discernible shrinkage or bloating above the detectable level of 3-5% and if its strength was such that it could not be broken manually without employing the aid of mechanical means (e.g., a vise and pliers). Such a composite bar prepared by using the $[\text{-B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2]_x$- polymer as a binder for B_4C powder was classified as excellent.

Procedure for the Preparation of Ceramic Bars from the $[\text{-B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2]_x$- Polymer. A 3.0-g sample of the polymer was finely powdered for 15 min in an alumina mortar and pestle in an inert-atmosphere box and then placed in a 0.5 in. × 1.5 in. rectangular die. Uniaxial pressing in a Carver press to 5000 pounds (~5 min) was followed by ambient temperature isostatic compaction at 50 000 psi (~15 min). The polymer bar thus obtained had the approximate dimensions 0.5 in. × 1.5 in. × 0.25 in.

The weighed and micrometer-measured polymer bar was introduced into a fused silica pyrolysis boat that then was inserted into a quartz tube that had been flushed with argon for 15 min and the end of the tube was connected to an oil bubbler. After ~5 min, the argon flow was reduced from ~100 mL/min to ~20-30 mL/min, and the quartz tube was placed in a Lindberg tube furnace and heated at a rate of 10 °C/min to a temperature of 1000 °C, held at 1000 °C for 0.5 h, and allowed to cool to ambient temperature over a period of ~3.5 h. The ceramic bar was removed to an inert-atmosphere box, weighed, micrometer measured and then subjected to further evaluation or transferred to the appropriate furnace for temperature treatment above 1000 °C. Heating rates for temperatures to 1500 °C were 25 °C/min. For temperatures above 1500 °C, the heating rate was 17 °C/min.

Preparation and Processing of a Boron Powder/$[\text{-B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2]_x$- Polymer Mixture. The average values of boron [(23.7 + 28.9)/2] and carbon [(57.4 + 60.2)/2] found in the 1000 and 1500 °C samples of fired $[\text{-B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2]_x$- polymer powder, 26.3 and 58.8, respectively, were used to calculate the necessary amount of boron required to provide a theoretical boron/carbon ratio of 4/1. Thus, a mixture of 0.80 g of $[\text{-B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2]_x$- polymer and 1.40 g of amorphous boron powder (Cerac, 94%, <5 μm) were mixed in an alumina mortar and pestle in an inert-atmosphere box for 15 min. A 2.00-g sample of this mixture pyrolyzed to 1000 °C resulted in 1.83 g (92%) of an amorphous, dull gray-black powder. Anal. Found: B, 73.23; C, 21.34; P, 4.18. Further heating to 1500 °C of 0.512 g of the material thus produced gave 0.476 g (7% weight loss from 1000-1500 °C; overall yield to 1500 °C, 85%) of a metallic, silver-black powder containing crystalline B_4C. Anal. Found: B, 76.88; C, 18.00; P, 2.58.

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Selective Syntheses of FeTe and $FeTe_2$ from Organometallic Precursors. Synthesis and Pyrolysis of $[Cp(Et_3P)(CO)Fe]_2(Te)_n$

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We have devised selective syntheses of the solid-state compounds FeTe and $FeTe_2$ using organometallic reagents. Bis(dicarbonylcyclopentadienyliron) reacts with either 1 or 2 equiv of triethylphosphine telluride in the presence of excess phosphine to give $[Cp(Et_3P)(CO)Fe]_2Te$, **1**, and $[Cp(Et_3P)(CO)FeTe]_2$, **2**, respectively. Each compound is stable, crystalline, and easily purified. Each is a mixture of diastereomers as shown by ^1H, ^{31}P, and ^{125}Te NMR spectroscopies. That **1** is an intermediate in the synthesis of **2** is shown by independent reaction of **1** with Et_3PTe to yield **2**. That this reaction is reversible is shown by removal of Te from **2** with Et_3P to give **1**. Low-temperature pyrolysis of **1** gives FeTe and of **2** gives $FeTe_2$, and each of these is specific with respect to solid-state product. Along with CO and Et_3P, ferrocene is produced quantitatively in these pyrolyses. These reactions demonstrate that (1) low-temperature preparation of solid-state compounds is possible using fairly complicated organometallic precursors, (2) product selectivity can be ensured by a proper choice of precursor, and (3) particularly stable organometallic leaving groups such as ferrocene are advantageous both by driving the pyrolysis and by conveniently removing unwanted organic residue.

Introduction

The syntheses of inorganic solid-state compounds are most typically achieved by combination of the proper stoichiometries of the elements as solids.[1] So that complete interdiffusion of the solid reagents may be ensured, these reactions are usually run at high temperature; however, this can be a severe limitation. Lower processing temperatures allow the isolation of metastable phases and give wider latitude in the fabrication of complicated structures (heterostructures, quantum wells, etc.) which would be unstable at higher temperatures. In part to avoid such harsh reaction conditions, there has been increasing interest in the use of precursor methods.[2] The general technique here is not to combine the elements but rather to combine molecular precursors to the elements such that when the precursors are heated or otherwise chemically treated the ancillary components are removed as the

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solid-state product is formed. Since the elements are intimately mixed in the molecular precursors, the problem of interdiffusion of the elements is avoided and the syntheses can be carried out at lower temperatures.

Organometallic molecular compounds have features that make them attractive as precursors to solid-state compounds. The most important of these is that they are masked inorganic elements that can be dispersed molecularly in a wide variety of innocent solvents. This obviates elemental interdiffusion since suitable precursors for each element can be dispersed in the same solvent. When the solvent is subsequently removed, the different precursors are left mixed on the molecular level. A second advantage is that there exists an extensive list of ligand systems in organometallic chemistry. The creative use of these ligand systems will allow molecular control over processing. (As an example, with the proper choice of ligands precursor compounds can be made volatile. This is crucial for the application of organometallic methods to the preparation of thin films by vapor-phase epitaxy.)

More importantly, the ligands determine and control the chemical reactions that actually take the precursors to the solid-state products, that is, the reactions that occur after the different precursors encounter one another and before the ultimate products are formed. Few such reactions have been studied in detail, and as a result fundamental questions concerning the transformation of organometallic molecules into inorganic solid-state materials remain unanswered. It cannot be predicted which ligand systems are useful and which are deleterious, nor is it known what sort of reactions should ultimately be used to remove the ligands or in what form the ligands should be removed. It is also not possible to predict a priori which inorganic phase will result from the pyrolysis of a given precursor, and as such it is not possible to design syntheses that are specific for a particular phase. A number of these very general questions must be addressed to fully exploit organometallics in solid-state synthesis.

With respect to selective syntheses, metal chalcogenides offer some fundamental challenges. Many binary metal chalcogenide systems show several different stable phases, and one clear goal is the design of organometallic syntheses that are selective for each stable phase. We have had experience in the organometallic syntheses of several metal tellurides and therefore sought a telluride system that shows a limited number of stable phases for which organometallic precursors could be prepared. We chose the iron–tellurium system since, aside from the trivial end points, two iron–tellurium phases are stable at standard temperature and pressure, FeTe and FeTe$_2$.[3] In this report we demonstrate that product-specific syntheses of solid-state compounds from organometallic precursors are possible and that rather unexpected ligands can serve in the ancillary role in such syntheses. We present our scheme for the selective syntheses of the compounds FeTe and FeTe$_2$, showing that (Cp(CO)$_2$Fe)$_2$ (hereafter denoted Fp$_2$) and Et$_3$PTe are valuable precursors, that organoiron tellurides are intermediates, and that ferrocene is a byproduct of each synthesis which both drives the reaction and allows for the complete removal of the cyclopentadienyl ligands.

Experimental Section

General. Tellurium and tellurium-containing compounds are generally regarded as toxic, and therefore special care must be exercised in their handling.

Elemental tellurium (−60 mesh, *m5n*) and bis(dicarbonyl(methylcyclopentadienyl)iron) ((Cp′(CO)$_2$Fe)$_2$) were used as purchased from Alfa. Triethylphosphine, Fp$_2$, and the anhydrous grade solvents toluene, heptane, and pentane were used as purchased from Aldrich. Cp$_2$(Et$_3$P)(CO)$_3$Fe$_2$[4] and Et$_3$PTe[5] were prepared according to the literature procedures. The new organoiron tellurides did show some sensitivity to air and were therefore prepared and handled with typical inert-atmosphere techniques.[6] IR spectra were recorded with a PE-583 spectrometer; electronic spectra were recorded on an HP-8451A spectrometer, and NMR spectra were recorded on either a GE QE-300 or a JEOL FX-90Q spectrometer. Chemical shifts are quoted with respect to TMS for the ^{1}H spectra, free triethylphosphine[7] for the ^{31}P, and diphenyl telluride for ^{125}Te. X-ray powder diffraction patterns were measured with a Rigaku Mini-flex diffractometer. Gas chromatographic (GC) analysis were done on an HP-5880 chromatograph (OV-101, 6 ft × $^1/_8$ in., temperature programmed from 150 to 250 °C, field ionization detector), with biphenyl as an internal standard.

Preparation of [Cp(Et$_3$P)(CO)Fe]$_2$Te (1). A solution of Fp$_2$ (2.03 g, 5.7 mmol) in toluene/PEt$_3$ (25 mL/1.7 mL) was added all at once to a freshly prepared solution of Et$_3$PTe (Te 0.71 g, 5.6 mmol; Et$_3$P 1.5 mL, 10.3 mmol; 25 mL of toluene). The mixture was heated to reflux for 1 h, after which time the volatile components were removed in vacuo, giving a dark oil. This oil was triturated with pentane and dried to give a dark powder. Soxhlet extraction (pentane) followed by concentration of the resulting solution and cooling to 0 °C gave 1 as large crystals (yield: 2.46 g, 3.7 mmol, 66%): IR (heptane) 1902 (vs), 1919 (m), 1930 cm^{-1} (sh); ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 0.91 (quintet, J = 6 Hz, 9 H), 1.60 (m, 3 H), 1.85 (m, 3 H), 4.54 (s, 1.5 H), 4.67 (s, 3.5 H); ^{31}P NMR (proton decoupled, C$_6$D$_6$, 36.19 MHz) δ 80.3 (two peaks, ratio 2.5:1 (large peak downfield) separated by 1.6 Hz, with satellite peaks at ±45 Hz); UV–vis (heptane) λ_{max} 414, 296. Anal. Calcd for C$_{24}$H$_{40}$Fe$_2$O$_2$P$_2$Te: C, 43.56; H, 6.09. Found (Schwartzkopf): C, 43.35; H, 6.05.

Preparation of [Cp(Et$_3$P)(CO)FeTe]$_2$ (2). A solution of Fp$_2$ (2.76 g, 7.7 mmol) in toluene/Et$_3$P (10 mL/3 mL) was added all at once to a freshly prepared solution of Et$_3$PTe (Te 2.0 g, 15.7 mmol; Et$_3$P 5 mL, 33.9 mmol; 40 mL of toluene). The mixture was heated to reflux for 1.5 h, after which most (90%) of the solvent was removed by distillation. The complex 2 crystallized upon addition of several volumes of heptane followed by cooling to 0 °C (yield: 5.0 g, 6.3 mmol; 81%): IR (CH$_2$Cl$_2$) 1919 cm^{-1} (br); ^{1}H NMR (C$_6$D$_6$, 90 MHz) δ 0.81 (quintet, J = 7.9 Hz, 9 H), 1.48 (quintet, J = 7.9 Hz, 6 H), 4.52 (d, J = 1.5 Hz, 2.5 H), 4.54 (d, J = 1.5 Hz, 2.5 H); ^{31}P NMR (proton decoupled, C$_6$D$_6$, 36.19 MHz) δ 80.4 (s, satellites at ±60 Hz); ^{125}Te NMR (proton decoupled, C$_6$D$_6$, 28.25 MHz) δ −863.1 (d, J = 120 Hz), −868.3 (d, J = 120 Hz); UV–vis (heptane) λ_{max} 508, 415, 354 nm. Anal. Calcd for C$_{24}$H$_{40}$Fe$_2$O$_2$P$_2$Te$_2$: C, 36.52; H, 5.11; Fe, 14.15; P, 7.85. Found: C, 36.07; H, 5.05; Fe, 14.03; P, 7.16.

Removal of Tellurium from 2. In the drybox a solution of 2 (26 mg, 3.3 × 10^{-5} mol in C$_6$D$_6$ (1 mL) was treated with Et$_3$P (30 μL, 2 × 10^{-4} mol), and the solution shaken. The ^{1}H NMR spectrum was recorded after 30 min at room temperature. This showed 1 and 2 in a ratio of approximately 1:2.3.

Insertion of Tellurium into 1. In the drybox three independent NMR-scale reactions were prepared: (a) 26 mg (0.039 mmol) of 1 and 13 mg (0.053 mmol) of Et$_3$PTe; (b) 23 mg (0.035

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mmol) of 1 and 20 mg (0.081 mmol) of Et_3PTe; (c) 22 mg (0.033 mmol) of 1 and 32 mg (0.13 mmol) of Et_3PTe (each in 1 mL of C_6D_6). Each reaction was heated to 60 °C for 5 min, after which time the ^1H NMR spectrum of each was recorded. Subsequent heating (up to 30 min) had no effect on the spectrum. In each reaction a mixture of 1 and 2 was observed. The final molar ratios were (a) 1:4, (b) 1:6, and (c) 1:14.

Transfer of Tellurium from 2 to $Cp_2(Et_3P)(CO)_3Fe_2$ (3). A solution of a mixture of 2 (20 mg, 0.025 mmol) and 3 (11 mg, 0.025 mmol) in C_6D_6 (1 mL) was treated with Et_3P (20 μL, 0.14 mmol) and heated to 60 °C. The ^1H NMR spectrum showed the absence of 2 after 5 min and complete conversion of 3 to 1 within 1 h.

Pyrolysis of 1. In the drybox 235 mg (3.55×10^{-4} mol) of 1 was added to a Pyrex tube that was subsequently evacuated and sealed. When the seal was cool, the tube was placed in a preheated furnace (temperature between 260 and 290 °C). Within minutes the solid melted and an orange vapor appeared. After 1 h the tube was removed from the furnace, cooled, and opened. Biphenyl (43 mg, 2.8×10^{-4} mol) was added as the GC standard, and the mixture was extracted exhaustively with diethyl ether. The insoluble black solid was dried (65 mg, 3.5×10^{-4} mol, 99%) and shown by X-ray diffraction to be FeTe.[3] The organic products (Et_3P and Cp_2Fe) were identified by NMR, and the ferrocene was quantified by GC (97%).

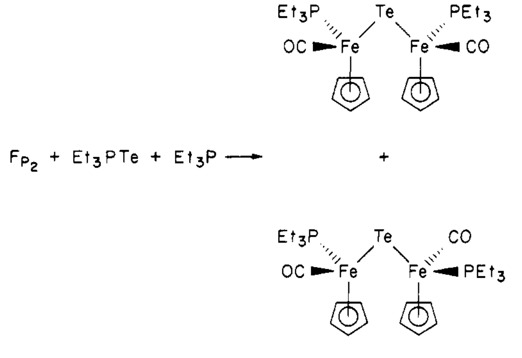
Pyrolysis of 2. The same procedure was followed as in the pyrolysis of 1. The pyrolysis of 435 mg (5.5×10^{-4} mol) of 2 gave 168 mg (5.4×10^{-4} mol, 98%) of $FeTe_2$ as the only detected solid-state product and ferrocene (96% based on eq 4b).

Copyrolysis of $[Cp(CO)_2Fe]_2$ and $[Cp'(CO)_2Fe]_2$. Independent experiments showed that $[Cp(CO)_2Fe]_2$ is pyrolyzed to give Cp_2Fe and $[Cp'(CO)_2Fe]_2$ is pyrolyzed to give Cp'_2Fe. Equimolar amounts of the two complexes were ground together, then transferred to a Pyrex tube, and sealed under vacuum. The mixture was heated to 250–300 °C for 2 h. During the pyrolysis an orange vapor appeared and a shiny metallic film coated the inside of the tube. Upon cooling the tube was opened carefully, and the contents were extracted with diethyl ether. GC analysis showed a statistical mixture of Cp_2Fe, $CpCp'Fe$, and Cp'_2Fe.

Copyrolysis of 2 and $[Cp(CO)_2Fe]_2$. Equimolar amounts of the two reagents were ground together by mortar and pestle. The resulting powder was transferred to a Pyrex tube and sealed. The mixture was pyrolyzed as above for 1 h. Workup as above showed ferrocene and FeTe as the only products.

Results

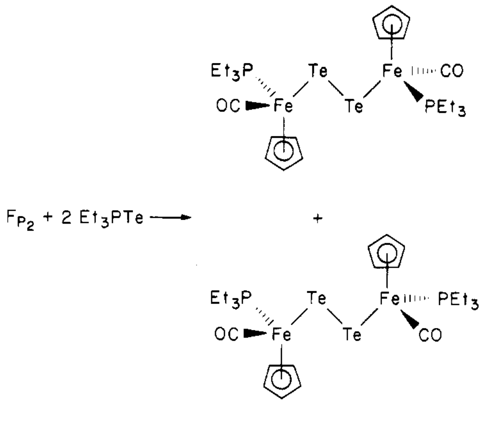
Preparation and Characterization of $[Cp(Et_3P)(CO)Fe]_2Te_n$. We have found that triethylphosphine telluride is a useful soluble equivalent of elemental tellurium and that it reacts with Fp_2 by inserting tellurium into the Fe–Fe bond. Addition of 1 equiv of Et_3PTe to Fp_2 in refluxing toluene yields the complexes $[Cp(Et_3P)(CO)Fe]_2Te$ (1) as the only observed products (eq 1). The IR spectrum of 1 shows only terminal, no bridging, CO ligands. The ^1H NMR spectrum shows only Cp and Et_3P ligands, and these are present in a 1:1 ratio. There are two distinct Cp resonances (intensity ratio of 1:2.5), and these show no signs of coalescence with increasing temperature (to 100 °C). This multiplicity is explained by the stereochemistry shown in 1. Each iron atom in 1 is asymmetrically tetrahedrally coordinated, and therefore 1 will exist in both meso and *d,l* isomers. Since our synthesis is in no way diastereoselective, both isomers are formed. As we did not attempt to separate the diastereomers, we see Cp resonances due to each. The ^{31}P NMR spectrum of 1 also shows two (and only two) resonances, which we similarly assign, one to each diastereomer. Finally, each ^{31}P resonance also shows a set of satellite peaks (J_{P-Te} = 90 Hz) that we assign to the P–Te coupling, which is expected from the P–Fe–Te array due to the 7% natural abundance ^{125}Te.[8]



(1)

1

The reaction of 2 equiv of Et_3PTe with Fp_2 in refluxing toluene also yields a pair of diastereomers, the diiron ditelluride complexes $[Cp(Et_3P)(CO)FeTe]_2$ being formed exclusively (eq 2). Here again we made no attempt to separate the two stereoisomers. The combined pair of complexes shows a broad, strong absorption in the IR, indicating terminal CO ligands. The ^1H NMR spectrum shows only Cp and Et_3P ligands, again in a ratio of unity. The Cp region shows four peaks, these actually being two closely spaced doublets. Each resonance is a doublet due to the P–H coupling, the analogue of which we did not observe in 1, and there are two such doublets, one due to each diastereomer. Nonetheless, the ^{31}P spectrum of 2 shows only one resonance; apparently the two different phosphorus sites implied by the diastereomers of 2 are not sufficiently different to be distinguished at 36.19 MHz. As in the ^{31}P spectrum of 1, there are small satellite peaks (J_{P-Te} = 120 Hz) accompanying the phosphorus signal from 2. These peaks are consistent with P–Te coupling as in 1.



(2)

2

The ^{125}Te NMR spectrum of 2 is particularly helpful (Figure 1). The spectrum shows two doublets (J_{P-Te} = 120 Hz for each). One doublet arises from each diastereomer, and the multiplicity of each is due to P–Te coupling. Since the Te_2 bridge is the ultimate source of the diastereomeric symmetry in 2, it is reasonable to expect the largest difference between the diastereomers of 2 to show up in the ^{125}Te NMR, particularly in view of the extreme sensitivity of ^{125}Te resonance frequencies to the chemical environment.

In the presence of either free phosphine or phosphine telluride, complexes 1 and 2 interconvert (eq 3). This is

$$2 + Et_3P \rightarrow 1 + Et_3PTe \tag{3a}$$

$$1 + Et_3PTe \rightarrow 2 + Et_3P \tag{3b}$$

$$2 + Cp_2(Et_3P)(CO)_3Fe_2 + Et_3P \rightarrow 1 \tag{3c}$$

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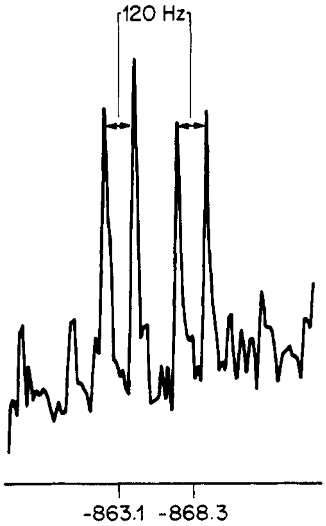

Figure 1. ^{125}Te NMR spectrum of 2. Chemical shifts are relative to external Ph_2Te at 0 ppm.

clearly shown by three different experiments. In the first a solution of 2 in C_6D_6 is treated with a large excess (6 equiv) of Et_3P. The ^1H NMR spectrum of this mixture shows both 1 and 2, in an equilibrium that is established at room temperature very quickly (<5 min). In a second experiment a solution of 1 in C_6D_6 is treated with a slight excess of Et_3PTe, and the mixture is heated. The subsequent ^1H NMR spectrum shows both 1 and 2, again indicating equilibration of the two. Since the concentration of free phosphine telluride is much lower here than is that of free phosphine in the previous experiment, this reaction appears slower at room temperature; nevertheless it is complete within 1 min at 60 °C. In the final experiment of this set, a solution of an equimolar mixture of 2 and $Cp_2(Et_3P)(CO)_3Fe_2$ (3) is treated with Et_3P and heated to 60 °C. As expected, 2 was consumed immediately, leaving a mixture of 1, 3, Et_3P, and Et_3PTe. On continued heating 3 was converted entirely to 1. This last reaction is slower, requiring approximately 1 h.

Complexes 1 and 2 as Precursors to $FeTe_n$. When either 1 or 2 is heated to modest pyrolysis temperatures, a remarkable transformation occurs (eq 4). From each

$$1 \rightarrow FeTe + Cp_2Fe + 2CO + 2Et_3P \qquad (4a)$$

$$2 \rightarrow FeTe_2 + Cp_2Fe + 2CO + 2Et_3P \qquad (4b)$$

unit of 1 or 2 the two-electron ligands, CO and Et_3P, are removed, as are one of the iron atoms and both of the cyclopentadienyl ligands. The remaining elements (the second iron atom and all of the tellurium) are polymerized (crystallized) to give the stoichiometric iron telluride as the only observed solid-state product. The formation of ferrocene is essentially quantitative; ferrocene is not simply one of a number of byproducts of eq 4, it is the only organometallic product. All of the cyclopentadienyl ligand in the precursor complexes is accounted for, and removed, by the extrusion of Cp_2Fe.

To examine the ferrocene extrusion more fully, we studied the pyrolysis of several CpFe complexes (eq 5).

$$Fp_2 \rightarrow Fe + Cp_2Fe + 4CO \qquad (5a)$$

$$Fp_2 + Fp'_2 \rightarrow Fe + (Cp_2Fe + Cp'_2Fe + 2CpCp'Fe) \qquad (5b)$$

Here again ferrocene is generated in high yield, and elemental iron is formed. This suggests that there are no features peculiar to 1 and 2 and that the pyrolytic extrusion of ferrocene is common. Equation 5b also shows that intermolecular scrambling can occur either in advance of or in conjunction with the solid-state compound forming reaction.

We emphasize the importance of this latter point in the following experiment. Having determined that Fp_2 is a precursor to elemental Fe and that 2 is a precursor to $FeTe_2$, we were curious about what would result from copyrolysis of the two. As shown in eq 6, this copyrolysis yields only FeTe, with no evidence for either Fe or $FeTe_2$.

$$2 + 3 \rightarrow 2FeTe + 2Cp_2Fe + 5CO + 3Et_3P \qquad (6)$$

Discussion

There is growing interest in complexes that have simple inorganic atomic or polyatomic bridges between transition-metal centers.[9] One aspect of this interest is that such heterometallic cluster complexes are not-so-distant relatives of solid-state inorganic compounds in the sense that the bridging atoms have no ancillary ligands other than the metal atoms to which they are directly bonded. Here we emphasize another relationship between the molecular and solid-state compounds, namely, that the heterometallic cluster compounds can be converted into solid-state compounds by processes that are in effect polymerizations of concealed inorganic monomers.

Although the family is growing, compounds analogous to 1 and 2 are comparatively rare. Compounds having the μ_2-Te ligand are known for Mn,[10] Cr, Mo, W,[11] V,[12] Rh,[13] Zr,[14] Co,[15] Re,[16] Fe,[17] and U.[18] Most of these complexes have been prepared by reaction with either elemental tellurium or tellurium salts; only the uranium complex was formed with use of a phosphine telluride. Compounds having the μ_2-$(\eta^1$-$Te)_2$ ligand are much less common,[19] as are those having the μ_2-$(\eta^2$-$Te_2)$ ligand.[20]

We have found phosphine tellurides to be very useful synthesis equivalents of elemental tellurium.[19,21] Phosphine tellurides are soluble in a wide variety of organic solvents;[5] and therefore their reactions should be faster than the corresponding reactions of elemental tellurium. Another advantage is that since there are no inorganic byproducts, as required in some of the "salt" methods; one possible source of side reaction or contamination is avoided. It should be emphasized that due in part to the phosphine tellurides the preparative reactions 1 and 2 are clean; when they are followed by NMR, no products other than 1 or 2 can be seen. Since there are no byproducts from reactions 1 and 2, the workups are quite easy, and this process is also adaptable to the direct synthesis of solid-state tellurides (see below). Were phosphine tellurides to be adapted to the related direct methods of

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chemical transport or vapor-phase epitaxy, this feature would be a critical benefit.[22]

The absence of byproducts in the formation of the Te-bridged complexes is due to the ability of the phosphine tellurides to insert tellurium directly into M–M bonds. If the phosphine telluride is viewed as a complex of zerovalent tellurium,[23] the tellurium is expected to act as if the atom were in the ^1D and ^1S states.[19] Concerted insertion reactions are known to occur through the excited singlet states of the chalcogenide atoms,[24] and therefore labile covalent bonds such as the Fe–Fe bond in Fp_2 are susceptible to attack.

With respect to insertion reactions, phosphine tellurides stand in interesting counterpoint to the lighter phosphine chalcogenides. Even the less basic phosphines such as triphenylphosphine have been used commonly to remove selenium, sulfur, or oxygen from chalcogenide compounds such as organometallic selenides and sulfides,[25,26] organic diselenides and disulfides,[27] and organic oxides such as oxiranes.[28] The corresponding insertion reactions are not seen. The phosphorus–chalcogenide bond energy dominates these processes, and since the bond of the phosphine to tellurium is substantially weaker than that to selenium, sulfur, or oxygen, the insertion and extrusion reactions in the phosphine–tellurium manifold can be pushed in either direction by independent variation of other reaction variables.

One potential disadvantage of phosphine tellurides is that the phosphine tends to become incorporated in the product complex.[19] We have not found this to be a particular drawback as yet, but in the present case the incorporation of the triethylphosphine does have interesting stereochemical consequences. Since FpX compounds (X = halide, alkyl, etc.) are known[29] to react with phosphines to give $Cp(R_3P)(CO)FeX$, it is not surprising that we isolate Fe–Te complexes that have a single CO on each Fe replaced by Et_3P. Flood and co-workers[30] have prepared mononuclear phosphine-substituted Fp–alkyl complexes in which the alkyl ligand itself is also asymmetric, and they were able to separate the resulting diastereomers, thereby showing that the stereochemistry about the pseudotetrahedrally coordinated iron atom is fixed. In the present example two such stereochemically rigid iron centers are linked by the tellurium bridges. This covalent connection of two asymmetric centers gives rise to the two diastereomers of each compound. Although no attempt was made to separate the diastereomers, they are easily distinguished spectroscopically.

The reactions that interconvert **1**, **2**, and **3** are important for several reasons. First, they help establish the already presumed mechanism of formation of the complexes, viz., (sequential) insertion reactions. While we have previously shown[19] that a dimetalladitelluride could be formed by the reaction of phosphine tellurides with a M–M bond, we were not able to show unequivocally that the process was stepwise, passing through the dimetallamonotelluride. Here we have clearly demonstrated this. Second, the interconversion reactions substantiate the assignment of structures to **1** and **2**. The simple interconversion reactions show that there must be an equally simple structural relationship between the two, as there is between the structures we propose for **1** and **2**. Third, the facility of eq 3a and 3b ensure that both **1** and **2** are isolable. If, for example, eq 3b did not proceed and eq 3a was quite rapid, eq 1 would yield, instead of **1**, half **2** and half **3**. Fourth, reactions 3 are critical when **1**, **2**, and **3** are further converted to solid-state compounds.

The preparation of FeTe and $FeTe_2$ by pyrolysis of the precursors **1** and **2**, respectively, is much milder than the preparations reported in the previous solid-state chemistry literature.[3] Synthesis from the elements requires heating to 900–950 °C for 24 h followed by prolonged annealing at from 300 to 700 °C. The pyrolysis of the organometallic precursors at 260–290 °C for 1 h is considerably less drastic. The lower reaction temperature clearly indicates the utility of the precursor approach.

On the basis of our previous synthesis of MnTe from organometallic precursors[19] and of the known chemistry of metal carbonyls,[31] we expected that the CO and phosphine ligands would be removed easily from **1** and **2**, and this expectation is directly supported by some related reports in iron–sulfur chemistry. Elemental sulfur and alkene sulfides have been used to add S_2 units to Fp_2.[32] In each case the cluster compound $(CpFeS)_4$ was isolated and characterized. Intermediates were not intercepted, but it is easy to imagine the tetranuclear cluster arising from the dimerization of the CpFeSSFeCp, which would result from the complete decarbonylation of $(Cp(CO)_2FeS)_2$, a sulfur analogue of **2**. This assertion was supported recently by McAlister and co-workers,[26] who, although they were unable to isolate the diiron disulfide, were able to show that closely related diiron polysulfides are converted to $(CpFeS)_4$ on heating to reflux in toluene. It is not clear at this point whether the tellurium analogue, $(CpFeTe)_4$, is an intermediate on the way to $FeTe_2$ or just a temporary shunt or even whether it occurs at all in these processes, but the sulfur example does make it clear that the two-electron ligands dissociate easily, generating unsaturated molecular fragments that may subsequently assemble into clusters.

We initially expected that the Cp ligands in **1**, **2**, **3**, and Fp_2 are bound too strongly to the iron centers, and they too strongly to their other ligands, for the pyrolyses to yield simple inorganic solids devoid of cyclopentadienyls. The ability of these precursors to generate ferrocene was therefore something of a surprise. Perhaps even more surprising is the fact that the ferrocene is produced in such high yields. As analyzed by GC it is formed quantitatively; thus the "extra" iron atom is an exceptionally effective Cp scavenger. It is clear that transfer of Cp ligands between iron centers must occur in these reactions, and this ligand transfer has some literature precedent. The complexes FpX (X = Br, $Cp(CO)_2Fe$) have been used to transfer the Cp ligand to other metal complexes in solution.[33] This

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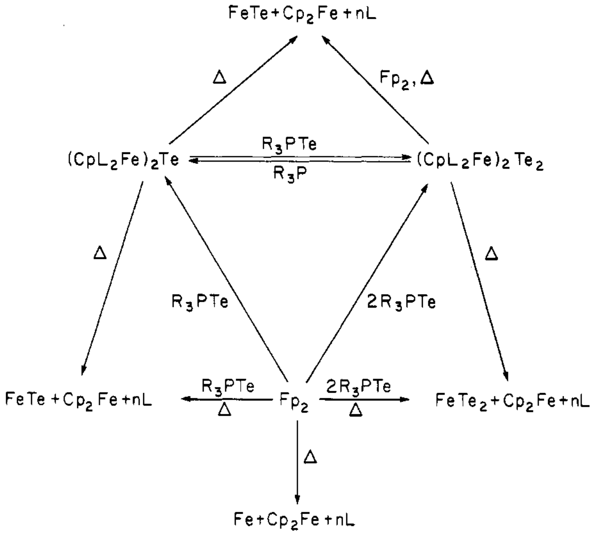

Figure 2. Interconversions and pyrolyses discussed in the text.

reaction is done at lower temperatures than in the present case, and no solid-state products are formed, but it is formally the same as the present case if the receiving metal atom as well as the donating atom is iron. While the mechanisms of the reactions that form the iron tellurides are certainly quite complicated, it is reasonable that a ligand migration of this type occurs at points along the path from the molecule to the solid.

The formation of ferrocene emphasizes two important aspects of precursor design. The first is that pathways for the removal of the organic ligands must be incorporated into the precursor. It is the ligands that make the precursor molecular, and correspondingly the ligands that are potential contaminants in the ultimate inorganic product. It is therefore necessary to provide ways for the ligands to be removed from the solid as it is formed. The present examples show two such paths, the first being the dissociation of the molecular ligands CO and Et_3P and the second being the much more involved process, the extrusion of ferrocene. In each case the evolution of stable, unreactive molecules ensures that the ligands will not remain as harmful organic residue in the growing solid. As an added benefit, ferrocene is quite volatile and is therefore readily removed along with the CO and Et_3P to the cooler zone of the reaction vessel. Ligand incorporation is a problem that plagues materials synthesis[22] and for which chemical solutions can be made available via precursor and pyrolysis design. The second aspect of precursor design that is implied by the extrusion of ferrocene is thermochemical. Ferrocene is an extraordinarily stable compound, and its formation is a driving force in each of the deposition reactions. Not only does this presumably accelerate the solid-forming reactions, but it also undoubtedly contributes to their selectivity by ensuring that the excess iron is not incorporated into the solid. These points may be summarized by claiming that ferrocene is a good "leaving group" for this solid-state compound preparation.

The fact that **1** gives FeTe and **2** gives $FeTe_2$ appears to indicate that the precursor determines the product. While this may seem self-evident, the copyrolysis of Fp_2 and **2** to give only FeTe appears to indicate that there is no direct correlation between precursor and product since independent pyrolyses of Fp_2 and **2** give Fe and $FeTe_2$, respectively, and neither of these is seen in the copyrolysis. These observations are all reconciled in Figure 2, in which it is reiterated that **1**, **2**, and **3** (or its equivalent, Fp_2) equilibrate under conditions much milder than those required to form the solid-state products. Therefore it is immaterial whether **1** or a 1:1 mixture of Fp_2 and **2** is used as precursor to FeTe because they are functionally equivalent by the time the production of FeTe begins.

It is evident that the isolation of **1** or **2** is not a strictly necessary step in the preparation of FeTe or $FeTe_2$. Since each complex is formed under conditions that are milder than those required for its eventual conversion to solid-state products, the solids could be prepared by direct pyrolysis of a simple mixture of the appropriate amounts of Fp_2 and Et_3PTe. (In this sense it is perhaps illustrative to view **1** and **2** as the first of many intermediates on the reaction pathway from the fundamental precursors, Fp_2 and Et_3PTe, to the ultimate solid-state products.) However, to avoid the isolation of **1** or **2** is to neglect an important benefit of the precursor method: the stoichiometry of the solid-state products is unambiguously set at the molecular level by the isolation and purification of the bimetallic complexes. Synthesis from the fundamental precursors is similar to synthesis from the elements in that the product stoichiometry is set at the macroscopic level and depends on the accuracy of the weighing of the starting materials.

Conclusion

We have prepared the compounds FeTe and $FeTe_2$ using organometallic precursors. The syntheses are specific, forming one of the tellurides to the exclusion of the other. The specificity is ensured either by using single-compound or multiple-component mixture precursors, inasmuch as low-temperature reactions make the single-compound and multicomponent precursors equivalent. We have also shown that ferrocene is a very useful leaving group in these reactions. It acts as a sink for the potentially troublesome cyclopentadienyl ligands and as an effective thermodynamic driving force.