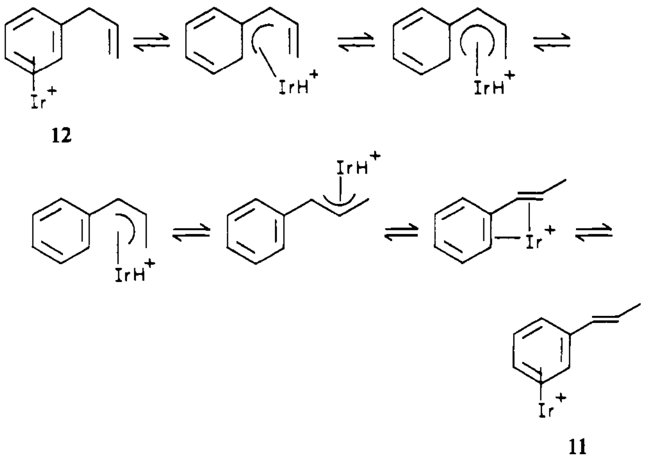
Scheme I. Proposed Intramolecular Isomerization of Coordinated Allylbenzene



and the starting arene complex would eventually result in total conversion to **11**. Sherman has recently presented evidence for a 1,3-hydrogen shift mechanism in the isomerization of allylbenzene by $\{Ru(\pi\text{-}CH_3CN)[P(C_6H_5)_3]_3\}(CH_3CN)$.[78]

Chloroform solutions of the allylbenzene complex isomerized to the *trans*-propenylbenzene complex at the same rate observed in acetone solutions (k_{obsd} = ca. 2×10^{-5} s^{-1}; see Figure 5). The reactions proceeded in a first-order fashion although some curvature in the rate plot was observed at higher concentrations and long reaction times. The *cis*-propenylbenzene complex also isomerized in chloroform solution. Since arene-exchange rates have been shown to be much slower in chloroform than in acetone, it seems clear that arene dissociation is not rate determining. Scheme I presents a plausible mechanism for the allylbenzene → *trans*-propenylbenzene conversion.

Acknowledgment. Important to this research was a loan of iridium chloride from Matthey-Bishop Co., Malvern, PA. We gratefully acknowledge the National Science Foundation for support of this research and for a Departmental Equipment Grant to the Department of Chemistry, University of California at Berkeley, for purchase of a 180-MHz NMR spectrometer. In addition, we thank Professor J. R. Shapley for helpful discussions.

Registry No. **1**, 75751-41-6; **3**, 75751-42-7; **6**, 75751-43-8; **7**, 75751-45-0; **8**, 75751-47-2; **11**, 75800-61-2; **12**, 75751-49-4; $[Ir(\eta^6\text{-}C_6H_5C_6H_5)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-51-8; $[Ir(\eta^4\text{-}COD)(CH_3CN)_2^+](BF_4^-)$, 32679-03-1; $[Ir(\eta^6\text{-}C_6H_6)(\eta^4\text{-}COD)^+](OSO_2CF_3^-)$, 75751-52-9; $[Ir(\eta^6\text{-}1,4\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](OSO_2CF_3^-)$, 75751-53-0; $[Ir(\eta^6\text{-}1,4\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](PF_6^-)$, 75751-54-1; $[Ir(\eta^6\text{-}1,4\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](B_{12}Cl_{12}^{2-})_{1/2}$, 75751-55-2; $[Ir(\eta^6\text{-}C_6H_6)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-34-9; $[Ir(\eta^6\text{-}1,3\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-40-7; $[Ir(\eta^6\text{-}1,2,3\text{-}C_6H_3(CH_3)_3)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-57-4; $[Ir(\eta^6\text{-}1,2,4\text{-}C_6H_3(CH_3)_3)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-59-6; $[Ir(\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-44-1; $[Ir(\eta^6\text{-}1,2,3,4\text{-}C_6H_2(CH_3)_4)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-46-3; $[Ir(\eta^6\text{-}1,2,3,5\text{-}C_6H_2(CH_3)_4)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-48-5; $[Ir(\eta^6\text{-}1,2,4,5\text{-}C_6H_2(CH_3)_4)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-48-5; $[Ir(\eta^6\text{-}1,2\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-38-3; $[Ir(\eta^6\text{-}\mathit{cis}\text{-}C_6H_5CH{=}CHCH_3)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-24-5; $[Ir(\eta^6\text{-}C_6H_5OH)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-26-7; $[Ir(\eta^6\text{-tetralin})(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-28-9; $[Ir(\eta^6\text{-naphthalene})(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-30-3; $[Ir(\eta^6\text{-}9,10\text{-dihydroanthracene})(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-32-5; $[Ir(\eta^6\text{-indene})(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-34-7; $[Ir(\eta^6\text{-}C_6(CH_3)_6)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-50-9; $[Ir(\eta^6\text{-}C_6H_5CH_3)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-36-1; $[Ir(\eta^6\text{-}1,4\text{-}C_6H_4(CH_3)_2)(\eta^4\text{-}COD)^+](BF_4^-)$, 74238-42-9; $[Ir(\eta^4\text{-}COD)HCl_2]_2$, 12148-12-8; $[Ir(\eta^4\text{-}COD)(\mu\text{-}OCH_3)]_2$, 33087-83-1; $[Ir(\eta^4\text{-}COD)Cl]_2$, 12112-67-3; $Ir(\eta^4\text{-}COD)(acac)$, 12154-84-6; $[Ir(\eta^6\text{-}C_6D_6)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-36-9; $[Ir(\eta^6\text{-}1,4\text{-}C_6D_4(CD_3)_2)(\eta^4\text{-}COD)^+](BF_4^-)$, 75751-38-1; $[Ir(\eta^4\text{-}COD)(S(C_2H_5)_2)_2^+](BF_4^-)$, 75751-40-5; C_6H_6, 71-43-2; $1,2\text{-}C_6H_4(CH_3)_2$, 95-47-6; $1,3\text{-}C_6H_4(CH_3)_2$, 108-38-3; $1,2,3\text{-}C_6H_3(CH_3)_3$, 526-73-8; $1,2,4\text{-}C_6H_3(CH_3)_3$, 95-63-6; $1,3,5\text{-}C_6H_3(CH_3)_3$, 108-67-8; $1,2,3,4\text{-}C_6H_2(CH_3)_4$, 488-23-3; $1,2,3,5\text{-}C_6H_2(CH_3)_4$, 527-53-7; $1,2,4,5\text{-}C_6H_2(CH_3)_4$, 95-93-2; C_6H_5OH, 108-95-2; $C_6H_5C_6H_5$, 92-52-4; $C_6H_5CH_2CH{=}CH_2$, 300-57-2; *cis*-$C_6H_5CH{=}CHCH_3$, 766-90-5; *trans*-$C_6H_5CH{=}CHCH_3$, 873-66-5; tetralin, 119-64-2; naphthalene, 91-20-3; 9,10-dihydroanthracene, 613-31-0; anthracene, 120-12-7; indene, 95-13-6.

Supplementary Material Available: Tables I–VIII (arene-exchange data), Table IX (kinetic data for isomerization of coordinated allylbenzene), and Table XV (^{1}H chemical shifts for iridium(I) *p*-toluenesulfonato complexes and salts) (14 pages). Ordering information is given on any current masthead page.

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Synthesis of Poorly Crystallized Platinum Metal Dichalcogenides

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Poorly crystallized RuS_2, OsS_2, PtS_2, and PdS_2 were prepared by the reaction of the anhydrous hexachlorometallate(IV) with hydrogen sulfide at various temperatures. Magnetic susceptibility measurements were obtained for the poorly crystallized materials as well as their annealed crystalline analogues. The magnetic susceptibility data indicate that the dichalcogenides are diamagnetic in both the poorly crystallized and crystalline phases. Powder X-ray diffraction analysis of the annealed materials indicates that RuS_2 and OsS_2 crystallize with the pyrite structure (a = 5.610 and a = 5.620 Å, respectively). PdS_2 crystallizes with an orthorhombic, distorted-pyrite structure (a = 5.457, b = 5.532, c = 7.524 Å). PtS_2 crystallizes in the hexagonal CdI_2 structure (a = 3.544, c = 5.029 Å).

Introduction

There has been recent interest in the "amorphous" or poorly crystallized transition-metal dichalcogenides, especially in the areas of electrochemistry and catalysis.[1-6] [X-ray diffraction patterns of these compounds resemble those obtained for materials which might be classified as being almost amorphous. The presence of only a small degree of short-range order, as evidenced by the shape of the X-ray diffraction pattern ob-

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Table I. Reaction Conditions

starting material	temp of reacn, °C	reacn time, h
$(NH_4)_2RuCl_6$	180	4
$(NH_4)_2OsCl_6$	220	3
$(NH_4)_2PdCl_6$	110	2
$(NH_4)_2PtCl_6$	130	1

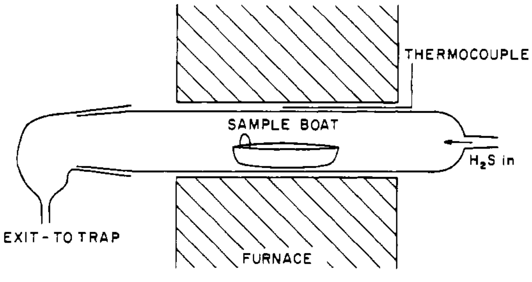

Figure 1. Reaction apparatus.

tained, form the basis for the term "poorly crystallized".] Previously, there has been reported[7,8] a technique for the preparation of a number of group 4B, 5B, and 6B poorly crystallized or amorphous transition-metal dichalcogenides and more recently for the preparation of poorly crystallized RuS_2.[9] These materials were prepared in nonaqueous solvents, at ambient temperature and pressure, by the reaction of an anhydrous transition-metal chloride with either Li_2S or NH_4HS. This paper discusses a new synthetic method for the preparation of poorly crystallized platinum metal dichalcogenides, RuS_2, OsS_2, PtS_2, and PdS_2, which is simpler than the procedures previously published. The properties of the "amorphous" platinum metal dichalcogenides are compared with those of their annealed crystalline analogues.

Experimental Section

Preparation. Poorly crystallized RuS_2, OsS_2, and PdS_2 were prepared by the reaction of anhydrous ammonium hexachlororuthenate(IV), ammonium hexachloroosmate(IV), ammonium hexachloroplatinate(IV), and ammonium hexachloropalladate(IV) with hydrogen sulfide at the conditions outlined in Table I. The reaction times and temperatures indicated are critical; too high a reaction temperature results in the decomposition of the ammonium hexachlorometallate(IV) complex to the metal, whereas too low a reaction temperature does not allow for a complete reaction to occur.

All of the platinum metal reactants were obtained from Engelhard Minerals and Chemicals Corp. The hydrogen sulfide was obtained from Matheson Gas Products Co. and was predryed through a column of aluminum sulfide (Cerac/Pure Inc.).

Preparation of RuS_2. Anhydrous ammonium hexachlororuthenate(IV) was prepared from $RuCl_3$.[10] The $(NH_4)_2RuCl_6$ complex was ground thoroughly under nitrogen with an agate mortar and pestle and placed into a silica boat, which was then placed inside a clamshell furnace as shown in Figure 1. The system was purged, at a flow rate of 55 cm^3/min, first with dry nitrogen and then with hydrogen sulfide, each for 30 min before the furnace was heated. When the ammonium hexachlororuthenate(IV) precursor was at the temperature indicated in Table I for half the stated time, the furnace was shut off. The material was cooled rapidly to room temperature while a hydrogen sulfide purge was maintained. The partially reacted material was removed from the furnace, reground thoroughly with an agate mortar and pestle, and treated in hydrogen sulfide for the time remaining. In the preparation of poorly crystallized RuS_2, there is an additional heat treatment with hydrogen sulfide that is not indicated in Table I. Without exposing the "amorphous" RuS_2 to air, following the second 2-h treatment under H_2S at 180 °C, the furnace temperature is increased to 250 °C and is maintained for an additional 2.5 h. Poorly crystallized RuS_2 tends to be pyrophoric, and this additional heat treatment is necessary to prevent air oxidation of the product.

Table II. Annealing Conditions

material	temp of annealing, °C	length of annealing, days
RuS_2	800	4
OsS_2	800	4
PtS_2	750	6
PdS_2	700	5

The reaction between the ammonium hexachlororuthenate(IV) and hydrogen sulfide is assumed to proceed by eq 1.

$$(NH_4)_2RuCl_6 + 2H_2S \xrightarrow[4\ h]{180\ °C} RuS_2 + 2NH_4Cl(s) + 4HCl(g) \qquad (1)$$

For removal of all traces of ammonium chloride, the products obtained by the above reaction were transferred to a Soxhlet extractor and extracted with methanol for 24 h. The materials were then extracted with carbon disulfide for 12 h to remove any sulfur that may have been deposited with the products. Decomposition of hydrogen sulfide at 250 °C was observed to occur in the presence of RuS_2. After extraction with carbon disulfide, the poorly crystallized RuS_2 was dried under vacuum.

Preparation of OsS_2, PdS_2 and PtS_2. Anhydrous $(NH_4)_2OsCl_6$ was obtained from Engelhard Minerals and Chemicals Corp. Anhydrous $(NH_4)_2PdCl_6$ was prepared from $PdCl_2$,[11] and anhydrous $(NH_4)_2PtCl_6$ was prepared from Pt metal.[12] The conditions for the synthesis of poorly crystallized OsS_2, PtS_2, and PdS_2 are outlined in Table I. The procedure is identical with that described for the synthesis of poorly crystallized RuS_2. However, it is not necessary to thermally treat "amorphous" OsS_2, PdS_2, and PtS_2 at an elevated temperature as it is for RuS_2, since these three products do not tend to be pyrophoric.

Annealing Experiments. The products obtained after the extractions with methanol and carbon disulfide were annealed with 10% by weight excess sulfur in evacuated sealed silica tubes at temperatures ranging from 250 to 800 °C. The temperatures and times of annealing necessary to form well-crystallized materials are outlined in Table II. Each time the samples were quenched to room temperature.

X-ray Analysis and Characterization. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromated high-intensity Cu Kα_1 radiation (λ = 1.5405 Å). Fast scans at 1° (2θ)/min of the products were examined for the presence of extraneous phases. Slow scans of $^1/_4$° (2θ)/min were obtained for all single-phase samples in the range $12° \le 2\theta \le 120°$. Lattice parameters for the crystalline phases OsS_2, RuS_2, PdS_2, and PtS_2 were determined by least-squares analysis using high-angle data ($2\theta > 50°$), corrected relative to an internal MgO standard.

Thermogravimetric Analysis. The sulfur to metal ratio in the amorphous materials was determined by thermogravimetric analysis (TGA) with use of a Cahn electrobalance (Model RG) with a 0.001-mg accuracy. Approximately 30 mg of finely powdered samples of each of the poorly crystallized products was placed in a silica bucket for heating. The maximum temperature reached was 900 °C, and the rate of heating was 30 °C/h. The sample was kept at 900 °C for 12 h after which time the furnace was shut off, allowing the sample to cool to room temperature.

Magnetic Measurements. Magnetic susceptibility data were obtained with a Faraday balance equipped with a Cahn RG electrobalance, described elsewhere,[13] over a temperature range of 80–300 K for poorly crystallized and crystalline RuS_2, OsS_2, PtS_2, and PdS_2. Measurements were performed at field strengths between 6.25 and 10.30 kOe. The balance was calibrated by using platinum wire (χ_g = 0.991×10^{-6} emu/g at 275 K). No corrections were made for core

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Table III. Thermogravimetric Analysis Results

material	starting wt, mg	final wt, mg	wt loss, mg	theor wt loss, mg	mole ratio M:S
RuS_2	17.19	10.14	7.05	6.67	1:2.19
OsS_2	19.05	14.13	4.92	4.80	1:2.07
PdS_2	12.99	8.27	4.72	4.88	1:1.89
PtS_2	15.15	10.60	4.55	3.75	1:2.43

Table IV. Crystallization Parameters

material	temp of onset of crystallization, °C	obsd phase	cell parameters, A	
			fnt *a*	fnt *b*
RuS_2	350	cubic pyrite	$a = 5.610$ (2)	$a = 5.610$[14]
OsS_2	400	cubic pyrite	$a = 5.620$ (2)	$a = 5.6196$[15]
PtS_2	425	hexagonal CdI_2	$a = 3.544$ (2), $c = 5.039$ (2)	$a = 3.543$, $c = 5.038$[16]
PdS_2	450	orthorhombic distorted pyrite	$a = 5.457$ (2), $b = 5.542$ (2), $c = 7.534$ (2)	$a = 5.460$, $b = 5.541$, $c = 7.531$[17]

[a] Cell parameters calculated from this work. [b] Cell parameters obtained for well-crystallized materials prepared by conventional methods (i.e., direct combination of the elements).

diamagnetism because of the large uncertainty in the magnitude of the corrections relative to the susceptibility of the material studied.

Results and Discussions

Thermogravimetric Analysis. Thermogravimetric analysis was carried out on the reaction products after extraction with methanol and carbon disulfide in order to obtain a value for the ratio of sulfur to metal. Results of the thermogravimetric analysis are summarized in Table III. In all cases, when the "amorphous" materials were subjected to the indicated conditions of thermogravimetric analysis, they decomposed to the metal and sulfur. X-ray powder diffraction patterns of the decomposed products confirmed the formation of metal.

X-ray Analysis. Powder X-ray diffraction analysis of the reaction products showed them to be poorly crystallized. The series of annealing experiments indicated that the poorly "amorphous" platinum metal dichalcogenides showed evidence of crystallization at the temperatures indicated in Table IV. The crystallized phases observed are also summarized in Table IV.

The changes in the crystalline character of RuS_2 as a function of annealing temperature can be seen in Figure 2. It can be seen that the Bragg peaks expected for the crystalline phase of RuS_2 develop from the corresponding X-ray powder diffraction envelope of the poorly crystallized disulfide. It should be noted that the vertical-line diffraction patterns shown in Figure 2 are a schematic representation of the X-ray powder diffraction patterns observed for the crystalline phase. There was no evidence for the existence of either metal or metal oxide in any of the X-ray patterns. Similar results were obtained for OsS_2, PdS_2, and PtS_2.

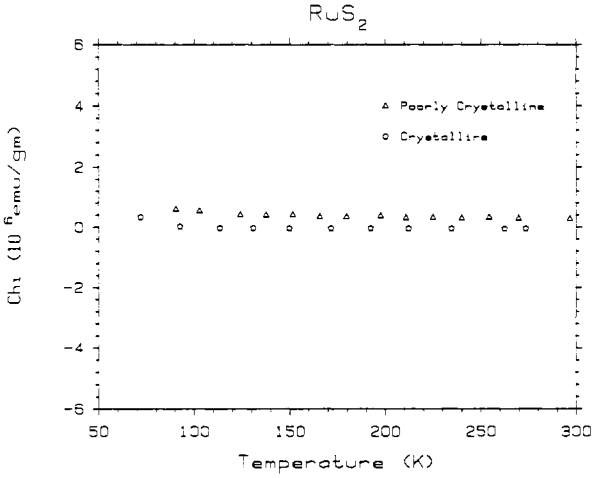

Figure 2. Powder X-ray diffraction pattern of "amorphous" and crystalline RuS_2.

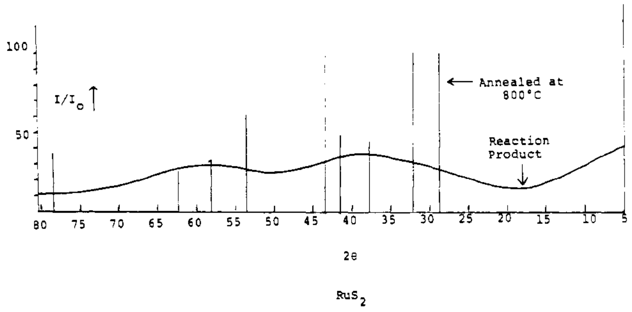

Figure 3. Magnetic susceptibility (χ vs. temperature) of "amorphous" and crystalline RuS_2.

Cell parameters were calculated for the well-crystallized materials and are summarized in Table IV. From Table IV, it can be seen that the calculated cell parameters are consistent with the parameters reported previously for the dichalcogenides prepared by conventional methods (i.e., direct combination of the elements).

Magnetic Measurements. RuS_2 and OsS_2 contain low-spin d^6 Ru and Os, respectively, and are known to be diamagnetic. PdS_2 and PtS_2 contain low-spin d^8 Pd and Pt, respectively, and are also known to be diamagnetic. Hence, magnetic susceptibility measurements on the four "amorphous" platinum metal dichalcogenides were an important means of confirming their composition. Magnetic susceptibility was also remeasured for the same material after annealing at the temperatures stated in Table II. At these temperatures the crystalline phases could be substantiated by X-ray analysis. Results of the magnetic susceptibility measurements are given in Figure 3. It can be seen that diamagnetic behavior is observed, as predicted for both the poorly crystallized and crystalline phases of RuS_2. Similar behavior was observed for OsS_2, PtS_2, and PdS_2.

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Registry No. RuS_2, 12166-20-0; OsS_2, 12137-61-0; PdS_2, 12137-75-6; PtS_2, 12038-21-0; $(NH_4)_2RuCl_6$, 18746-63-9; $(NH_4)_2OsCl_6$, 12125-08-5; $(NH_4)_2PdCl_6$, 19168-23-1; $(NH_4)_2PtCl_6$, 16919-58-7; H_2S, 7783-06-4.

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