

Figure 3. UV-vis spectrum of $[\text{Os}(\text{TMP})(\text{O})_2]$ in CH_2Cl_2 .

Table VII. Oxidation of Cyclohexene by $[\text{Os}(\text{P})(\text{O})_2]$ at 52 °C under Aerobic Conditions

complex	$10^5 \times$ amt of Os complex used, mL	$10^5 \times$ amt of cyclohexenol formed, mol	no. of equiv
$[\text{Os}(\text{TPP})(\text{O})_2]$	3.0	7.6	2.5
$[\text{Os}(\text{TMP})(\text{O})_2]$	1.7	5.5	3.2

complexes $[\text{Os}(\text{TPP})(\text{PPh}_3)_2]$, 2.044 (2); $[\text{Os}(\text{OEP})(\text{OPPh}_3)_2]$, 2.029 (8); $[\text{Os}(\text{Me}_2\text{OEP})(\text{CO})(\text{py})]$, 2.067 (3) Å.^{16,17} The porphyrin skeleton is approximately planar. Deviations from the least-squares plane of the core atoms vary from 0.007 to 0.070 Å (rms displacement 0.036 Å). The phenyl rings are essentially planar, and the mean C-C distance (1.375 ± 0.005 Å) is normal. The dihedral angles between the two peripheral phenyl rings and the porphyrin core are 92.3 (2) and 64.5 (2)°. The geometry of the *p*-Me-TPP moiety (the average N-C_q, C_q-C_p, C_p-C_m, and C_q-C_m distances are 1.369 (9), 1.438 (5), 1.333 (7), and 1.399 (20) Å respectively)¹⁸ is very similar to that found in other (tetraphenylporphyrinato)metal complexes.^{16,19}

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The electronic spectra of $[\text{Os}(\text{TMP})(\text{O})_2]$ and $[\text{Os}(p\text{-X-TPP})(\text{O})_2]$ are distinctly different from that of $[\text{Ru}(\text{TMP})(\text{O})_2]$. The osmium complexes show a three-band pattern at 580–590, 460–480, and 390–400 nm, as illustrated in Figure 3 for $[\text{Os}(\text{TMP})(\text{O})_2]$. The visible spectrum of $[\text{Ru}(\text{TMP})(\text{O})_2]$ features an intense band at 516 nm, and it resembles more closely the spectrum of $[\text{Os}(p\text{-X-TPP})(\text{OR})_2]$ (for example, $[\text{Os}(\text{TPP})(\text{OEt})_2]$ λ/nm (log ε): 507 (4.07), 408 (5.02))¹² than that of $[\text{Os}(p\text{-X-TPP})(\text{O})_2]$. We offer no explanation for this difference, and future studies will be necessary to elucidate this point.

The reactivities of the $[\text{Os}(\text{P})(\text{O})_2]$ complexes toward organic substrates have been investigated. At 20 °C, cyclohexene was not oxidized by $[\text{Os}(\text{OEP})(\text{O})_2]$, $[\text{Os}(\text{TPP})(\text{O})_2]$, and $[\text{Os}(\text{TMP})(\text{O})_2]$, as neither cyclohexene oxide, cyclohexenone, nor cyclohexenol was formed after the reactions. With other organic substrates such as norbornene and benzyl alcohol, no detectable reaction was observed, even at 52 °C. When $[\text{Os}(\text{TMP})(\text{O})_2]$ or $[\text{Os}(\text{TPP})(\text{O})_2]$ was stirred with cyclohexene at 52 °C, cyclohexenol was formed. No cyclohexene oxide was found. The results are listed in Table VII. Since the reaction of $[\text{Ru}(\text{TMP})(\text{O})_2]$ with cyclohexene yields cyclohexene oxide as one of the major products, the ruthenium and osmium complexes may react by different pathways. No catalytic aerobic oxidation of organic substrates has yet been observed with the $[\text{Os}(\text{P})(\text{O})_2]$ complexes.

Acknowledgment. Financial support by the Department of Chemistry, University of Hong Kong, is gratefully acknowledged.

Registry No. *m*-CPBA, 937-14-4; $[\text{Os}(\text{TMP})(\text{O})_2]$, 115076-43-2; $[\text{Os}(p\text{-MeO-TPP})(\text{O})_2]$, 115076-44-3; $[\text{Os}(p\text{-Me-TPP})(\text{O})_2] \cdot 2\text{C}_4\text{H}_8\text{O}$, 115076-45-4; $[\text{Os}(\text{TPP})(\text{O})_2]$, 110589-22-5; $[\text{Os}(p\text{-Cl-TPP})(\text{O})_2]$, 115076-46-5; $[\text{Os}(\text{TMP})(\text{CO})(\text{EtOH})]$, 115076-47-6; $[\text{Os}(p\text{-MeO-TPP})(\text{CO})(\text{EtOH})]$, 115076-48-7; $[\text{Os}(p\text{-Me-TPP})(\text{CO})(\text{EtOH})]$, 66082-87-9; $[\text{Os}(\text{TPP})(\text{CO})(\text{EtOH})]$, 115076-49-8; $[\text{Os}(p\text{-Cl-TPP})(\text{CO})(\text{EtOH})]$, 115076-50-1; $[\text{Os}(\text{OEP})(\text{O})_2]$, 51349-77-0; $[\text{Os}(\text{OEP})(\text{OH})_2]$, 115092-12-1; cyclohexene, 110-83-8; cyclohexenol, 25512-63-4.

Supplementary Material Available: Tables of atomic and thermal parameters for hydrogen atoms, anisotropic thermal parameters, bond distances, and bond angles (4 pages); tables of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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New Low-Temperature Synthesis of Transition-Metal Sulfides

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The reaction of hexamethyldisilthiane with transition-metal halides at room temperature results in the rapid synthesis of transition-metal sulfides. Sulfides that are normally difficult or even impossible to produce by using classical methods are readily produced. This method allows great control of reaction conditions and can be used with a wide range of transition metals and oxidation states. The sulfides that are synthesized are anhydrous, unlike those produced by many other low-temperature methods. This is a concern in applications such as the use of the materials as cathodes in secondary lithium batteries. The reactions were fast and usually exothermic, producing sulfides that were amorphous to X-ray diffraction. The only coproducts of the reaction between hexamethyldisilthiane and the metal halides are trimethylsilyl halides. These compounds are all volatile liquids and are easy to separate from the sulfides produced. Retention of the formal oxidation state of the metal from the halide was found in the sulfide in all cases.

Introduction

Transition-metal sulfides are of interest for many applications. Uses range from common ones such as dry lubrication to more specialized ones such as ionic intercalation for secondary batteries and catalysts.^{1,2} The sulfides are well suited for these applications

because of their physical structure as well as their chemical properties. Many of them, especially the dichalcogenides, have layered or sandwich-type structures.¹ These layers are bound to each other only by van der Waals forces, and therefore the layers can be easily pushed apart or slid alongside each other. The

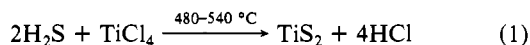
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movement allowed by this phenomenon makes intercalation easy and accounts for the excellent lubricating properties. However, physical properties and morphology of the transition-metal sulfides are strongly affected by the processes used to synthesize them.

There are many methods for making transition-metal sulfides, and each has various advantages and disadvantages. Of course, the simplest and most straightforward method is by direct combination of the elements. This requires intimate mixing of the metal and sulfur in the desired ratio and heating them at elevated temperatures, usually sealing them in an evacuated tube.³⁻⁸ By varying the temperature at which the reaction is taking place, one can obtain some control of the resulting stoichiometry.^{6,9-11} Because of favorable enthalpies of formation as observed in standard phase diagrams, higher sulfides can often be reduced to less sulfur-rich sulfides by raising the temperature. Combining the elements under elevated pressure at room temperature is also effective in forming sulfides in some cases.^{12,13} Mole and Hocart¹² report forming Cu₂S at 1600 kg/cm² this way, and Zubova and Korotaeva formed sulfides of nickel, cobalt, and iron.¹³

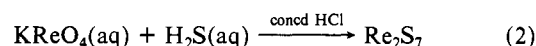
Another common sulfurizing agent at elevated temperatures is hydrogen sulfide. Some sulfides can be made simply by passing H₂S vapor over the metal at high temperature, such as Zr₃S₅,¹⁴ FeS,¹⁵ and Co₃S₄.¹⁶ More commonly, however, the H₂S is reacted with metal chlorides,^{5,7,17,18} hydroxides,^{19,20} or even oxides.²¹⁻²³ For example, Biltz et al.¹⁷ report



Biltz and co-workers did much work investigating synthetic parameters and products of these moderate- to high-temperature reactions.^{6,17,24-27} Only those sulfides that are stable at these temperatures or pressures can be made by these methods. In general, sulfides synthesized at these conditions generally have moderate surface area and are crystalline.²⁸

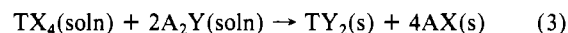
Sulfides can also be produced by degradation of an intermediate metal-sulfur compound. Examples would be the thermal or acidic degradation of sulfur-containing ammonium salts of metals,^{22,27,29-31} such as the decomposition of ammonium thiomolybdate to molybdenum trisulfide²⁷ or the basic degradation of metal thiosulfates (NiS₂O₃ is reduced to NiS₂ by a 10% solution of KOH³²).

Aside from the conditions discussed above, transition-metal sulfides may also be produced near room temperature. These reactions are usually done in solution. Hydrogen disulfide is as common a sulfurizing agent in these conditions as it is at high temperatures. When H₂S is bubbled through an acidified transition-metal salt solution, a sulfide will precipitate.³³⁻³⁶ For example³⁶



It has been reported that there is some control of the stoichiometry obtained by varying the pH of the solution.^{37,38} When Fe₂O₃ is reacted with aqueous H₂S in acid, FeS is produced, while in base, Fe₂S₃ is made.³⁷ Using aqueous solutions presents the problem of forming hydrated compounds. This is especially a concern in applications that require an anhydrous system, such as the intercalation of lithium ions in secondary batteries.^{39,40} In addition, this technique cannot be used when the oxide can not readily be transformed to the sulfide.

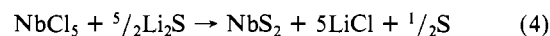
Chianelli and Dines²⁸ desired to produce sulfides at low temperatures in a nonhydroxylic environment to prevent contamination by hydroxides or oxides. Using polar organic solvents and transition-metal chlorides as the metal source, they found H₂S to be a poor reactant. By the use of other alkali-metal and alkali-metal-like sulfides in place of H₂S, a metathetical reaction was achieved. The reaction proceeds according to the scheme



T = transition metal; X = Cl; A =

Na⁺, Li⁺, NH₄⁺; Y = S, Se

This reaction allows the synthesis at low temperatures of dichalcogenides free of hydroxyl contamination. There is also control of physical properties such as particle size and crystallinity. Unfortunately, alkali-metal chloride, which is produced as a co-product, must be removed. Also, in higher oxidation state metal chlorides, a reduction takes place during the reaction, for example



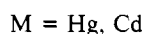
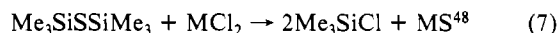
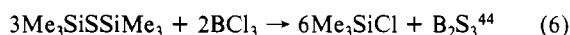
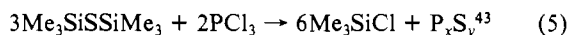
This reduction prevents the use of this technique to prepare certain sulfur-rich compounds such as MoS₃.

Molybdenum trisulfide had shown promise as a cathode material in secondary batteries with a very high potential energy density of 767 Wh/kg.⁴¹ We were interested in finding a route to direct synthesis of MoS₃, which has previously been available only through thermal (200–250 °C) or aqueous degradation of ammonium thiomolybdate.⁴²

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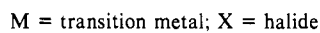
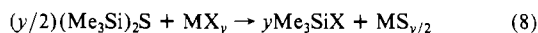
We needed a covalent sulfur source that would allow a nonionic, metathetic reaction to take place so as to avoid the possibility of reduction. Our attention was drawn to work reported by Abel and co-workers.⁴³⁻⁴⁸ They investigated the reactions of a series of organosilyl sulfides. It was found that when these compounds were reacted with various halides, invariably the silicon-sulfur bond broke and a silicon-halogen bond formed. The sulfur in turn bonded to the metal atom to which the halogen had previously been bound. They investigated primarily main-group-metal halides. While their principal interest was in forming organo-metallic and coordination complexes,⁴⁸ they reported that hexamethyldisilthiane (HMDST, $\text{Me}_3\text{SiSSiMe}_3$) produced sulfides rather than complexes:



Jenkins and Willey⁴⁹ further investigated the reactions of HMDST with metal halides, including TiCl_4 . They were attempting to produce cyclic compounds and so reacted equimolar quantities of HMDST and TiCl_4 . Their main product was TiSCl_2 ; however, trace amounts of a black precipitate, which they thought was probably amorphous TiS_2 , was formed. The reports on HMDST indicated that this reagent deserved further study as a low-temperature, nonaqueous, covalent sulfur source for the formation of transition-metal sulfides.

Experimental Section

The general reaction can be expressed as



Reaction parameters could easily be controlled to provide a variety of conditions. We explored reactions in the vapor phase, in the liquid phase with various solvents (from -78 to $+100$ °C), and in the neat liquid phase. The reactions were fast, usually exothermic, and in the case of the fluorides, exothermic, requiring cooling. Because of the reactivity of both the halides and HMDST toward moisture, all manipulations and reactions had to take place in an inert atmosphere with anhydrous solvents.

General Method A: Formation of Sulfides from Soluble Halides (Ti_2S_3 , TiS_2 , VS_2 , Nb_2S_5 , CrS , MoS_2 , Mo_2S_5 , WS_2 , W_2S_5 , WS_3 , FeS , Fe_2S_3). In all of these cases, 2–4 g of the corresponding metal chloride (or bromide in the case of WS_2) (as shown in Table IV) was dissolved in 150 mL of dry methylene chloride and sealed in a round-bottom flask with a rubber septum. An argon-filled balloon was attached to maintain atmospheric pressure. A 10% excess of HMDST (based on one sulfur atom per two halogen atoms) was slowly injected into the solution while stirring. In most cases an exothermic reaction occurred immediately, producing a fine precipitate. In all cases, reaction was complete after stirring for 16–24 h. The precipitate was filtered out in a drybag with methylene chloride. The filtered precipitate was washed with dried acetonitrile in a Soxhlet extractor to ensure complete removal of any unreacted halides that may have adhered to the sulfide particles. After vacuum-drying, the materials were sealed in evacuated Pyrex tubes. Metal content was determined by atomic absorption on a Perkin-Elmer 305 spectrometer and sulfur content was determined gravimetrically.

General Method B: Formation of Sulfides from Volatile Halides (MoS_3 , WS_3). The fluorides of molybdenum and tungsten are highly volatile and extremely reactive, even toward glass. MoF_6 and WF_6 both have extremely narrow liquid ranges, 17–35 and 2.5–17.5 °C, respectively. Because of this, special methods were necessary to introduce each into solution in methylene chloride. The fluoride vapor was vacuum-

Table I. Chemical Analysis To Show M/S Ratio (by Weight)

compd	theor	obsd	compd	theor	obsd
MoS_3	1.00	1.00	W_2S_5	2.30	2.30
Mo_2S_5	1.20	1.17	WS_2	2.88	2.86
MoS_2	1.50	1.52	Nb_2S_5	1.16	1.16
WS_3	1.92	1.83	VS_2	0.79	0.80

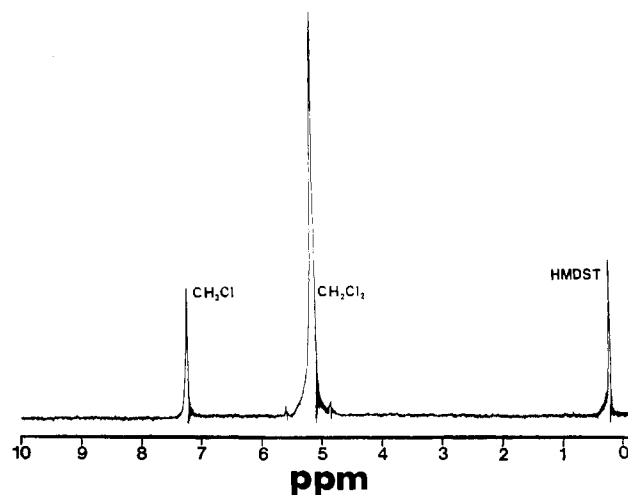


Figure 1. NMR spectrum of hexamethyldisilthiane and chloroform in methylene chloride.

distilled into a calibrated dry ice trap. When a sufficient quantity had condensed (3–4 mL), an argon atmosphere was introduced, and the fluoride was warmed and allowed to vapor-transport to a round-bottom flask containing cooled methylene chloride. This was then sealed and stirred while HMDST was introduced through a syringe as in method A above. Reaction was very rapid, even at -78 °C, and much heat evolved. After stirring for 16–24 h, the precipitate was filtered out, cleaned, and analyzed as above.

General Method C: Formation of Sulfide from CrCl_3 (Cr_2S_3). Chromium trichloride is very inert and is difficult to dissolve. We had to use zinc as a catalyst to extract 2–3 g of CrCl_3 into acetonitrile in a Soxhlet extractor. Once the chromium trichloride was in solution, the procedure was as in method A. The reaction proceeded quickly, and the purple solution changed to a black slurry. Filtration and washing were as above.

Analytical Methods. To determine sulfur content, the precipitated compounds were oxidized in a hot mixture of bromine, carbon tetrachloride, and nitric acid. Hydrochloric acid was then added to dissolve the resulting oxidized precipitate. After cooling, $\text{Ba}(\text{NO}_3)_2$ was added, which caused the formation and precipitation of BaSO_4 . This was filtered out, dried, and weighed to gravimetrically determine sulfur content.

Transition-metal content of the precipitates was determined by using a Perkin-Elmer Model 305 atomic absorption spectrometer. The precipitates were dissolved in aqua regia or, if necessary, by the procedure used above for sulfur analysis. Standard solutions of the transition elements of interest were made as suggested by the Perkin-Elmer handbook.⁵⁰ The sample solutions were diluted and their concentrations compared with the standards to determine the metal content.

A Varian EM390 NMR spectrometer was used to measure the proton NMR shifts of the organic components of the reaction system. X-ray diffraction patterns were observed on a Phillips XRG 3100 spectrometer, using $\text{CuK}\alpha$ radiation and a graphite monochromator. Scans were taken with 2θ between 5 and 70° at a rate in 2θ of 1.2°/min. FTIR measurements were taken on a BIO-RAD Digilab Division FTS-60 system.

Results

After initial success using this chemistry to produce molybdenum sulfides,⁵¹ we extended our research to investigate its application to a wider range of transition-metal halides.

We were able to use proton NMR spectroscopy to monitor the organic components of the reaction system. Chloroform, with a singlet peak at 7.3 ppm, was used as a standard to compare the positions of the organic reactants and products. The singlet from the solvent CH_2Cl_2 was not located in the area of interest and

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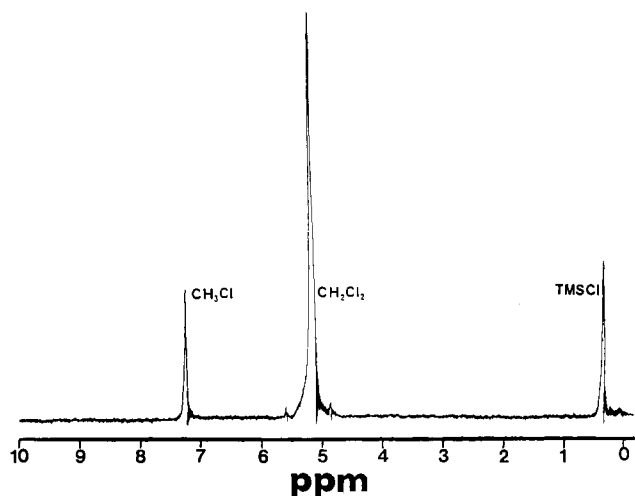


Figure 2. NMR spectrum after the stoichiometric reaction of hexamethyldisilthiane with molybdenum pentachloride in methylene chloride with chloroform used as a marker.

Table II. Silicon-Halide and Silicon-Sulfur Bond Energies

bond	bond energy, kcal/mol ⁵²	bond	bond energy, kcal/mol ⁵²
Si-Br	403	Si-F	807
Si-Cl	471	Si-S	293

so did not interfere with the observations. Before reaction with the metal halide, only chloroform, methylene chloride, and HMDST singlets were visible (see Figure 1). After the addition of half the necessary amount of transition-metal chloride for a complete reaction to sulfide, the size of the HMDST peak was reduced by half and a peak corresponding to trimethylsilyl chloride appeared at 0.4 ppm with a height equal to that of the consumed HMDST. Figure 2 shows the NMR spectrum of the product of the reaction of stoichiometric amounts of HMDST and transition-metal chloride. The HMDST peak has been completely replaced by the trimethylsilyl chloride peak. Trace amounts of hexamethyldisiloxane are visible. This resulted from the trimethylsilyl chloride reacting with the trace amounts of water, forming $(\text{CH}_3)_3\text{SiOH}$, which then dimerizes. This confirmed that the organic components of the reaction reacted as expected. Comparison of silicon-halogen and silicon-sulfur bond energies may explain the driving force for this reaction. Table II shows these bond strengths.⁵² The obvious strength of the silicon-halide bonds relative to the weaker silicon-sulfur bond probably accounts for the easy exchange.

A principal feature of this general reaction is that the organic coproducts of the reaction between HMDST and halides are trimethylsilyl halides. These compounds are all volatile liquids and therefore easy to separate from the sulfides produced. The boiling points are 79 °C for Me_3SiBr , 57 °C for Me_3SiCl , and 18 °C for Me_3SiF .

The results of elemental analysis showed sulfur to metal ratios that were consistent with those of the sulfides that we had expected to produce in the reactions. Some of these ratios are shown in Table I.

X-ray powder diffraction patterns of all samples prepared at low temperature indicated that they were amorphous. Since some of the materials are unstable at higher temperatures, no X-ray data could be obtained (MoS_3 , Mo_2S_5 , WS_3 , W_2S_5). Others, such as TiS_2 and Cr_2S_3 , are stable phases at elevated temperatures and so could be heated and crystallized such that diffraction patterns could be observed. We see excellent agreement between the diffraction patterns observed and those in the JCPDS files. Figure 3 shows the correspondence of peaks between the file pattern of Cr_2S_3 and the thermally crystallized powder resulting from the

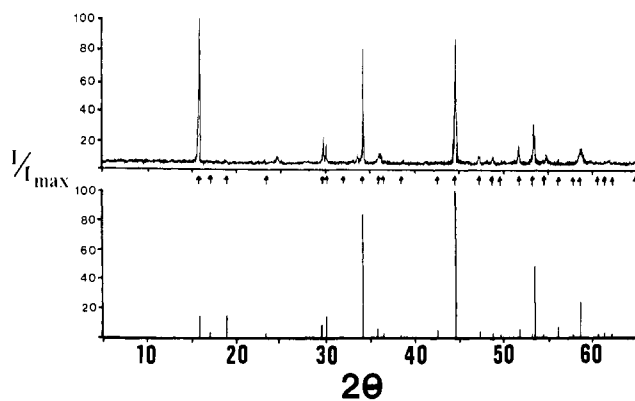


Figure 3. XRD pattern of the heated product from the reaction of hexamethyldisilthiane with chromium trichloride compared with JCPDS file No. 11-0007 (Cr_2S_3).

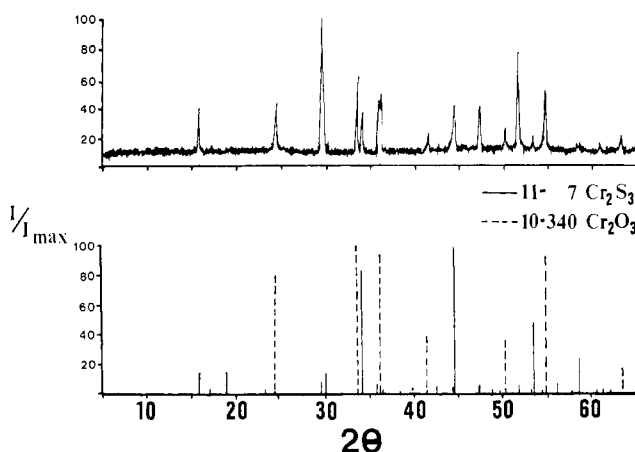


Figure 4. XRD pattern of the product prepared as in Figure 3 except that insufficiently dried solvent was used.

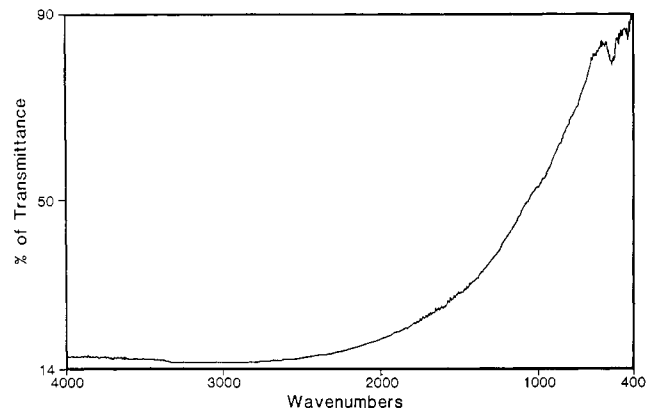


Figure 5. FTIR spectrum of MoS_3 as made from the reaction of MoF_6 with hexamethyldisilthiane.

reaction of CrCl_3 with HMDST. XRD also helps to point out the need for keeping moisture out of the system. In Figure 4 the result of using insufficiently dried acetonitrile as the solvent in the aforementioned reaction is seen. The sulfide prepared is contaminated with a large percentage of oxide. Table III presents comparisons of the d spacings of those sulfides that were crystallized with the JCPDS files to which they are expected to correspond. The vanadium sulfide, when heated for crystallization, visibly gave off some sulfur. This is expected and, as shown in the table, corresponds to decomposition of VS_2 to the more thermally stable V_5S_8 .

XRD and elemental analysis are good techniques for determining the gross composition and major phases of the compounds, but they are relatively insensitive to impurities and tell nothing of amorphous structure. Although the X-ray patterns may indicate that our samples correspond to the expected sulfides after heating,

(52) Ewborth, E. A. V. *Organometallic Compounds of the Group IV Elements*; MacDiarmid, A. G., Ed.; Dekker: New York, 1968; Vol. I.

Table III. *d* Spacings (Å) and Intensities (I/I_m in Parentheses) of Thermally Crystallized Products Compared with Those of the Corresponding Sulfides and Oxides from the JCPDS Files

FeS			Cr ₂ S ₃	Cr ₂ O ₃
MM166A	24-80	MM148A	10-340	6-504
	4.73 (5)	5.53 (23.94)	5.55 (16)	
2.99 (22.73)	2.98 (56)		4.91 (10)	
2.89 (3.29)	2.93 (9)		4.37 (8)	
2.66 (31.02)	2.66 (36)			3.63 (74)
2.53 (8.23)	2.52 (4)	2.96 (21.38)	2.96 (16)	
	2.16 (4)	2.66 (8.43)		2.67 (100)
2.08 (100.00)	2.09 (100)	2.61 (100.00)	2.61 (80)	
	1.93 (5)	2.47 (6.12)		2.48 (94)
	1.75 (4)			2.18 (40)
1.73 (29.63)	1.72 (28)	2.03 (97.86)	2.02 (100)	
1.62 (9.23)	1.64 (4)			1.82 (40)
1.48 (4.27)	1.49 (3)	1.71 (65.04)	1.71 (50)	
1.44 (12.86)	1.47 (5)	1.67 (6.39)		1.67 (90)
		1.64 (8.74)	1.64 (8)	
		1.57 (17.14)	1.57 (25)	
		1.46 (4.62)	1.48 (4)	1.46 (25)
		1.43 (15.83)	1.43 (10)	1.43 (40)
		1.39 (4.40)	1.39 (12)	
MoS ₂			TiS ₂	TiO ₂
MoS ₂ A	6-97	MM163B	15-853	12-1272
6.08 (100.00)	6.15 (100)	5.74 (57.31)	5.69 (54)	
3.06 (1.93)	3.08 (4)	3.53 (8.94)		3.52 (100)
2.72 (21.47)	2.74 (16)	2.63 (100.00)	2.62 (100)	
2.65 (16.44)	2.67 (10)			2.43 (10)
	2.50 (8)	2.37 (9.51)		2.38 (20)
2.28 (14.61)	2.28 (44)			2.33 (10)
2.04 (6.89)	2.05 (14)	2.06 (58.73)	2.05 (44)	
1.83 (4.35)	1.83 (25)			1.89 (34)
	1.64 (4)	1.71 (66.11)	1.70 (25)	1.70 (20)
1.58 (29.22)	1.58 (12)	1.67 (11.96)		1.67 (20)
		1.61 (16.15)	1.60 (16)	
		1.43 (23.62)	1.43 (10)	1.48 (14)
MM156D		VS ₂	V ₂ O ₃	V ₅ S ₈
		36-1139	26-278	29-1381
5.69 (100.00)	5.73 (100)			5.64 (76)
				5.09 (24)
3.67 (17.24)			3.65 (60)	2.87 (14)
			2.70 (80)	
2.72 (44.82)				2.54 (100)
2.56 (22.52)				
2.48 (51.89)	2.51 (70)	2.47 (60)		
2.20 (31.28)		2.18 (20)		
2.01 (9.83)	2.00 (40)	2.03 (2)		2.00 (40)
				1.98 (23)
	1.92 (10)			
1.83 (15.2)		1.83 (25)		
1.70 (56.89)		1.69 (100)		
				1.66 (17)
	1.60 (30)			1.64 (34)
				1.58 (14)
1.47 (13.90)		1.47 (25)		
1.43 (21.72)		1.43 (30)		

they give no guarantee that this was also the case before they were heated. We found that FTIR spectroscopy is very sensitive to slight impurities and can reveal bonding structure even in amorphous compounds. For example, Figure 5 shows the FTIR spectrum of the precipitate resulting from the reaction of MoF₆ and HMDST. No evidence of organic impurities in the compound is seen. Also easily visible is the sulfur-sulfur stretch at 530 cm⁻¹, in agreement with amorphous MoS₃ made by other methods. This peak is not visible in MoS₂. Also, previous electrochemical studies indicated that MoS₃ prepared from HMDST cycled identically

Table IV. Results of Reactions^a

halide	solvent	product
MoF ₆	CH ₂ Cl ₂	MoS ₃
MoCl ₅	CH ₂ Cl ₂	Mo ₂ S ₅
MoCl ₄	CH ₂ Cl ₂	MoS ₂
MoCl ₃	CH ₂ Cl ₂ , THF, neat	
WF ₆ , WCl ₆	CH ₂ Cl ₂	WS ₃
WCl ₅	CH ₂ Cl ₂	W ₂ S ₅
WBr ₄	THF, CH ₃ CN	WS ₂
CrCl ₃	THF, CH ₃ CN	Cr ₂ S ₃
CrCl ₂	THF, CH ₃ CN	CrS
TiCl ₄	CH ₂ Cl ₂	TiS ₂
VCl ₄	CH ₂ Cl ₂	VS ₂
NbCl ₅	CH ₂ Cl ₂	Nb ₂ S ₅
FeCl ₃	CH ₂ Cl ₂	Fe ₂ S ₃
FeCl ₂	CH ₂ Cl ₂	FeS

^aOnly MoCl₃ failed to produce any product.

with MoS₃ prepared from ammonium thiomolybdate when used as a cathode in a lithium battery.⁴¹

Conclusion

We have been able to react a wide range of transition-metal halides in various oxidation states with hexamethyldisilthiane. Only MoCl₃ failed to produce a reaction. This compound was insoluble in the solvents that we tried, including HMDST. All of the other halides reacted to completion when sufficient HMDST was present and produced amorphous materials, as shown in Table IV. Retention of the formal oxidation state of the metal from the halide was found in the sulfide in all cases. Aside from facilitating the direct synthesis of a variety of sulfides, the reaction conditions of the process can be easily varied to affect the physical properties of the resulting sulfide. We have used temperatures as low as -78 °C and up to 230 °C to produce MoS₃ from a vapor-phase reaction. The upper limit of this temperature range was determined by the thermal stability of the sulfide to be formed. Various solvent environments and, as just noted, the vapor phase will permit the reaction.

Another aspect worth noting is that the reaction proceeds very swiftly, usually instantaneously. This may account for the fact that all sulfides prepared so far have had very small particle sizes. Since the materials formed are amorphous, it is difficult to determine their actual compositions. In the case of MoS₃, electrochemical measurements⁴¹ justify our arguments that single-phase amorphous materials are prepared. In addition, thermal analysis plots on all samples never indicate the existence of pure sulfur. The analysis of the resulting byproducts have indicated that only formation of trimethylsilyl halides occurs in all reactions. This is helpful since they are volatile and can readily be removed from the precipitates with the solvent. As we cannot imagine any type of radical or silicon "carbanion" type mechanism, it seems reasonable that a multicoordinated intermediate species is formed, which allows for rapid metathesis reactions between the solvated metal halides and HMDST. It is our feeling that if the metal halide is soluble, the reaction will proceed.

We recognize a need for additional physical characterization of many of the amorphous materials that have been formed to further understand their physical properties and local bonding arrangements.

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