chemistry, we first note that apart from our work, only two compounds containing the $W_3S_4^{4+}$ core have been described, both by Shibahara.^{33,34} These contain the $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(NCS)_9]^{5-}$ ions. Shibahara has also reported compounds containing some mixed oxo-thio species,^{6c,35,36} viz., W_3S_3O , $W_3S_2O_2$, and W_3SO_3 (all having μ_3 -S). We have now provided for the first time a route to $W_3S_4^{4+}$ compounds that does not involve the aqua ion. Unfortunately, as in the molybdenum case, the yields of the $[W_3S_4Cl_3(dmpe)_3]^+$ and analogous *depe* species are only a modest 20%.

Perhaps the most remarkable aspect of the work reported here is the preparation and characterization, for the first time, of a hydrido complex containing a M_3X_4 ($M = Mo, W; X = O, S, Cl, \text{etc.}$) core. It turns out that these can be obtained from, and reversibly converted back into the $[W_3S_4Cl_3(PP)_3]^+$ species ($PP = dmpe$ or *depe*), as indicated in the following equation:



The yields in both directions are good, being about 70% (isolated) to the hydride and substantially quantitative for the reverse reaction.

(27) Müller, A.; Pohl, S.; Dartmann, M.; Cohen, J. P.; Bennett, J. M.; Kirchner, R. M. *Z. Naturforsch., B* **1979**, *34*, 434.

(28) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72.

(29) Halbert, T. R.; McGauley, K. Pau, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.

(30) Cotton, F. A.; Llusar, R.; Marler, D. O.; Schwotzer, W.; Dori, Z. *Inorg. Chim. Acta* **1985**, *102*, L25. $H_3NTA =$ nitrilotriacetic acid; $H_2C_2O_4 =$ oxalic acid.

(31) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 3654. $[9]aneN_3 = 1,4,7$ -triazacyclononane.

(32) Kathirgamanathan, P.; Martinez, M.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1437.

(33) Shibahara, T.; Takeuchi, A.; Ohtsujii, A.; Kohda, K.; Kuroya, H. *Inorg. Chim. Acta* **1987**, *127*, L45.

(34) Shibahara, T.; Kohda, K.; Ohtsujii, A.; Yasuda, K.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 2757.

(35) Shibahara, T.; Takeuchi, A.; Nakajima, M.; Kuroya, H. *Inorg. Chim. Acta* **1988**, *143*, 147.

(36) Shibahara, T.; Takeuchi, A.; Kuroya, H. *Inorg. Chim. Acta* **1987**, *127*, L39.

(21) Further details will be found in the supplementary material.

(22) Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *Inorg. Chem.* **1982**, *21*, 302.

(23) Wiegardt, K.; Herrmann, W.; Müller, A.; Eltzner, W.; Zimmermann, M. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1984**, *39B*, 876.

(24) Richens, D. T.; Sykes, A. G. *Inorg. Chim. Acta* **1981**, *54*, L3.

(25) Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1982**, *21*, 418.

(26) Paffet, M. T.; Anson, F. C. *Inorg. Chem.* **1983**, *22*, 1347.

The unambiguous identification and characterization of the hydrido species required both X-ray and NMR data. The X-ray crystallographic results, as shown in Figure 3, provide an excellent picture of the $[\text{W}_3\text{S}_4\text{H}_3(\text{dmpe})_3]^+$ cation except for its most critical feature, the hydrogen atoms. We are left to infer that they occupy the apparently empty positions in the coordinated spheres of the tungsten atoms. The fact that the rest of the cation retains almost identically the same structure as the $[\text{W}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3]^+$ ion leaves no doubt that we are still dealing with $[\text{W}_3\text{S}_4\text{X}_3(\text{dmpe})_3]^+$ ion in which X is a monatomic, uninegative anion that has an extremely small scattering factor for X-rays. Only H^- fits these requirements. Even though the H^- ion (formally speaking) should be a softer, more electron-donating ligand than Cl^- , the W–W distances in the two clusters are identical within the uncertainties. There are

some small differences in the W–S and W–P distances, however. Both the Cl and H atoms lie trans to one W–(μ_2 -S) bond.

Acknowledgment. We are grateful to both the National Science Foundation and the Robert A. Welch Foundation for financial support. We also thank Professor Zvi Dori of the Technion as well as Drs. Larry R. Falvello and Willi Schwotzer for their interest and assistance.

Supplementary Material Available: Tables of positional parameters, bond lengths, bond angles, and anisotropic displacement parameters for **1–4** and cyclic voltammograms of $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmpe})_3][\text{PBh}_4]$ and $[\text{W}_3\text{S}_4\text{Cl}_3(\text{depe})_3][\text{BPh}_4]$ (31 pages); tables of observed and calculated structure factors for **1–4** (63 pages). Ordering information is given on any current masthead page.

The Use of Very Crowded Silylamide Ligands –N(SiMe_nPh_{3–n})₂ (n = 0, 1, or 2) To Synthesize Crystalline, Two-Coordinate Derivatives of Mn(II), Fe(II), and Co(II) and the Free Ion [Ph₃SiNSiPh₃][–]

Hong Chen, Ruth A. Bartlett, H. V. Rasika Dias, Marilyn M. Olmstead, and Philip P. Power*

Contribution from the Department of Chemistry, University of California, Davis, California 95616. Received November 17, 1988

Abstract: The synthesis, spectroscopy, and structures of several lithium salts of very bulky silylamides and some of their transition-metal derivatives are described. In addition, the structures of two of the bis(silyl)amine precursors, $\text{HN}(\text{SiMePh}_2)_2$ and $\text{HN}(\text{SiPh}_3)_2$, are reported. The lithium derivatives include the monomeric solvates $\text{Li}(\text{THF})_2\text{N}(\text{SiMePh}_2)_2$, **1**, $\text{Li}(\text{THF})_2\text{N}(\text{SiPh}_3)_2$, **2**, and $\text{Li}(12\text{-crown-4})\text{N}(\text{SiMePh}_2)_2$, **3**, and the salt $[\text{Li}(12\text{-crown-4})_2][\text{N}(\text{SiPh}_3)_2]\cdot\text{THF}$, **4**, involving the free $[\text{N}(\text{SiPh}_3)_2]^-$ ion with a wide SiNSi angle. Four transition-metal derivatives, $\text{M}[\text{N}(\text{SiMePh}_2)_2]_2$ (M = Mn, **5**; Fe, **6**; Co, **7**) and $\text{Fe}[\text{N}(\text{SiMe}_2\text{Ph})_2]_2$, **8**, are also reported. All compounds were characterized by X-ray crystallography, and the transition-metal species were further examined by ¹H NMR, UV-vis, and EPR spectroscopy and magnetic measurements. The transition-metal complexes are all high spin with essentially two coordination and near linear geometries for **5**, **6**, and **8**, whereas **7**, the Co derivative, has an NCoN angle 147.0 (1)° with the possibility of further weak metal ligand interactions that could not be confirmed by ¹H NMR. The structures of the silylamine precursors and the lithium salts **1** to **4** provide evidence of crowding through wide SiNSi angles in the case of the former and monomeric or dissociated structures including wide SiNSi angles for **1–4**. The species **6** and **7**, which were described in a preliminary communication, were the first crystalline, two-coordinate derivatives of iron and cobalt to be reported. In addition, the recently communicated structure of the ion $[\text{Ph}_3\text{SiNSiPh}_3]^-$ was the first of its kind. It is isoelectronic to $[\text{PPN}]^+$ and has short (1.634 Å) Si–N bonds. Crystal data with Mo K α ($\lambda = 0.71069$ Å) radiation at 130 K: $\text{HN}(\text{SiMePh}_2)_2$, $\text{C}_{26}\text{H}_{27}\text{NSi}_2$, $a = 13.683$ (4) Å, $b = 7.953$ (1) Å, $c = 22.196$ (6) Å, $\beta = 104.12$ (2)°, $Z = 4$, monoclinic, space group $P2_1/n$, $R = 0.039$; **1**, $\text{C}_{34}\text{H}_{42}\text{LiNO}_2\text{Si}_2$, $a = 17.675$ (4) Å, $b = 12.111$ (3) Å, $c = 15.986$ (2) Å, $\beta = 107.89$ (1)°, $Z = 4$, monoclinic, space group $C2/c$, $R = 0.044$; **2**, $\text{C}_{44}\text{H}_{46}\text{LiNO}_2\text{Si}_2$, $a = 24.945$ (11) Å, $b = 10.296$ (3) Å, $c = 20.658$ (9) Å, $\beta = 134.29$ (2)°, $Z = 4$, monoclinic, space group $C2/c$, $R = 0.048$; **3**, $\text{C}_{34}\text{H}_{42}\text{LiNO}_4\text{Si}_2$, $a = 11.664$ (3) Å, $b = 13.971$ (6) Å, $c = 19.537$ (7) Å, $Z = 4$, orthorhombic, space group $Pbcn$, $R = 0.058$; **5**, $\text{C}_{52}\text{H}_{52}\text{MnN}_2\text{Si}_4$, $a = 10.893$ (1) Å, $b = 15.399$ (6) Å, $c = 27.049$ (4) Å, $\beta = 91.73$ (1)°, $Z = 4$, monoclinic $P2_1/c$, $R = 0.040$; **6**, $\text{C}_{32}\text{H}_{44}\text{FeN}_2\text{Si}_4$, $a = 15.137$ (5) Å, $b = 12.996$ (4) Å, $c = 17.662$ (5) Å, $\beta = 90.85$ (2)°, $Z = 4$, monoclinic, space group $P2_1/c$, $R = 0.042$.

Hexamethyldisilazane, $\text{HN}(\text{SiMe}_3)_2$, first characterized in 1944,¹ has proved to be an extremely convenient starting material for the synthesis of many hundreds of compounds involving the bulky $-\text{N}(\text{SiMe}_3)_2$ group.² The utility of this ligand in the stabilization of compounds with low coordination numbers or unusual bonding was first recognized in 1963 with the synthesis

of several transition-metal derivatives.^{3,4} In addition, its alkali metal salts may function as good proton abstractors, and these have found wide use in organic chemistry. However, with the exception of the related $-\text{N}(t\text{-Bu})\text{SiMe}_3$ ligand⁵ and an isolated report⁶ on Ge(II), Sn(II), and Pb(II) derivatives of $-\text{N}(\text{SiEt}_3)_2$ and $-\text{N}(\text{GePh}_3)_2$ there has been little exploration of the novel coordination which might result from changing the size of the silyl

(1) Sauer, R. O. *J. Am. Chem. Soc.* **1944**, *66*, 1707.

(2) (a) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, England, 1980. (b) Bradley, D. C. *Chem. Br.* **1975**, *11*, 393. (c) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1. (d) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271.

(3) Bürger, H.; Wannagat, U. *Monatsh.* **1963**, *94*, 1007.

(4) Bürger, H.; Wannagat, U. *Monatsh.* **1964**, *95*, 1099.

(5) Harris, D. H.; Lappert, M. F. *J. Organomet. Chem. Libr.* **1976**, *2*, 13.

(6) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Riviere, P.; Riviere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.