

# Effect of Diverse Ligands on the Course of a Molecules-to-Solids Process and Properties of Its Intermediates

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Received February 23, 1994<sup>Ⓞ</sup>

We have been studying chemical processes that use discrete molecular reagents to form extended solid inorganic materials. The goals of this program have been to determine how best to design and implement these molecular precursor reactions and to discover what chemical intermediates lie on the molecules-to-solids paths. In this manuscript we report studies of the reactions of the low-valent iron complex  $\text{Fe}(\text{C}_8\text{H}_8)_2$  with low-valent tellurium compounds of the form  $\text{TePR}_3$  (R = various hydrocarbon groups) that lead ultimately to the exclusively inorganic extended solid compounds  $\text{Fe}_x\text{Te}_y$ . We have found four Fe/Te cluster types that are chemical intermediates in this process:  $\text{Fe}_4\text{Te}_4(\text{PEt}_3)_4$ , **1**;  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , **2**;  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , **3**;  $(\text{dmpe})_2\text{FeTe}_2$ , **4**;  $(\text{depe})_2\text{FeTe}_2$ , **5**;  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , **6**. (Here  $i\text{Pr} = \text{CHMe}_2$ ,  $\text{dmpe} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ , and  $\text{depe} = \text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ .) The different clusters form when different supporting phosphine ligands are employed. We report the syntheses, structures, and properties of these intermediates and the comparisons and contrasts between these molecular intermediates and the extended solid products. We note that when larger ligands are used smaller clusters are formed. We also note what features of the molecular structures lead to ferromagnetic versus antiferromagnetic coupling of the distinct Fe centers. We have determined the structures of the following materials crystallographically: **2** ( $\text{C}_{36}\text{H}_{84}\text{Fe}_4\text{Te}_4\text{P}_4$ ; tetragonal,  $P4_21c$ ;  $a = 14.0469(7) \text{ \AA}$ ,  $c = 13.5418(9) \text{ \AA}$ ;  $Z = 2$ ); **3** ( $\text{C}_{18}\text{H}_{54}\text{Fe}_6\text{Te}_8\text{P}_6$ ; trigonal,  $R\bar{3}$ ;  $a = 11.859(2) \text{ \AA}$ ,  $c = 26.994(5) \text{ \AA}$ ;  $Z = 3$ );  $\text{dmpe}\cdot 2\text{Te}$  ( $\text{C}_6\text{H}_{16}\text{Te}_2\text{P}_2$ ; monoclinic,  $P2_1/c$ ;  $a = 6.0890(4) \text{ \AA}$ ,  $b = 10.7934(7) \text{ \AA}$ ,  $c = 9.8200(5) \text{ \AA}$ ,  $\beta = 104.63(7)^\circ$ ;  $Z = 2$ ); **5** ( $\text{C}_{20}\text{H}_{48}\text{FeTe}_2\text{P}_4$ ; orthorhombic,  $Pbnn$ ;  $a = 10.997(3) \text{ \AA}$ ,  $b = 14.157(3) \text{ \AA}$ ,  $c = 18.345(4) \text{ \AA}$ ;  $Z = 4$ ); **6** ( $\text{C}_{24}\text{H}_{64}\text{Fe}_4\text{Te}_6\text{P}_8$ ; orthorhombic,  $Abaa$ ;  $a = 12.056(3) \text{ \AA}$ ,  $b = 17.725(5) \text{ \AA}$ ,  $c = 21.403(8) \text{ \AA}$ ;  $Z = 4$ ).

## Introduction

The study of chemical processes that lead from molecular reagents to extended solid products has several goals. Among these is the determination of methods by which the otherwise runaway reactions can be controlled in a purposeful way. Were the appropriate methods of control available, one could envision the construction of very complex solids *via* strictly chemical means. At present such a level of fine control is not generally available.

In the present manuscript we describe our efforts to control the processes that lead from the initial combination of bis(cyclooctatetraene)iron,  $\text{Fe}(\text{COT})_2$ , and triethylphosphine telluride,  $\text{TePEt}_3$ , to the ultimate products, solid-state tellurides of iron,  $\text{Fe}_x\text{Te}_y$ . We find that the addition of different phosphine ligands to the reaction mixture results in the formation of different Fe/Te-containing molecular compounds. We describe the syntheses of these materials, their molecular structures and properties, and their physical and chemical relationships among one another and to the associated extended solids.

## Experimental Section

Unless noted to the contrary all manipulations were conducted under inert atmosphere using conventional techniques. Triethylphosphine ( $\text{PEt}_3$ , Aldrich), trimethylphosphine ( $\text{PMe}_3$ , 1 M solution in toluene, Aldrich), triisopropylphosphine ( $\text{P}^i\text{Pr}_3$ , Strem), bis(dimethylphosphino)ethane ( $\text{dmpe}$ , Strem), bis(diethylphosphino)ethane ( $\text{depe}$ , Strem), and tellurium (Aldrich) were used as received. Solvents were anhydrous and used as received from Aldrich. Simple trialkylphosphine tellurides<sup>1</sup> and bis(cyclooctatetraene)iron<sup>2</sup> were prepared using literature methods. Magnetic susceptibility measurements were made on a SQUID magnetometer using standard techniques.

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‡ Abstract published in *Advance ACS Abstracts*, June 15, 1994.

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**Synthesis of  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , **2**.**  $\text{Fe}(\text{COT})_2$  (1.00 g, 3.79 mmol) dissolved in toluene (15 mL) was treated with a mixture of  $\text{TeP}^i\text{Pr}_3$  (1.09 g, 3.79 mmol) and  $\text{P}^i\text{Pr}_3$  (1.82 g, 11.4 mmol) in toluene (15 mL). The resulting solution was heated to reflux 4.5 h, after which the deep brown mixture was cooled to room temperature and filtered through a medium-porosity glass frit. The solution was condensed *in vacuo* to roughly half its original volume. Cooling this latter solution to  $-20^\circ\text{C}$  overnight gave crystallization of  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$  that was isolated, washed with pentane ( $2 \times 5 \text{ mL}$ ), and dried ( $0.293 \text{ g}$ ,  $8.53 \times 10^{-5} \text{ mol}$ , 23%). Anal. Calcd for  $\text{C}_{36}\text{H}_{84}\text{Fe}_4\text{Te}_4\text{P}_4$ : C, 31.45; H, 6.16; Fe, 16.25; P, 9.01; Te, 37.13. Found: C, 31.57; H, 6.12; Fe, 16.50; P, 8.83; Te, 37.05.

**Synthesis of  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , **3**.** A solution of  $\text{Fe}(\text{COT})_2$  (1.00 g, 3.79 mmol) in toluene was distributed equally in three vials. Additional toluene ( $3 \times 10 \text{ mL}$ ) was carefully layered onto each. In a separate vessel elemental Te (0.65 g, 5.1 mmol) was dissolved in a solution of  $\text{PMe}_3$  in toluene/pentane (13 g of a stock 1 M toluene solution of  $\text{PMe}_3$  plus an additional 10 mL of toluene and 15 mL of pentane). The phosphine telluride solution was filtered and then layered evenly onto each of the three  $\text{Fe}(\text{COT})_2$  solutions. After 3 days at room temperature the layers had interdiffused and crystals of  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$  had formed. This solid was isolated, washed ( $2 \times 5 \text{ mL}$  of pentane), and dried ( $0.12 \text{ g}$ ,  $6.6 \times 10^{-5} \text{ mol}$ , 10%). Anal. Calcd for  $\text{C}_{18}\text{H}_{54}\text{Fe}_6\text{Te}_8\text{P}_6$ : C, 11.93; H, 3.00; Fe, 18.49; P, 10.25; Te, 56.32. Found: C, 12.20; H, 2.91; Fe, 18.55; P, 10.15; Te, 56.40.

**Pyrolysis of  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ .** A Pyrex ampule was charged with  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$  (0.044 g, 0.024 mmol), connected through a liquid-nitrogen trap to a vacuum pump, and heated to  $170^\circ\text{C}$  for 5 min. During this time the trimethylphosphine evolved as evidenced by the increase and subsequent decrease in the observed pressure. The residual solid (0.033 g, corresponding to 100%  $\text{PMe}_3$  loss) was sealed in an evacuated Pyrex tube and annealed for 2 h at  $350^\circ\text{C}$ . The residual solid was collected, washed with pentane, and dried *in vacuo* (0.030 g). Powder X-ray diffraction showed this to be a mixture of  $\beta$ - and  $\epsilon$ - $\text{FeTe}$ .<sup>3,4</sup> (N.B., during the annealing process a small amount of Te was transported to the cool end of the tube. This accounts for the small mass loss.)

**Synthesis of  $\text{dmpe}\cdot 2\text{Te}$ .** A solution of  $\text{dmpe}$  (0.15 g, 1.0 mmol) in toluene (5 mL) was treated with a solution of  $\text{TePEt}_3$  (0.5 g, 2 mmol)

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**Table 1.** Crystallographic Data for  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ ,  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ ,  $\text{dmpe}\cdot 2\text{Te}$ ,  $\text{FeTe}_2(\text{depe})_2$ , and  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ 

	$\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$	$\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$	$\text{mpe}\cdot 2\text{Te}$	$\text{FeTe}_2(\text{depe})_2$	$\text{Fe}_4\text{Te}_6(\text{dmpe})_4$
chem formula	$\text{Fe}_4\text{Te}_4\text{P}_4\text{C}_{36}\text{H}_{84}$	$\text{Fe}_6\text{Te}_8\text{P}_6\text{C}_{18}\text{H}_{54}$	$\text{Te}_2\text{P}_4\text{C}_6\text{H}_{16}$	$\text{FeTe}_2\text{P}_4\text{C}_{20}$	$\text{Fe}_4\text{Te}_6\text{P}_6\text{C}_{24}\text{H}_{64}$
fw	1374.75	1812.35	405.35	675.16	1589.56
space group	$P4_21c$	$R\bar{3}$	$P2_1/c$	$Pbnm$	$Abaa$
<i>a</i> (Å)	14.0469(7)	11.859(2)	6.0890(4)	10.997(3)	12.056(3)
<i>b</i> (Å)			10.7934(7)	14.157(3)	17.725(5)
<i>c</i> (Å)	13.5418(9)	26.994(5)	9.8200(5)	18.345(4)	21.403(8)
$\beta$ (deg)			104.63(7)		
<i>V</i> (Å <sup>3</sup> )	2672.0(3)	3287.7(8)	621.63(7)	2856(1)	4574(3)
<i>Z</i>	2	3	2	4	4
<i>T</i> (°C)	23	23	23	23	23
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.71	2.75	2.17	1.57	2.31
$\mu$ (mm <sup>-1</sup> )	3.35	8.12	4.91	2.76	4.04
$\lambda$ (Å)	0.709 30	0.709 30	0.709 30	0.709 30	0.709 30
$R_f^a$	0.053	0.022	0.027	0.041	0.033
$R_w^b$	0.059	0.021	0.029	0.046	0.043

$$^a R_f = \sum(F_o - F_c)/\sum F_o. \quad ^b R_w = \sum w(F_o - F_c)^2/\sum (wF_o^2).$$

in toluene (5 mL). The precipitation of  $\text{dmpe}\cdot 2\text{Te}$  began immediately. The mixture was left undisturbed several hours. The pale yellow microcrystalline solid was isolated by filtration, washed with pentane (3  $\times$  5 mL), and dried (0.23 g, 0.51 mmol, 51%). Anal. Calcd for  $\text{C}_6\text{H}_{16}\text{P}_2\text{Te}_2$ : C, 17.78; H, 3.98; P, 15.28; Te, 62.96. Found: C, 17.80; H, 3.94; P, 15.52; Te, 62.70. This compound is quite insoluble in toluene and pentane but is soluble in toluene to which several equivalents of  $\text{PET}_3$  have been added. Crystals suitable for diffraction were prepared by allowing the same two solutions to interdiffuse slowly at room temperature.

**Synthesis of  $(\text{dmpe})_2\text{FeTe}_2$ , 4.** A solution of  $\text{Fe}(\text{COT})_2$  (0.264 g, 1.0 mmol) in toluene (10 mL) was treated with a solution of  $\text{dmpe}$  (0.30 g, 2.0 mmol),  $\text{TePET}_3$  (0.49 g, 2.0 mmol), and  $\text{PET}_3$  (0.80 g, 6.8 mmol) in toluene (20 mL). The resulting mixture was filtered into a Schlenk tube and subsequently evaporated to dryness *in vacuo*. The resulting solid was extracted with toluene (15 mL). The extract was condensed and cooled to  $-20^\circ\text{C}$ , at which point crystallization of  $(\text{dmpe})_2\text{FeTe}_2$  occurred. The solid was isolated, washed (2  $\times$  5 mL of pentane), and dried (0.14 g, 0.23 mmol, 23%). Anal. Calcd for  $\text{C}_{12}\text{H}_{32}\text{FeP}_4\text{Te}_2$ : C, 23.58; H, 5.28; Fe, 9.14; P, 20.27; Te, 41.75. Found: C, 23.86; H, 5.28; Fe, 9.30; P, 20.03; Te, 41.65. UV-visible absorption (toluene):  $\lambda_{\text{max}} = 478, 584, 782$  nm.

**Pyrolysis of  $(\text{dmpe})_2\text{FeTe}_2$ .** A Schlenk tube was charged with  $(\text{dmpe})_2\text{FeTe}_2$  (44 mg,  $7.2 \times 10^{-5}$  mol). While the tube was open to vacuum (approximately 0.1 Torr), it was plunged into an oil bath whose temperature had been adjusted to  $210^\circ\text{C}$ . As indicated by the vacuum gauge, volatile material evolved as the solid changed appearance from dark red to metallic black. After 25 min, the tube was cooled and the solid collected (23 mg; complete removal of  $\text{dmpe}$  from 44 mg of  $(\text{dmpe})_2\text{FeTe}_2$  would leave 22 mg of solid). X-ray powder diffraction by showed only  $\text{FeTe}_2$ .<sup>3,4</sup>

**Synthesis of  $(\text{depe})_2\text{FeTe}_2$ , 5.** A solution of  $\text{Fe}(\text{COT})_2$  (264 mg, 1.0 mmol) in toluene (13 mL) was treated with a solution of  $\text{depe}$  (412 mg, 2.0 mmol) and  $\text{TePET}_3$  (491 mg, 2.0 mmol) in toluene (10 mL). The resulting solution was agitated to ensure complete mixing and then was left at room temperature overnight. At this point the volatile components of the mixture were removed *in vacuo* and the resulting dark, sticky solid was washed with pentane (15 mL), dried, and subsequently extracted with toluene (10 mL). The extract was condensed to approximately half its original volume and then cooled to  $-20^\circ\text{C}$ . The densely colored product formed as a crystalline solid (0.22 g, 30%). Anal. Calcd for  $\text{C}_{20}\text{H}_{48}\text{FeP}_4\text{Te}_2$ : C, 33.20; H, 6.69; Fe, 7.72; P, 17.12; Te, 35.27. Found: C, 33.08; H, 6.63; Fe, 7.86; P, 16.94; Te, 35.50. This compound is soluble in toluene and thf. UV-vis absorption (toluene):  $\lambda_{\text{max}} = 498, 615, 772$  nm.

**Synthesis of  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , 6.** A solution of  $\text{Fe}(\text{COT})_2$  (0.27 g, 1.0 mmol) in toluene (5 mL) was treated with a solution of  $\text{dmpe}$  (0.15 g, 1.0 mmol) in toluene (5 mL), and the combined solution was filtered. A solution of  $\text{TePET}_3$  (0.25 g, 1.0 mmol) in toluene (5 mL) was carefully layered onto the Fe-containing solution. The resulting mixture was left undisturbed at room temperature for 5 days, during which time crystals of  $(\text{dmpe})_4\text{Fe}_4\text{Te}_6$  formed. The supernatant solution was decanted, and the solid was washed thoroughly (5  $\times$  1 mL of toluene, 5  $\times$  1 mL of pentane). Drying gave 10.0 mg ( $6.3 \times 10^{-6}$  mol, 2.5%). This solid is absolutely insoluble in toluene, thf, and pentane. The crystals formed by this procedure can be used directly for X-ray crystallography.

**X-ray Crystallography.** In each of the systems for which we determined structures crystallographically a suitable crystal was mounted in a

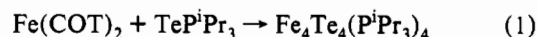
Lindemann capillary in an inert-atmosphere drybox. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized  $\text{Mo K}\alpha$  radiation and the NRCCAD program package.<sup>5</sup> The diffraction data are summarized in Table 1. Calculations were performed using the NRCVAX program package.<sup>6</sup> Absorption corrections were applied in each case. In each case the structure was solved by direct methods.

Disorder of the isopropyl carbon atoms was found in  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ . Although an ordered model could be refined, the difference Fourier maps clearly indicated rotational disorder of the  $\text{P}^i\text{Pr}_3$  groups.

## Results

We have previously reported<sup>7</sup> that the reaction of  $\text{Fe}(\text{COT})_2$  with  $\text{TePET}_3$  in the presence of additional  $\text{PET}_3$  yields the cluster compound  $\text{Fe}_4\text{Te}_4(\text{PET}_3)_4$ , **1**. The structure of this compound is a tetrahedron of four Fe atoms in which each tetrahedral face is capped with a triply-bridging Te atom. The structure is completed by four phosphine ligands, one coordinated to each Fe. We sought the answer to the question of how strongly the nature of the cluster product resulting from the combination of  $\text{Fe}(\text{COT})_2$  with phosphine tellurides depends on the supporting ligand by conducting a series of similar reactions in which we simply varied the phosphine.

When we used  $\text{P}^i\text{Pr}_3$  in place of  $\text{PET}_3$ , the first observation was that the Fe/Te reaction required more forcing conditions. While  $\text{Fe}(\text{COT})_2$  and  $\text{TePET}_3$  react upon combination at room temperature, the same iron compound reacts with  $\text{TeP}^i\text{Pr}_3$  only on heating to reflux in toluene. After this reaction mixture had been at reflux for 4.5 h, it was cooled, filtered, and condensed. The cluster product  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , **2**, formed as a crystalline solid (eq 1). We determined the structure of this compound by



X-ray crystallography (Tables 1 and 2, and Figure 1) and found that it is essentially that of **1**, i.e., formed by concentric  $\text{Fe}_4\text{Te}_4$  and  $\text{P}_4$  tetrahedra. Compound **2** is thus the latest member of the large family of  $\text{Fe}_4\text{E}_4$  cubane cluster compounds<sup>8-15</sup> and of the

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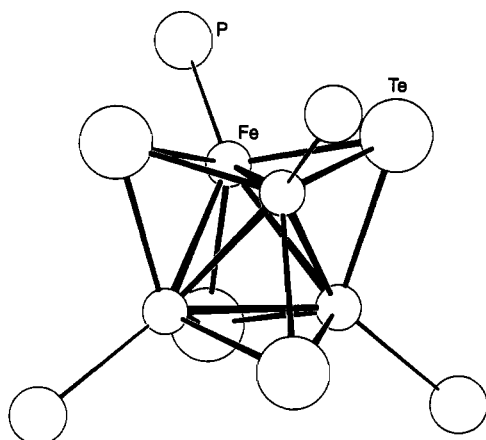
**Table 2.** Structural Comparison of  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$  and  $\text{Fe}_4\text{Te}_4(\text{PEt}_3)_4$ <sup>a</sup>

Distances (Å)			
ligand	Fe-Fe	Fe-Te	Fe-P
$\text{P}^i\text{Pr}_3$	2.687(5)	2.623(3)	2.447(6)
	2.675(5)	2.620(3)	
	2.687(5)	2.614(3)	
$\text{PEt}_3$	2.623(4)	2.609(1)	2.390(6)

Angles (deg)		
ligand	Fe-Te-Fe	Te-Fe-Te
$\text{P}^i\text{Pr}_3$	61.73(7)	112.71(9)
	61.36(7)	111.62(9)
	61.77(8)	111.71(9)
$\text{PEt}_3$	60.36(6)	112.70(5)

<sup>a</sup> Data concerning  $\text{Fe}_4\text{Te}_4(\text{PEt}_3)_4$  were taken from ref 6.



**Figure 1.** Structure of  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , **2**. The largest circles represent Te atoms, the smallest circles represent Fe atoms, and the medium circles represent the P atoms of the  $\text{P}^i\text{Pr}_3$  ligands. Selected distances and angles are given in Table 2.

much smaller family of  $\text{Fe}_4\text{Te}_4$  compounds.<sup>16-19</sup> The data in Table 2 show that the bond distances in **2** are generally longer than the corresponding distances in **1**. This is best explained by the greater steric bulk of  $\text{P}^i\text{Pr}_3$ . While **1** is crystallographically cubic, **2** is distorted from this ideal. This is ultimately due to the structural asymmetry of  $\text{P}^i\text{Pr}_3$ . The cluster **2** differs from **1** in solubility; while **1** is only slightly soluble in toluene, **2** is exceedingly so. Both the sluggish reactivity of  $\text{TeP}^i\text{Pr}_3$  and the increased solubility of **2** can be rationalized by the bulk of the trisopropylphosphine ligands.

Since an increase in the size of the phosphine gave the same cluster core, the effect of a comparable decrease in phosphine size was at issue. When  $\text{Fe}(\text{COT})_2$  is treated with a mixture of  $\text{TePMe}_3$  and  $\text{PMe}_3$ , and the solutions of the Fe and Te reagents are allowed to interdiffuse slowly, a cluster product, **3**, appears as large crystals. We determined the structure of **3** and found that it has a  $\text{Fe}_6\text{Te}_8$  core and not the  $\text{Fe}_4\text{Te}_4$  core of **1** and **2**. The crystallographic data collection is reviewed in Table 1, and the structure of the cluster is summarized in Table 3 and Figure 2.

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) in  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ <sup>a</sup>

Distances			
Fe-Te1a	2.541(1)	Te1a-Te1c'	3.684(1)
Fe-Te1b	2.544(1)	Te1-Te2	3.485(1)
Fe-Te1c	2.542(2)		
Fe-Te2	2.566(1)	(Fe-Te) <sub>vic</sub> <sup>b</sup>	2.548
Fe-Fe*	2.818(2)	(Fe-Fe) <sub>vic</sub> <sup>b</sup>	2.895
Fe-Fe#	2.972(2)	(Te-Te) <sub>vic</sub> <sup>b</sup>	3.585
Fe-P	2.245(2)		

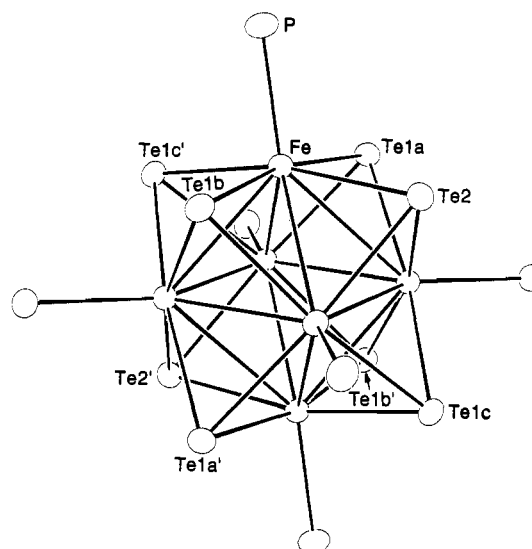
  

Angles around Fe			
Te1a-Fe-Te2	86.06(2)	Te1b-Fe-Te2	86.02(2)
Te1b-Fe-Te1c'	92.83(3)	Te1b-Fe-P	90.79(5)
Te1a-Fe-P	94.32(5)	Te1a-Fe-Te1c'	92.83(3)
Te2-Fe-P	102.94(5)	Te1c'-Fe-Te2	166.27(3)
Te1a-Fe-Te1b	168.42(4)	Te1c'-Fe-P	95.67(5)

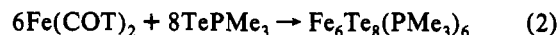
Angles around Te	
Fe-Te1-Fe*	67.33(5)
Fe-Te1-Fe#	71.58(4)
Fe-Te2-Fe*	70.78(3)

<sup>a</sup> The six Fe atoms form a trigonal antiprism. The labels Fe and Fe\* refer to iron atoms in the same basal plane, Fe# refers to an iron atom in the opposite basal plane. <sup>b</sup> Average values; vic = vicinal.



**Figure 2.** Structure of and labeling for  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , **3**. The structure contains an inversion center. Selected distances and angles are given in Table 3.

Compound **3**,  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , is a member of the  $\text{M}_6\text{E}_8$  family of "Chevrel-type" clusters.<sup>20-29</sup>



In this system smaller monodentate phosphines yield larger clusters than do larger phosphines. The next issue is the effect

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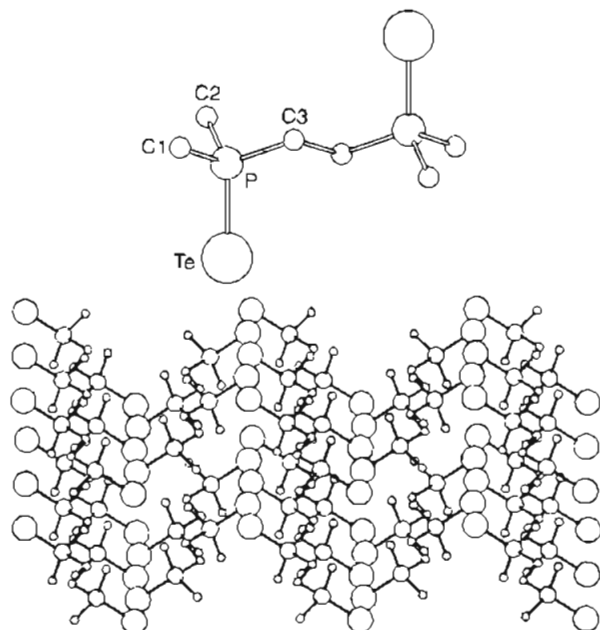


Figure 3. (a) Top: Structure of and labeling for  $\text{dmpe}\cdot 2\text{Te}$ . Selected distances and angles are given in Table 4. (b) Bottom: Crystal packing diagram for  $\text{dmpe}\cdot 2\text{Te}$ .

Table 4. Selected Interatomic Distances (Å) and Angles (deg) in  $\text{dmpe}\cdot 2\text{Te}$

Distances			
Te-P	2.357(2)	P-C2	1.796(7)
P-C1	1.825(6)	P-C3	1.803(7)
Angles			
Te-P-C1	112.9(3)	C1-P-C3	107.04(4)
C1-P-C2	103.24(4)	Te-P-C3	113.63(3)
Te-P-C2	113.93(3)	C2-P-C3	105.3(4)

of multidentate phosphines on the  $\text{Fe}(0)/\text{Te}(0)$  reaction. The most direct experiment in the series would be to allow  $\text{Fe}(\text{COT})_2$  to react with  $\text{dmpe}\cdot 2\text{Te}$ ; however, this is hampered by the virtually complete insolubility of  $\text{dmpe}\cdot 2\text{Te}$  in toluene. In order to understand this phosphine telluride and its behavior, we prepared it and examined its structure. As distinct from the usual synthesis (direct combination of elemental Te with the phosphine), the most convenient method of preparation of  $\text{dmpe}\cdot 2\text{Te}$  is to deliver Te to  $\text{dmpe}$  in the form of  $\text{TePEt}_3$  (eq 3). As the  $\text{dmpe}$  telluride forms, it precipitates from toluene as a microcrystalline solid. (In order to form crystals that are suitable for crystallography, the slow interdiffusion of solutions of the two reagents is required.) The crystallographic description of  $\text{dmpe}\cdot 2\text{Te}$  is summarized in Tables 1 and 4 and in Figure 3. The molecular structure is that of a typical phosphine telluride; however, the source of the insolubility of  $\text{dmpe}\cdot 2\text{Te}$  is apparent from the crystal packing diagram (Figure 3b): the molecules pack together very tightly in a zipper-like arrangement, aligning the Te atoms from adjacent layers.



The solubility of  $\text{dmpe}\cdot 2\text{Te}$  is greatly enhanced by including a monodentate phosphine such as  $\text{PEt}_3$  in the solvent mixture. One can imagine that the dynamic exchange of Te between  $\text{dmpe}$  and  $\text{PEt}_3$  (the transition state for which process contains the  $\text{R}_3\text{P}\cdot\text{Te}\cdot\text{PR}'_3$  array that is, in the limit of triphenylphosphine, a stable molecule<sup>30,31</sup>) interferes with the formation of the densely packed  $\text{dmpe}\cdot 2\text{Te}$  crystal. This feature accounts for the low isolated yield of  $\text{dmpe}\cdot 2\text{Te}$  when the latter is prepared from  $\text{dmpe}$

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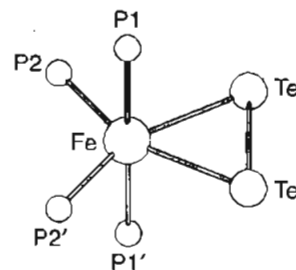


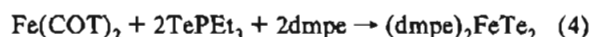
Figure 4. Structure of and labeling for  $\text{FeTe}_2(\text{depe})_2$ , 5. Selected distances and angles are given in Table 5.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) in  $\text{FeTe}_2(\text{depe})_2$

Distances			
Fe-Te	2.660(2)	Fe-P2	2.220(3)
Fe-P1	2.273(3)	Te-Te'	2.674(2)
Angles			
Te-Fe-Te'	60.35(5)	P1-Fe-P2'	84.3(1)
Te-Fe-P2	94.85(8)	Fe-Te-Te'	59.82(3)
P1-Fe-P2	96.2(2)	Te-Fe-P1'	86.69(9)
Te-Fe-P2	94.85(8)	P1-Fe-P1'	179.2(2)
Te-Fe-P1	92.57(9)	P2-Fe-P2'	110.0(2)
Te-Fe-P2'	155.18(9)		

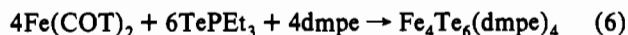
and  $\text{TePEt}_3$  and also allows the study of the reactions of  $\text{Fe}(\text{COT})_2$  with the reaction-equivalent of  $\text{dmpe}\cdot 2\text{Te}$ .

When  $\text{Fe}(\text{COT})_2$  is treated with  $\text{dmpe}$  and  $\text{TePEt}_3$  in toluene ( $\text{dmpe})_2\text{FeTe}_2$ , 4, forms at room temperature (eq 4). The stoichiometry used in this reaction is not critical as 4 forms readily. This compound appears to form good crystals, and we attempted to determine its molecular structure; however, there is disorder in the system and the structure did not refine well. The disorder is with respect to a crystallographic mirror plane that passes approximately through the Fe atom and one of the Te atoms. We hoped that the replacement of  $\text{dmpe}$  with a closely related bidentate phosphine would give the same inorganic molecular core but one which would pack into regular crystalline order. With this in mind we combined  $\text{Fe}(\text{COT})_2$  with  $\text{TePEt}_3$  in the presence of  $\text{depe}$ . The reaction with  $\text{depe}$  follows the same path, and ( $\text{depe})_2\text{FeTe}_2$ , 5, is formed as a crystalline solid (eq 5). We were able to determine the structure of this material crystallographically, and those results are summarized in Tables 1 and 5 and Figure 4. The iron atom in 5 is coordinated by four phosphorus and two tellurium atoms that form a very distorted octahedron. The Fe-Te and Te-Te distances within the  $\text{FeTe}_2$  triangle are within the ranges considered normal, although the Fe-Te distance is on the long side and the Te-Te distance is on the short side (see below).



The room-temperature absorption spectrum of 5 in the visible region shows three distinct features, all of which are quite intense. There is a strong similarity between this spectrum and that of 4. On the basis of this, and on the elemental analysis of 4, and the information to be gleaned from the incomplete X-ray structural refinement, we conclude that 4 is isostructural with 5.

When the compounds that are formed by  $\text{dmpe}$  and  $\text{depe}$  are compared with those based on monodentate phosphines, it is tempting to suggest that cluster growth is very effectively curtailed by the bidentate ligands. This deduction must be modified in view of the formation of  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , 6. Compound 6 is also formed by the reaction of  $\text{Fe}(\text{COT})_2$ ,  $\text{dmpe}$ , and  $\text{TePEt}_3$ ; however, in this case a minimum amount of  $\text{dmpe}$  is used, and the iron reagent and the tellurium reagent are allowed to combine only very slowly (eq 6). The synthesis of 6 is frustratingly unreliable;



however it is repeatable, and we have been able to prepare enough of the material to both determine its structure and measure its magnetization. The crystallographic structure determination is summarized in Tables 1 and 6 and in Figure 5. The structure of **6** is best appreciated as a dimer of  $(\text{dmpe})_2\text{Fe}_2\text{Te}_3$  in which the two subunits are connected by four equivalent Te-to-Fe donor/acceptor bonds. Discounting the potential Fe-Fe interaction (see below), each Fe atom is coordinated by six atoms, the six describing a distorted octahedron. Within each  $\text{Fe}_2\text{Te}_3$  subunit the three crystallographically distinct Fe-Te bonds are practically identical, and the Fe-Te internuclear distance of 2.586 Å as well within the normal range for covalent bonding.<sup>19,32</sup> The Te-Te internuclear distances are all well over 3 Å; therefore, no Te-Te bonding is evident. Given this, the Fe atoms are conveniently viewed as being in oxidation state III, again ignoring Fe-Fe bonding.

We have measured the magnetization of **1**, **2**, and **6**. Both **1** and **2** are paramagnetic. Above 100 K, each has a temperature-independent effective magnetic moment (8.3 and 8.49  $\mu_B$ , respectively) that corresponds roughly to 8 parallel spins. Compound **6** is diamagnetic.

We have shown previously<sup>7</sup> that complexes of the form  $\text{Fe}_4\text{-Te}_4(\text{PR}_3)_4$  undergo pyrolytic condensation to give solid-state tellurides of iron. Here we report that in the same way  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$  can be converted to  $\text{FeTe}_{1\pm x}$  and  $(\text{dmpe})_2\text{FeTe}_2$  can be converted to  $\text{FeTe}_2$ ; thus, all of these Fe/Te molecular and cluster compounds are chemically related to Fe/Te extended compounds.

## Discussion

From the results described above it is clear that a variety of clusters result from the interaction of  $\text{Fe}(\text{COT})_2$  with zerovalent tellurium in the form of  $\text{TePR}_3$  and that which of that variety one is able to isolate depends critically on which supporting phosphine is used. This suggests a level of reaction control that is available for moderating molecules-to-solids processes and raises the question of why a given phosphine results in a particular cluster. One explanation is crystallization: perhaps all of the cluster types we have observed in this system are present to greater or lesser degrees in all of the reactions, and the particular phosphine that is used selects the particular inorganic cluster core that we observe only because that phosphine-cluster superstructure crystallizes most promptly.

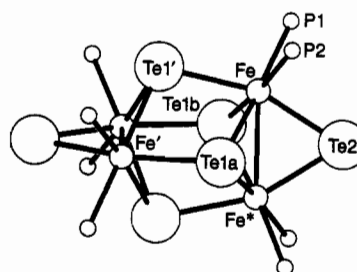
A second explanation is essentially kinetic. When the supporting ligands effectively hide the growing Fe/Te core from the reaction environment, the cluster so-hidden will be kinetically trapped since the ligands must be moved out of the way for further cluster growth to occur. It is reasonable that phosphines that are larger (all else being equal) will cover smaller clusters more effectively than will smaller phosphines. This reasoning predicts that the use of larger phosphines (all else being equal) will result in the isolation of smaller Fe/Te clusters. This rationalization is consistent with what we find.

In the limit of bidentate phosphines one might conjecture that this steric effect would shut down cluster growth entirely and that for this reason the  $\text{FeTe}_2$  compounds, **4** and **5**, result. The simple explanation based on steric protection is alone not sufficient to rationalize the formation of the  $\text{FeTe}_2$  compounds, however, since the  $\text{Te}_2$  unit in each is still quite exposed to the reaction environment. One might expect that the Te-Te bond would be reactive toward the (essentially) zerovalent iron remaining in the reaction mixture, but in fact neither **4** nor **5** reacts even with added  $\text{Fe}(\text{COT})_2$ . The resolution of this puzzle lies in the electronic structure of the complex. The Te-Te bond in **5** is short for a Te-Te single bond: the bond in **5** is 2.674 Å, while the

**Table 6.** Selected Interatomic Distances (Å) and Angles (deg) in  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$

Distances			
Fe-Te1a	2.586(2)	Te1a-Te1'	3.269(2)
Fe-Te1b	2.587(2)	Te1b-Te1'	3.216(2)
Fe-Te1'	2.593(2)	Te1a-Te2	3.655(2)
Fe-Te2	2.585(2)	Te1b-Te2	3.660(2)
Fe-Fe*	2.795(4)		
Fe-P1	2.217(4)	(Fe-Te) <sub>vic</sub> <sup>a</sup>	2.59
Fe-P2	2.224(4)	(Te-Te) <sub>vic</sub> <sup>a</sup>	3.45
Angles around Fe			
Te1a-Fe-Te2	89.94(5)	Te1'-Fe-P1	102.2(2)
Te1a-Fe-P1	171.6(2)	P1-Fe-P2	83.6(2)
Te1'-Fe-Te2	160.41(7)	Te1a-Fe-Te1'	76.75(5)
Te1b-Fe-Te2	90.10(6)	Te1b-Fe-Te1'	78.40(5)
Te1a-Fe-Te1b	100.19(6)	Te1'-Fe-P2	102.1(2)
Te1a-Fe-P2	88.5(2)		
Angles around Te			
Fe-Te1a,b-Fe*	65.31(6)	Fe-Te1a-Fe'	99.77(6)
Fe-Te2-Fe*	65.43(6)	Fe*-Te1a-Fe'	98.99(6)

<sup>a</sup> Average values; vic = vicinal.



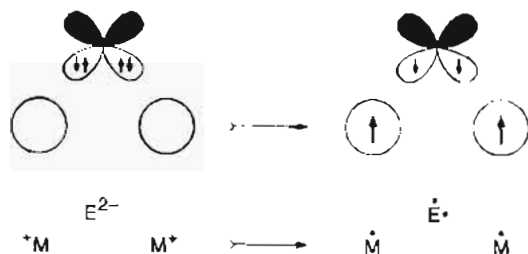
**Figure 5.** Structure of and labeling for  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , **6**. Selected distances and angles are given in Table 6.

Te-Te bond length is 2.715 Å in bis(4-methoxyphenyl) ditelluride,<sup>33</sup> 2.763 Å in  $\text{L}_3\text{MnTe-TeMnL}_3$ ,<sup>34</sup> 2.765 Å in  $\text{L}_4\text{CoTe-TeCoL}_4$ ,<sup>35</sup> 2.784 Å in  $[\text{Cr}_4(\text{CO})_{20}(\text{Te}_2)]^{2-}$ ,<sup>36</sup> 2.892 Å in  $\{\text{Fe}_4\text{Te}_4(\text{CO})_{10}\}_2(\text{Te}_2)^{2-}$ ,<sup>36,37</sup> and 2.926 Å in  $\text{FeTe}_2$  (marcasite structure type).<sup>39</sup> While the bond in **5** is not as short as the bond in free  $\text{Te}_2$  (2.59 Å<sup>40</sup>), it is nonetheless short enough to imply a Te-Te bond order greater than one. To the extent that the Te-Te bond order exceeds one, the Fe-Te bonds are not simple covalent bonds. In the limit the  $\text{Te}_2$  unit would be a simple donor ligand, and the complex would be better viewed as a trigonal bipyramidal, five-coordinate complex of Fe(0). The description of the Fe in **4** and **5** as zerovalent is supported by the fact that the four phosphorus donors stabilize the low-spin  $d^8$  configuration of zerovalent Fe. This description is also consistent with the lack of reactivity of the Te-Te bond, since such  $\eta^2\text{-Te}_2$  units are apparently not prone to oxidative addition to low-valent metal centers: Di Vaira, Peruzzini, and Stoppioni reported<sup>41</sup> the synthesis and characterization of  $(\text{ppp})\text{NiTe}_2$  ( $\text{ppp}$  = bis((2-diphenylphosphino)methyl)phenylphosphine), a complex that is best viewed as a complex of Ni(0) based on the pseudo-tetrahedral coordination around Ni and the short Te-Te bond (2.668 Å). When this complex is treated with  $\text{Ni}(\text{COD})_2$ , the Te-Te moiety

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**Figure 6.** Diagram of the mechanism of anion-mediated superexchange. The central anion ( $E^{2-}$ ) is shown with two perpendicular valence p-orbitals, and each metal atom is represented by a single s-orbital for simplicity. The normal anionic configuration is represented at the left. In this configuration each p-orbital is doubly-occupied. The associated reverse-charge-transfer configuration is shown at the right. In this configuration each E-centered p-orbital is singly-occupied. Since the two p-orbitals are orthogonal, the low energy intra-atomic coupling on E is high-spin. This gives the ferromagnetic coupling of the two metal centers.

simply coordinates in a donor/acceptor sense to the Ni(0) rather than adding to the Ni center oxidatively.

Given these observations, we conclude that the bidentate phosphines quench cluster growth both by covering the metal center sterically and by electronically protecting the zerovalent metal from oxidation.

The magnetic properties of **1**, **2**, and **6** deserve comment. The two  $Fe_4Te_4$  clusters are paramagnetic and have effective moments that are temperature-independent above approximately 100 K<sup>42</sup> and are close to the value of  $8.9 \mu_B$  that is characteristic of a spin-only paramagnet having  $S = 4$  (i.e., 8 parallel spins.) One can rationalize the observed moments in **1** and **2** by noting that in each case each Fe(II) center is in a  $d^6$  configuration in a tetrahedral ligand field and is therefore expected to be (locally) a triplet ( $S = 1$ ). The four triplet Fe centers are then coupled ferromagnetically to give a molecular  $S = 4$  ground state.

On the basis of literature precedents, the overall high-spin coupling in a complex such as **1** or **2** is unexpected. For example, the apparently related charge-neutral complexes  $Fe_4(NO)_4(\mu_3-S)_4$ ,<sup>14</sup>  $Fe_4E_4(CO)_{12}$ <sup>13</sup> ( $E = S, Se$ ), and  $Cp_4Fe_4S_4$ <sup>11</sup> are all diamagnetic. (The case of  $Fe_4(NO)_4(\mu_3-S)_4$  is all the more noteworthy since the Fe-Fe distance therein is 2.651 Å—intermediate between the Fe-Fe distances in **1** and **2**. Presuming that direct Fe-Fe two-electron covalent bonding is responsible for the diamagnetic coupling of the Fe(I) centers in  $Fe_4(NO)_4(\mu_3-S)_4$ , one would expect, on the basis of internuclear distances, that the same Fe-Fe bonding, and therefore overall diamagnetism, would occur in **1** and **2**.) In the other  $Fe_4Te_4L_4$  complexes for which the information is available ( $Fe_4Te_4[EPh]_4$ ,<sup>3</sup>  $E = S, Te$ ), the antiferromagnetic coupling of the Fe centers is significant.<sup>17</sup>

Superexchange accounts for the ferromagnetic coupling of the Fe centers in **1** and **2**. According to the accepted description of anion-mediated superexchange,<sup>43,44</sup> when the metal-anion-metal internuclear angle is  $90^\circ$  the sense of the metal-metal spin coupling is ferromagnetic. The Fe-Te-Fe angles in **1** and **2** are significantly less than  $90^\circ$ , but the same electronic coupling mechanism is implied and ferromagnetic superexchange is anticipated. This superexchange interaction is represented in Figure 6.

The question arises of why such ferromagnetic coupling is not observed in other  $Fe_4E_4$  clusters. One reason is that the strength of the superexchange interaction is determined in part by the energetic accessibility of the reverse charge transfer that is implied by the configuration shown in Figure 6. This configuration is

**Table 7.** Comparison of  $Fe_2Te_3$  Fragments in  $FeTe$  and  $Fe_4Te_6(dmpe)_4$

	$Fe_4Te_6$ $(dmpe)_4$		$Fe_4Te_6$ $(dmpe)_4$	
	$FeTe^a$	$FeTe^a$	$FeTe^a$	$FeTe^a$
$r(Fe-Te)$ (Å)	2.609	2.586	$\theta(Fe-Te-Fe)$ (deg)	65.3
$\theta(Fe-Te-Te)$ (deg)	93.5	93.4	$r(Fe-Fe)$ (deg)	2.83
				2.80

<sup>a</sup> Values based on data from refs 3 and 45.

more accessible the closer the metal and the anion are in electronegativity. Since Fe and Te are closer in electronegativity than Fe and S, the ferromagnetic coupling is expected to be stronger in  $Fe_4Te_4$  clusters than in  $Fe_4S_4$  clusters. If the reverse charge transfer is energetically inaccessible, then antiferromagnetic coupling is expected to dominate *via* conventional through-bond coupling (albeit in this case "through-lone pair" coupling).

Another reason for the ferromagnetic coupling in **1** and **2** is the high local spin state ( $S = 1$ ) on each Fe. The coupling between the Fe-centered Fe-Te bonding electrons and the nonbonding (yet magnetically active) d electrons on the same Fe atom is stronger the larger the number of high-spin coupled d electrons there are. Since this spin-polarization is one of the components of superexchange, the ferromagnetic coupling is expected to weaken as electrons are removed from the Fe centers. This is a plausible explanation for the increased importance of antiferromagnetic coupling in  $Fe_4Te_4(EPh)_4$ <sup>3</sup>.

The diamagnetism of **6** implies the antiferromagnetic coupling of the Fe(III) centers. The antiferromagnetic coupling can be due either to the formation of direct Fe-Fe bonds or to superexchange. The shorter Fe-Fe internuclear distance in **6** (2.795 Å) is long for a direct Fe-Fe covalent bond, but it is within the reported range. (For example, the Fe-Fe bond in  $[(\eta^3-C_3H_5)_2Fe(CO)_3]_2$  is 3.138 Å.<sup>45</sup>) As mentioned above, the conventional description of superexchange would predict ferromagnetic coupling of the Fe centers in **6** since the Fe-Te-Fe angle is less than  $90^\circ$ , therefore direct Fe-Fe bonding seems the more plausible reason for the observed antiferromagnetic ground state.

Note that even though the Fe-Fe internuclear distances are shorter in **1** and **2** than in **6**, our data indicate that covalent bonds exist between the Fe centers in the latter but not in the former.

We have shown that complexes of the form  $Fe_4Te_4(PR_3)_4$ ,  $Fe_6Te_6(PR_3)_6$ , and  $FeTe_2(PR_3)_4$  can all be converted to corresponding  $Fe_xTe_y$  solid-state compounds. We have not been able to isolate **6** in sufficient quantity to test its conversion to FeTe; however, we are confident that that molecules-to-solids process will occur. Since these chemical relationships exist between the clusters and the solids, we sought other comparisons and contrasts between the molecular materials and their extended-solid relatives. The most striking structural relationship between any of the clusters we report here and the corresponding extended solid occurs in the case of **6**. The  $Fe_2Te_3$  subunit that constitutes the core of **6** can be found directly in the NiAs-type FeTe solid.<sup>46</sup> Crystalline  $Fe_{1-x}Te$  (NiAs structure type) can be viewed as being constructed by Fe-centered  $Te_6$  octahedra. The  $Fe_2Te_3$  unit is found in the FeTe structure, the  $Te_3$  triangle being a single face of a  $Te_6$  octahedron that is shared between the two Fe centers. The Fe-Fe internuclear direction in the  $Fe_2Te_3$  unit corresponds to the *c*-direction in the NiAs-type solid. The two  $Fe_2Te_3$  fragments (one from  $Fe_4Te_6(dmpe)_4$ , the other from  $FeTe$ )<sup>3,4,46</sup> are compared in Table 7. The numerical comparison shows that the two structures are quite similar.

(42) The low-temperature magnetic behavior of these materials will be reported separately.

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(44) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: Cambridge, U.K., 1986; Chapter 6.

(45) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinski, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.

(46) Useful descriptions of the NiAs structure are included in the following texts: (a) West, A. R. *Solid State Chemistry and Its Applications*; John Wiley & Sons: Chichester, U.K., 1984. (b) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984.

In this case the cluster-to-solid similarity is more than just structural. The ideal NiAs structure is described as an hexagonally close-packed array of anions in which the octahedral interstitial sites are occupied by the cations. Assuming hard sphere atoms, this predicts a crystallographic  $c/a$  ratio of 1.633.<sup>47</sup> Few metal chalcogenides or pnictides show this ideal value of  $c/a$ . Most show  $c/a$  ratios less than 1.633, and the departure from the ideal is rationalized by the presence of metal-metal bonding along the  $c$ -direction. This metal-metal bonding shrinks the  $c$ -axis and thereby leads to values of  $c/a$  less than the ideal. The Fe-Fe vector in the  $\text{Fe}_2\text{Te}_3$  fragment of FeTe referred to in Table 7 is coincident with the  $c$ -direction, and therefore, the metal-metal bonding implied by  $(c/a) = 1.487$  in FeTe corresponds to the Fe-Fe covalent bonding between these two Fe atoms. Thus, the diamagnetism of **6** (which implies Fe-Fe covalent bonding in **6**) and the lattice contraction in FeTe (which implies Fe-Fe covalent bonding along the  $c$ -direction in FeTe<sup>48</sup>) are distinctly related.

### Conclusion

We have found that the reaction of  $\text{Fe}(\text{COT})_2$  with  $\text{TePR}_3$  leads to solid-state iron tellurides, and that when the reaction conditions are moderated, molecular compounds can be retrieved from the mixture. As a general rule, the use of larger phosphines

leads to lower nuclearity molecular clusters. Bidentate phosphines also tend to yield small molecular compounds. The Fe(II)-based clusters  $\text{Fe}_4\text{Te}_4(\text{PR}_3)_4$  ( $\text{R} = \text{ethyl, isopropyl}$ ) are high-spin compounds while the Fe(III)-based compound  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$  is diamagnetic, showing direct Fe-Fe bonding. The latter compound is clearly identifiable as a fragment of FeTe in the NiAs modification.

**Supplementary Material Available:** Table S-1, listing crystallographic data for  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ ,  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ ,  $\text{dmpe}\cdot 2\text{Te}$ ,  $\text{FeTe}_2(\text{depe})_2$ , and  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , Table S-2, listing positional and thermal parameters for  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , Table S-3, listing interatomic distances and angles in  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , Figure S-1, showing an ORTEP diagram for  $\text{Fe}_4\text{Te}_4(\text{P}^i\text{Pr}_3)_4$ , Table S-4, listing positional and thermal parameters for  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , Table S-5, listing interatomic distances and angles in  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , Figure S-2, showing an ORTEP diagram for  $\text{Fe}_6\text{Te}_8(\text{PMe}_3)_6$ , Table S-6, listing positional and thermal parameters for  $\text{dmpe}\cdot 2\text{Te}$ , Table S-7, listing interatomic distances and angles in  $\text{dmpe}\cdot 2\text{Te}$ , Figure S-3, showing an ORTEP diagram for  $\text{dmpe}\cdot 2\text{Te}$ , Table S-8, listing positional and thermal parameters for  $\text{FeTe}_2(\text{depe})_2$ , Table S-9, listing interatomic distances and angles in  $\text{FeTe}_2(\text{depe})_2$ , Figure S-4, showing an ORTEP diagram for  $\text{FeTe}_2(\text{depe})_2$ , Table S-10, listing positional and thermal parameters for  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , Table S-11 listing interatomic distances and angles in  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$ , and Figure S-5, showing an ORTEP diagram for  $\text{Fe}_4\text{Te}_6(\text{dmpe})_4$  (28 pages). Ordering information is given on any current masthead page.

(47) Reference 45a, p 250.

(48) Terzieff, P. *Physica B* **1981**, *103*, 158.