

of oxygenated organic molecules.¹⁸ Thus, the new chiral imides **13** and **14** have immediate preparative value. Further studies will determine whether these auxiliaries will be generally useful for other types of thermal additions and cycloadditions. At present, we know that they show exceptional selectivity in asymmetric alkylations.¹² Lastly, we note that imides **7** and **8** possess an N-H bond in an asymmetric microenvironment, and preliminary studies on asymmetric protonations are very encouraging.¹⁹

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Supplementary Material Available: Full details of the crystal structure of **11b**, procedures for the preparation of **13** and **14**, and tables giving spectroscopic characterization of all new compounds (18 pages). Ordering information is given on any current masthead page.

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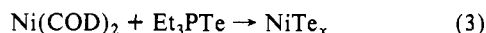
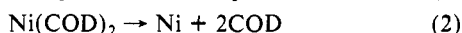
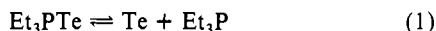
The Transition from Molecules to Solids: Molecular Syntheses of Ni₉Te₆(PEt₃)₈, Ni₂₀Te₁₈(PEt₃)₁₂, and NiTe

J. G. Brennan, T. Siegrist, S. M. Stuczynski, and M. L. Steigerwald*

AT&T Bell Laboratories
Murray Hill, New Jersey 07974
Received August 17, 1989

Molecular precursors offer some attractive practical advantages in the synthesis of solid-state compounds. The intimate mixing of the elements that comes with the use of precursors allows lower reaction temperatures than the traditional ceramic preparative route, which in turn should allow for the preparation of solid-state phases that are inaccessible to the ceramic method. In order to exploit the precursor method to its fullest, it is important to characterize as completely as possible reactions that take the molecular starting materials to solid-state products. One straightforward method is the interception and characterization of reaction intermediates.¹ In most cases it is expected that these chemical species will not only be intermediates in the sense of reaction coordinate diagrams but also intermediate in size, describable as either large molecules or small fragments of the bulk. In this view, the study of the isolated chemical intermediates will give insight into both the chemistry of formation of a bulk solid and the evolution of the size-dependent physical properties.¹

Trialkylphosphine tellurides are useful as organometallic equivalents of elemental tellurium for the preparation of solid-state metal tellurides.² The initial indication of the utility of phosphine tellurides is their ability to reversibly deposit zerovalent tellurium³ (eq 1). This is reminiscent of the ease with which bis(cyclooctadiene)nickel (Ni(COD)₂) thermally liberates zerovalent nickel (albeit irreversibly)⁴ (eq 2). The similarity between eq 1 and 2 raises the question as to whether the combination of R₃P₂Te and Ni(COD)₂ would result in the formation of the solid-state compound⁵ NiTe (eq 3).



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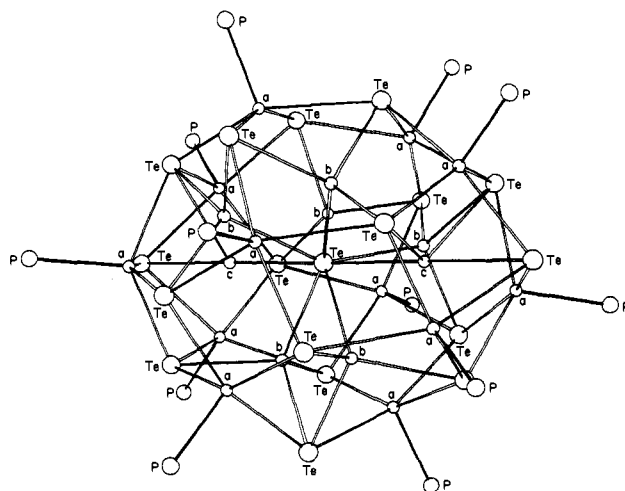


Figure 1. Structure of Ni₂₀Te₁₈(PEt₃)₁₂. The labels a, b, and c refer to Ni_a, Ni_b, and Ni_c, respectively. The ethyl groups are omitted for clarity. Ni_a coordination is square-based pyramidal with Ni-Te distances between 2.55 and 2.69 Å and Ni-P distances approximately 2.2 Å. Ni_b coordination is tetrahedral with Ni-Te distances between 2.45 and 2.64 Å. Ni_c coordination is (very distorted) trigonal bipyramidal with two short (2.52-2.59 Å) and three long (2.8-2.9 Å) Ni-Te distances. The central Te-Ni_c-Te-Ni_c-Te array is almost exactly linear and contains the shorter Ni-Te bonds.

This communication describes the synthesis of the solid-state compound nickel telluride, NiTe, using these organometallic reagents as the sources of Ni and Te. In addition, we report the isolation and crystallographic characterization of two intermediates: the clusters Ni₉Te₆(PEt₃)₈ and Ni₂₀Te₁₈(PEt₃)₁₂.

Ni(COD)₂, Et₃P, and Et₃P₂Te were combined in toluene at room temperature to give a black, optically very dense solution. This solution was homogeneous and quite stable at room temperature (see below), but when heated to reflux for several hours, the solution became colorless and polycrystalline nickel telluride precipitated in quantitative yield. Powder X-ray diffraction measurements confirm that polycrystalline NiTe was formed at low temperature. This should be compared to the ceramic route in which the elements are combined⁵ at 400-600 °C for several days to several weeks.

It is clear from this experiment not only that NiTe can be made by using molecular equivalents of the zerovalent elements but also that Ni-Te bonds are formed quickly and that the intermediate Ni-Te complexes are stable at room temperature. Fenske and co-workers⁶ have shown that a variety of nickel chalcogenide clusters are stable under similar conditions, so we set out to characterize the molecular species that formed initially in this reaction.

Ni(COD)₂, Et₃P₂Te, and Et₃P were combined in toluene at room temperature in the relative molar ratio of 1:1:1, and a black, apparently homogeneous solution resulted. Pentane was added to this mixture, and large crystals of a black solid, **1**, grew during the next several days (yield: 26%). The structure of this compound, whose stoichiometry is Ni₂₀Te₁₈(PEt₃)₁₂, was determined crystallographically, and a drawing of that structure is shown in Figure 1.

The evaluation of the entire structure in terms of its constituent parts shows that there is a great deal of local symmetry. Covering the surface of the cluster molecule are the 12 phosphine ligands, each attached to a surface Ni atom (Ni_a in Figure 1). Each of these Ni atoms is also bonded to four Te atoms such that each

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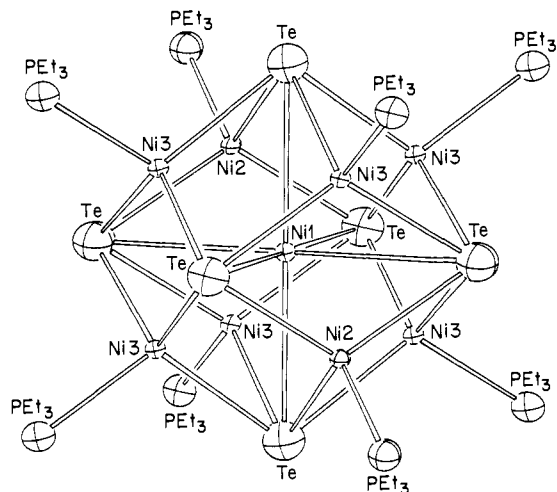


Figure 2. Structure of $\text{Ni}_9\text{Te}_6(\text{PEt}_3)_8$. Significant distances: $\text{Ni}_1\text{-Ni}_2$, 2.486 (4) Å; $\text{Ni}_1\text{-Ni}_3$, 2.4671 (23) Å; $\text{Ni}_1\text{-Te}$, 2.981 (2) Å; $\text{Ni}_2\text{-Ni}_3(\text{av})$, 2.87 Å; $\text{Ni}_3\text{-Ni}_3(\text{av})$, 2.84 Å; $\text{Ni}_2\text{-Te}$, 2.5489 (16) Å; $\text{Ni}_3\text{-Te}(\text{av})$, 2.55 Å. For related structures, see ref 6 and 10.

Ni_a has a square-pyramidal coordination environment. Inside the Ni_a layer are the other eight Ni centers (each of which, curiously, bonds to the central Te atom). Six of these (Ni_b in Figure 1) are tetrahedrally coordinated by four Te atoms. The remaining two Ni atoms (Ni_c) are each bonded to five Te atoms in a distorted trigonal bipyramid. This analysis shows that although the combination of the Ni-centered coordination polyhedra seems almost random, there are only three types of Ni coordination and each of these is regular.

It is important to note that although reaction 3 leads to NiTe in refluxing toluene, the structure of this Ni-Te cluster apparently has no features in common with that of the bulk solid-state compound. From this it is clear that the activation energy for atomic movement within the cluster (the molecular equivalent of solid-state diffusion in the bulk material) is low. In contrast, nanometer-sized clusters of CdSe prepared at room temperature are crystalline and mimic the structure of the bulk solid.⁷

A distinctly different cluster results when $\text{Ni}(\text{COD})_2$, Et_3PTe , and Et_3P are combined in heptane in the ratio of 2:1:22. Rhombohedral crystals form directly from the optically dense brown reaction mixture in several hours (yield: 45%). We have also characterized this compound crystallographically, and a representation of this cluster, whose stoichiometry is $\text{Ni}_9\text{Te}_6(\text{PEt}_3)_8$, is shown in Figure 2.

The structure of this smaller cluster is much more symmetrical than that of **1**. A single, central Ni atom is surrounded by an octahedron of six Te atoms and a cube of eight Ni atoms, with each exterior Ni atom being capped with a single phosphine. There are a number of interesting features in this structure. First, if each Te is considered Te^{2-} , then there are six Ni(II) and three Ni(0) centers. This assignment is consistent with the fact that the cube of external Ni atoms is slightly elongated along one of the body diagonals. This suggests that the three "Ni(0)" sites are the central Ni and two antipodal Ni vertices. A second noteworthy aspect in the central Ni which is surrounded by an octahedron of Te^{2-} centers. This is the same as the Ni environment in bulk NiTe. In this sense, this structure mimics that of the related solid-state compound.⁸ Finally, the concentric cube of metal atoms and octahedron of chalcogens is reminiscent of the well-known Chevrel⁹ solid-state phases. In these materials, each cluster is a combination of a cube of chalcogens and an octahedron

of metals. The present case is an example of an anti-Chevrel cluster.

In this communication we have shown that organometallic complexes of Ni(0) and Te(0) can be combined to yield the solid-state material NiTe and that this process can be interrupted and large molecular clusters isolated by the appropriate choices of stoichiometry, solvent, and reaction temperature. It is hoped that the isolation and characterization of a larger number of such intermediates in molecule-to-solid reactions will help elucidate the pathways by which these complicated reactions occur.

Supplementary Material Available: Tables listing positional and thermal parameters, significant distances and angles, and calculated and observed X-ray diffraction powder patterns for $\text{Ni}_9\text{Te}_6(\text{PEt}_3)_8$ and $\text{Ni}_{20}\text{Te}_{18}(\text{PEt}_3)_{12}$ and experimental details (synthesis of NiTe, **1**, and **2** and crystallography of **1** and **2**) (28 pages); tables of calculated and observed structure factors (133 pages). Ordering information is given on any current masthead page.

Enzymatic Asymmetric Hydroxylation of Pentadienols Using Soybean Lipoxygenase

P. Zhang and Keith S. Kyler*

Department of Chemistry, University of Miami
Coral Gables, Florida 33124

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Despite the high regio- and stereoselectivity of lipoxygenase-catalyzed oxidations of unsaturated fatty acids,¹ the potential utility of these enzymes for synthesizing chiral alcohols has attracted little attention. Previous studies of modified substrates with soybean lipoxygenase (SBLO) suggest that the essential structural requirements are a single ω -6 (*Z,Z*)-1,4-pentadienyl moiety and an appropriately spaced proximal² carboxyl group as characterized by the natural substrate linoleic acid.³ On the basis of this premise, we envisaged an enzymatic method for the asymmetric hydroxylation of unsaturated alcohols **1** via their adipate monoesters **2** (Scheme I) where the adipoyl prosthesis provides the additional lipophilic scaffold required for SBLO recognition. We now report our results for the asymmetric oxidation of these surrogate substrates to afford, after reduction and hydrolysis, the chiral diols **3**.

Substrates were prepared by the condensation of (*Z*)- $\text{THPOCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{PPh}_3$ ⁴ with the appropriate aldehyde (RCHO; cf. Table I), followed by deprotection (*p*-TsOH, MeOH, 23 °C) to afford the (*Z,Z*)-dienols⁵ **1** containing small amounts (5–10%) of the *Z,E* isomers.⁶ The alcohols were transformed to their adipate monoesters **2** by using adipic anhydride monomer⁷ and pyridine/DMAP (cat.) in CH_2Cl_2 .

As shown in Table I, all substrates were enzymatically oxidized when treated with SBLO (Sigma Co., type I) and O_2 (0.2 L min^{-1}) at 0 °C in 0.20 M borate buffer, pH 8.5. Control experiments

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