facile propellor rotation. As emphasized previously by others,[3] there should be no correlation between acceptor properties of an olefin and the activation barrier to this form of stereochemical nonrigidity; differences in the barrier may arise from variations in the cylindrical properties and energies of the orthogonal π-orbitals presented to the olefin by the metal fragment, differences in orbital overlap along the rotational pathway, and other attractive or repulsive interactions in the transition state. Theoretical studies of the molecules discussed herein are in progress.

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Supplementary Material Available: Structure determination, data collection, and solution and refinement summaries and tables of atomic coordinates and isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for complex **3a** (6 pages); observed and calculated structure factor tables for complex **3a** (19 pages). Ordering information is given on any current masthead page.

$(Et_3P)_4Fe_4Te_4$: An Intermediate between Molecular Reagents and Solid-State Products

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We have reported a number of reaction sequences in which molecular reactants are converted into extended inorganic solids.[1] Our goals have been to design simple and general methods for the transformation of molecules to solids and to learn as much as possible about the pathways connecting the two. In this paper we report the synthesis of a mixture of β- and ϵ-FeTe and the isolation and characterization of $(Et_3P)_4Fe_4Te_4$, a cluster compound that is formed directly from the molecular reagents and that is subsequently converted to the solid products.

Compounds of low-valent transition metals react with phosphine tellurides[1-4] to form metal-tellurium bonds. We sought to extend this synthesis methodology and became particularly interested in the chalcogenides of iron because of the remarkable and confusing magnetic properties of the bulk materials.[5] (One hope is that the structure and behavior of iron-chalcogen clusters might shed some light on the properties of the extended solids.) We therefore looked for a low-valent complex of iron with which Et_3PTe might be expected to react. $Fe(COT)_2$ was an attractive candidate.[6] The metal is easily oxidized,[7] and the COT ligands are molecular and could be expected to fall off the metal[7,8] on reaction with phosphine telluride. We find[9] that this is the case. $Fe(COT)_2$ reacts quickly at room temperature in toluene with Et_3PTe to lose the COT ligands and yield the cluster compound $(Et_3P)_4Fe_4Te_4$ (eq 1). We determined the structure of this molecule crystallographically,[10] and a drawing of the molecular structure is shown in Figure 1.

$$4Fe(COT)_2 + 4TePEt_3 \rightarrow (Et_3P)_4Fe_4Te_4 \quad (1)$$

The molecule has cubic symmetry and therefore has only one independent Fe, Te, and P atom and two independent C atoms. The core of each molecule is a tetrahedron of Fe atoms with an Fe-Fe distance of 2.623 (4) Å. Each face of the tetrahedron is capped with a single Te atom, the resulting Te_4 tetrahedron having a characteristic Te-Te distance of 4.343 (1) Å. The structure is capped and completed by a phosphine ligand at each Fe. The Fe-Te distance is 2.609 (1) Å. This is in the range normal for Fe-Te bonds[11,17a,b] and implies that the bonding in the cluster is dominated by the direct Fe-Te interactions. It is significant, however, that the Fe-Fe distance is only 0.14 Å longer than the nearest-neighbor distance in elemental Fe. This suggests the presence of a substantial stabilizing interaction among the Fe atoms, particularly when compared to other $[FeTe]_4$ compounds (see below).

The $[FeTe]_4$ core may be viewed as a severely distorted cube. In this sense this compound is a member of the large family of iron-chalcogen cubanes.[12-17] One $[FeTe]_4$-based solid[17d] and two other molecular $[FeTe]_4$ complexes (of the type $[(PhE)_4Fe_4Te_4]^{3+}$, E = S, Te) have been structurally characterized to date.[17a,b] The present compound differs from these in having only neutral

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(9) Preparation of $[(Et_3P)FeTe]_4$: All manipulations were carried out under an inert atmosphere. $Fe(COT)_2$ (1.0 g, 3.8 mmol) was dissolved in toluene (30 mL) to which Et_3P (1.7 mL, 11.5 mmol) had been added. In a separate vessel, Et_3PTe (0.93 g, 3.8 mmol) was dissolved in 10 mL of toluene. The Te-containing solution was added to the Fe-containing solution at room temperature. After 16 h, the solid which had deposited was separated by filtration, washed (2 × 5 mL of pentane), and dried. Yield: 0.82 g (0.68 mmol = 72%). Anal. ($C_{24}H_{60}Fe_4P_4Te_4$) C, H, Fe, P, Te. The material was crystallized from 10/1 toluene/Et_3P, cooling slowly from 80 to 90 °C. The UV-visible absorption spectrum of this material shows broad, featureless absorption across the visible region. The cluster is not sufficiently soluble for NMR spectroscopy.

(10) Crystal data: space group $I\bar{4}3m$; cubic; a = 12.9548 (5) Å; V = 2174.16 (8) Å^3. Details of the crystallography are included in the supplementary material.

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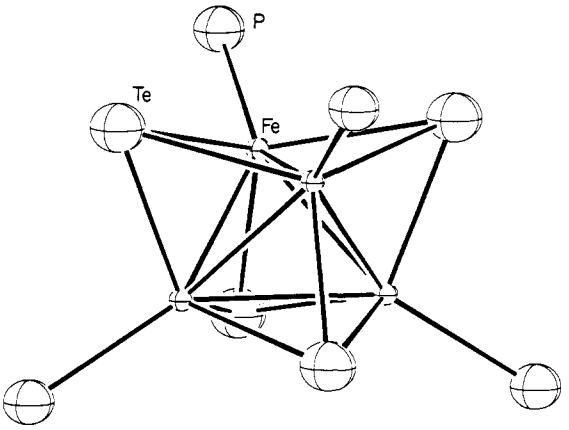

Figure 1. Drawing of the molecular structure of $[(Et_3P)FeTe]_4$. The large circles represent Te atoms, and the small circles Fe atoms. The ethyl groups on the phosphines are omitted for clarity. The molecule is tetrahedrally symmetric. Selected distances (Å): Fe–Fe, 2.623 (4); Fe–Te, 2.609 (1); Fe–P, 2.390 (6). Selected angles (deg): Fe–Fe–Fe, 60.00 (6); $(Fe–Fe–Te)_{small}$, 59.82 (5); $(Fe–Fe–Te)_{large}$, 109.25 (9), Fe–Fe–P, 144.74 (5); Fe–Te–Fe, 60.36 (6); Te–Fe–Te, 112.70 (5).

phosphine ligands bound to the inorganic core (important for the subsequent conversion to extended solids) and in having a lower average oxidation state at iron (2.00+ versus 2.25+). These differences result in the very symmetrical cubic structure of $(Et_3P)_4Fe_4Te_4$ and its shorter Fe–Fe distances (2.623 (4) Å versus 2.847, 2.818 (6), and 2.747 (2) Å in $Cs_7Fe_4Te_8$, $[Fe_4Te_4(SPh)_4]^{3-}$, and $[Fe_4Te_4(TePh)_4]^{3-}$, respectively). It is interesting that in the related compounds, $Fe_4E_4(CO)_{12}$ (E = S, Se)[15] (in which each Fe is in the 2.00+ oxidation state and bears three CO ligands), the Fe_4E_4 cores are only slightly distorted from ideal cubes. They also show substantially larger Fe–Fe distances (3.466 Å, E = S; 3.617 Å, E = Se) than in $(Et_3P)_4Fe_4Te_4$. Assuming that the Te analogue[17c] has a similar structure, it is clear that the additional eight two-electron donors have a dramatic effect on the Fe_4E_4 structure.

We find that heating $[(Et_3P)FeTe]_4$ releases the phosphine and polymerizes the $[FeTe]_4$ unit to form polycrystalline iron tellurides.[18] It is known[5] that stoichiometric FeTe disproportionates to give β-FeTe and ε-FeTe (Fe rich and Te rich, respectively); this is what we observe, powder X-ray diffraction showing both phases.

To summarize, we have found that $Fe(COT)_2$ reacts rapidly with Et_3PTe to give $[(Et_3P)FeTe]_4$. The structure of this cluster shows Fe–Te bonding and suggests Fe–Fe bonding as well. Thermolysis of the cluster gives extended solid iron tellurides; thus the cluster is an allowable chemical intermediate between the molecular reagents and the solid-state products. We are investigating how the properties of the cluster might also be considered intermediate between those of the molecules and of the solid.

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Supplementary Material Available: Tables S1 of crystallographic data, S2 of positional and thermal parameters, and S3 of interatomic distances and angles for $(Et_3P)_4Fe_4Te_4$ (5 pages); Table S4 of observed and calculated structure factors for $(Et_3P)_4Fe_4Te_4$ (6 pages). Ordering information is given on any current masthead page.

(18) Pyrolysis of $[(Et_3P)FeTe]_4$: Differential scanning calorimetry (DSC) shows an endothermic reaction of this compound at approximately 193 °C. To determine the products of this process, a Pyrex tube was charged with $[(Et_3P)FeTe]_4$ (98 mg, 81 μmol), after which the tube was evacuated (0.1 Torr), sealed, and heated to 280 °C for 18 h. This gave a black solid (61 mg, 102% recovery of Fe and Te). Powder X-ray diffraction showed only β-FeTe and ε-FeTe.[5a]

Automated Synthesis of Peptide C-Terminal Aldehydes

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Peptide C-terminal aldehydes (PAs) are an important class of transition-state analogues, which have drawn considerable attention since their initial discovery as natural products.[1] PAs of various structures are potent inhibitors of the diverse enzymes which are implicated in a wide range of disease states.[2] We report here the development of an automated synthetic technique that dramatically facilitates the preparation of PAs. These peptide analogues represent formidable synthetic targets due to their inherent chemical lability and their multifarious functionalities, which often require orthogonal protection. As part of our program to develop potent selective inhibitors of enzymes, we desired a rapid and efficient general synthesis of PAs. The ready availability of these derivatives would allow for the rational investigation of the structure–activity relationships for peptide analogue based inhibitors of medically relevant enzymes.

The solid-phase method of synthesis has dramatically increased the accessibility of synthetic peptides and oligodeoxynucleotides. In particular, the extension of the solid-phase technique to allow for the automated synthesis of peptides and oligonucleotides has facilitated significant advancement in several areas of science and technology. We chose, therefore, to develop an automatable solid-phase method for the synthesis of PAs.

Of the several strategies for the synthesis of PAs,[3-5] we determined that one was suitable for adaptation to a solid-phase method.[6] This method relies on the protection of the aldehyde function as the stereochemically stable semicarbazone. This method involves the following general steps. The protected amino acid aldehyde semicarbazones are deprotected at the N-terminus and coupled with protected amino acids or protected peptides to give a protected peptide C-terminal semicarbazone. After the desired number of deprotection/coupling cycles are complete, the protected peptide semicarbazone is treated with aqueous acid/formaldehyde to regenerate the aldehyde and cleave it from the solid support. The resulting protected PA can then be deprotected if necessary. This general strategy has been used to prepare PAs in solution[5] and on a *soluble* support.[7] We report here a method that allows for the synthesis of PAs in a way which is fully compatible with conventional peptide synthesizers.

Several approaches were explored for the preparation of amino acid aldehyde semicarbazone resins. The most efficient approach found is shown in Scheme I. This method uses the solution synthesis of the complete semicarbazone carboxylic acid linker **4**. The synthesis of this linker began with the reaction of *tert*-butylcarbazate with carbonyldiimidazole in dimethylformamide (DMF) followed by treatment with *trans*-4-(aminomethyl)-cyclohexanecarboxylic acid benzyl ester[8] (which was prepared in

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