$(CO)_2]_2$[5] with **1**, the CO bond order decreases from 3 to less than 2 and uranium becomes tightly bonded to oxygen. This ability of the uranium-carbon multiple bond to react with and reduce coordinated carbon monoxide indicates potential use of **1** and related compounds as reagents in organometallic synthesis and may have relevance to the catalytic reduction of CO.

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Registry No. 1a, 77357-85-8; **2**, 92472-03-2; **2**·$C_7H_8·C_4H_8O$, 92472-04-3; $CpMn(CO)_3$, 12079-65-1; CO, 630-08-0; U, 7440-61-1; C, 7440-44-0.

Supplementary Material Available: Table II, crystal, data collection, and reduction parameters; Table III, bond distances for $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$; Table IV, bond angles for $Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph$; Table V, positional and thermal parameters for anisotropically refined atoms of $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2·C_7H_8·C_4H_8O$; Table VI, positional and thermal parameters for isotropically refined atoms of $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2·C_7H_8·C_4H_8O$; Table VII, observed and calculated structure factors for $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2·C_7H_8·C_4H_8O$ (19 pages). Ordering information is given on any current masthead page.

Chemical Alloying, a Novel Method for the Preparation of Homogeneous Se_xTe_{1-x} Alloys

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Metals are unique among the elements in that they are often miscible with each other; i.e., they can be blended in the melt to form alloys, metallic composites consisting of two or more metals. In certain instances, homogeneous alloys (substitutional solid solutions, interstitial solid solutions, and/or intermetallic compounds) can be formed over a wide range of compositions. These homogeneous alloys are generally formed in the melt, and, accordingly, the possibility of their formation by stoichiometric reaction of two or more elements or compounds to yield a new metallic compound (alloy) has been generally overlooked.

We have found that metallic alloys, homogeneous crystalline compounds of trigonal Se and Te, can be formed quantitatively via the stoichiometric coreduction of compounds (esters) of Se and Te. The formation of chalcogenide alloys by chemical reaction is not unique to Se and Te. In fact, we have prepared homogeneous crystalline binary alloys of Se with S and As as well as crystalline ternary alloys of Se-Te-As via coreduction of stoichiometric mixtures of their corresponding esters.[1] We predict, given the identification of chemistry suitable for the generation of two or more metals from soluble metal precursors of the same genre, that a wide range of metal alloys can be formed by chemical reaction.

Specific interchalcogenide compounds have been prepared by redox reactions;[2] however, we do not know of any reports in the literature of the alloying of metals across a continuous range of composition by chemical reactions. There are also analogies between our observation of alloying of Se-Te by coreduction and the formation of intermetallic compounds of transition metals by redox condensation.[3,4] While this chemistry is generally directed toward the formation of discrete covalent organometallic clusters, it is not difficult to see these intermetallic clusters as precursors to crystalline metallic alloys.

Table I. Chemical Alloying of Se and Te

mole ratio of Se and Te esters	alloy compn[a] obtained	mp,[b] °C
0.93/0.07	$Se_{0.93}Te_{0.07}$	232
0.86/0.13	$Se_{0.85}Te_{0.15}$	251
0.61/0.39	$Se_{0.62}Te_{0.38}$	317
0.41/0.59	$Se_{0.41}Te_{0.59}$	374
0.28/0.72	$Se_{0.29}Te_{0.71}$	412
0.15/0.85	$Se_{0.16}Te_{0.84}$	437

[a] Alloy compositions were determined by X-ray fluorescence spectroscopy. [b] Melting points were determined by differential scanning calorimetry, and the values listed are for the center of the peak.

Following on our earlier work in which chalcogenide esters were reduced to their corresponding elements,[5] we have found that crystalline alloys can be simply prepared by the coreduction of mixtures of chalcogenide esters. The chemistry is typified by Se and Te. We have reduced solutions of Se^{IV} and Te^{IV} compounds (dialkyl selenites,[5-7] tetraalkoxytelluranes,[6,8,9] or glycol solutions of SeO_2 and TeO_2) with hydrazine to obtain stoichiometric crystalline alloys of Se_xTe_{1-x}.

$$\underset{x\text{ mol}}{\mathrm{Se^{IV}}} + \underset{1-x\text{ mol}}{\mathrm{Te^{IV}}} \xrightarrow{N_2H_4} \mathrm{Se}_x\mathrm{Te}_{1-x} + \mathrm{N_2}\uparrow$$

In a typical procedure, anhydrous hydrazine, 98%, is added dropwise and at ambient temperature to stirred solutions of diethyl selenite and tetraalkoxytellurane. The mole ratio of the esters is selected to correspond to the specific composition of crystalline Se-Te alloy desired. Immediately upon addition of N_2H_4, a black colloidal precipitate forms. The reaction is exothermic, and the exotherm is controlled by the rate of N_2H_4 addition. Completion of the reaction is normally indicated by the cessation of N_2 gas evolution. By this procedure, Se_xTe_{1-x} alloys have been obtained in which x has been varied between 0.1 and 0.9. Yields of alloy are quantitative.

Table I summarizes our work on the preparation of Se-Te alloys by stoichiometric coreduction of Se and Te esters.

There are a number of important aspects of the data in Table I that deserve discussion. First, and most surprising, is the fact that the mole ratio of the esters in the solution is mirrored in the composition of the resulting alloy. If we view the process as one in which atoms of Se and Te are formed on reduction of the esters, followed by nucleation of colloidal alloy particles, then, for alloying to occur, the rate of reduction of the Se and Te esters must be comparable.[10] In fact, the rates of reduction must be nearly identical for the stoichiometry of the alloy to mirror the stoichiometry of the esters. The formation of homogeneous alloys during the precipitation of particles is an indication that Se-Te alloys are substitutional solid solutions. All of the Se_xTe_{1-x} samples prepared by coreduction are homogeneous and crystalline. The homogeneity and crystallinity of the alloys was confirmed by X-ray diffraction analysis (XRD).[11-13] The melting points, determined by differential scanning calorimetry (DSC) and shown in the table, correspond very well with those that one would calculate by in-

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(1) Badesha, S. S.; Smith, T. W. U.S. Pat. 4460408.

(2) Alicino, J. F.; Kowald, J. A. In "Organic Selenium Compounds, Their Chemistry and Biology"; Klayman, D. L.; Gunther, W. H. H., Eds.; Wiley: New York, 1973; p 1058.

(3) Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977**, *71*, 1.

(4) Chini, P.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285.

(5) Badesha, S. S.; Monczka, P.; Smith, S. D. *Can. J. Chem.* **1983**, *61*, 2199.

(6) Meerwein, H.; Bersin, T. *Justus Liebigs Ann. Chem.* **1929**, *476*, 113.

(7) Mehrotra, R. C.; Mathur, S. N. *J. Indian Chem. Soc.* **1965**, *42*, 748.

(8) Simon, A.; Heintz, G. *Naturwissenschaften* **1960**, *47*, 468.

(9) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Hus, Y. F. *J. Am. Chem. Soc.* **1981**, *103*, 2340.

(10) A detailed study of the reduction and hydrolysis kinetics of the esters is in progress at the present time.

(11) Watanabe, H.; Kao, K. C. *Jpn. J. Appl. Phys.* **1979**, *18*, 1849.

(12) Dutchak, Ya. I.; Ignat'av, E. G.; Mudryi, S. I.; Okhotin, A. S., *Kosm. Tekhnol. Materialoved.* **1982**, 138; *Chem. Abstr.* **1982**, *97*, 169382*q*.

(13) Vermaak, J. S.; Petruzzelo, J. *J. Appl. Phys.* **1982**, *53*, 6809.

0002-7863/84/1506-7247$01.50/0

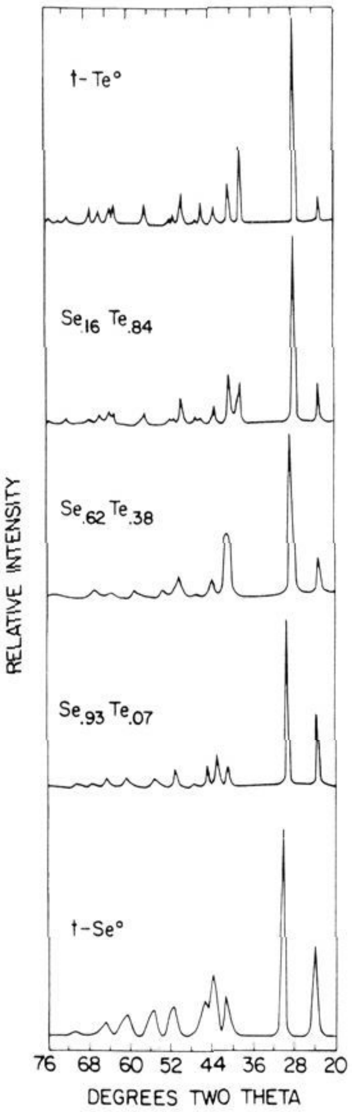

Figure 1. X-ray diffraction spectra (Cu Kα radiation) of precipitated Se_xTe_{1-x} alloy powders.

terpolation of literature values[14-18] for Se–Te alloys of the same composition prepared by conventional melt–quench processes.[18]

Figure 1 shows XRD traces, intensity vs. 2θ, of trigonal Te and trigonal Se along with traces for alloys of composition $Se_{0.1}Te_{0.9}$, $Se_{0.5}Te_{0.5}$, and $Se_{0.9}Te_{0.1}$. The flat base line indicates that the specimens are completely crystalline. It is evident from the absence of splitting, the constant full widths at half-maximum (fwhm), and the well-defined peaks that the materials are single phased. Although the fwhm remains constant for the peaks in each sample, this value differs among the various powders due to differences in average crystallite size. If one looks closely at the intense peak in trigonal Te at 28° 2θ, it can be seen that the position of this reflection gradually moves to larger angle as the mole fraction of Se in the alloy is increased. This shift is in keeping with the different lattice parameters of trigonal Te and trigonal Se.

The homogeneity of the composition of the crystalline alloys was demonstrated by energy-dispersive X-ray analysis (EDXA), wherein diffraction patterns were sampled from various ~1-μm regions of the samples. Scanning electron micrographs (Figure 2a–d) show that the gross morphology of the crystals changes significantly with composition going from rod-shaped faceted crystals at $Se_{0.93}Te_{0.07}$ to faceted-spheroidal crystals at $Se_{0.41}Te_{0.59}$ and back to rod-like crystals at $Se_{0.16}Te_{0.84}$. In light of the common trigonal unit cell evidenced in the XRD, it is surprising to see such dramatic variations in the morphology of the precipitated crystals of different composition.

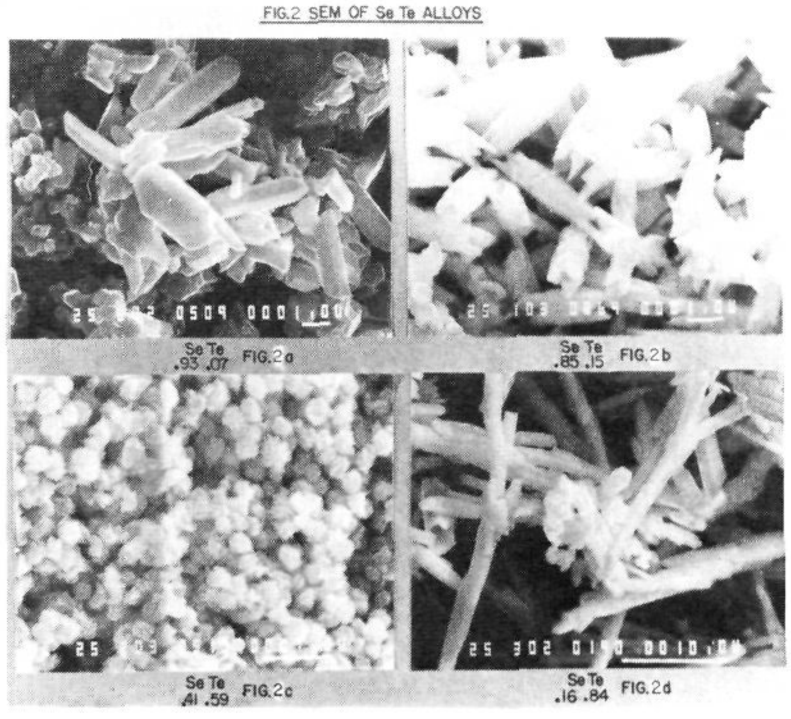

Figure 2.

It has thus been demonstrated that homogeneous crystalline alloys of Se and Te can be prepared by coreduction of solutions of Se^{IV} and Te^{IV} esters. The composition of the alloys mirrors the mole ratio of the esters in solution prior to reduction. The crystalline alloys thus formed exhibit diffraction patterns analogous to those obtained by annealing Se and Te alloyed in the melt.[19,20] There may be subtle structural differences that will manifest themselves in the electronic properties of these materials and such structural differences might be probed by vibrational spectroscopy.[21]

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Registry No. SeO_2, 7446-08-4; TeO_2, 7446-07-3; diethyl selenite, 14364-97-7.

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(14) Das, G. C.; Bever, M. B. *Metall. Trans.* **1973**, *4*, 1457.
(15) Bever, M. B.; Uhlmann, D. R.; Moss, S. C. *J. Non-Cryst. Solids* **1972**, *7*, 251.
(16) Pellini, G.; Vio, G. *Gazz. Chim. Ital.* **1906**, *36*, 469.
(17) Kimata, Y. *Mem. Coll. Sci., Kyoto Imp. Univ.* **1915**, *1*, 119.
(18) Hansen, P. M.; Anderko, K. "Constitution of Binary Alloy", 2nd ed.; McGraw-Hill: New York, 1958; p 1188.
(19) Bhatnagar, A. K.; Subrahmanyam, S. V. *Solid State Commun.* **1982**, *42*, 281.
(20) Grison, E. *J. Chem. Phys.* **1951**, *19*, 1109.
(21) Lucovsky, G. *Mater. Res. Bull.* **1969**, *4*, 505.

Recognition of a Semibridging Carbonyl Group in $Mn_2(CO)_9$ from Plane-Polarized Photolysis of $Mn_2(CO)_{10}$ in Ar Matrices at 12 K

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Photolysis of $Mn_2(CO)_{10}$ has long been acknowledged to proceed via homolytic cleavage of the Mn–Mn bond, producing $Mn(CO)_5$ radicals.[1] Later studies[2] also suggested the participation of nonradical species $Mn_2(CO)_n$, where $n = 9$ or 8. These were initially considered to arise by thermal ejection of CO from $Mn(CO)_5$,[2c] but recent work by Yesaka et al.[3] has shown these species to arise from an alternative decomposition of $Mn_2(CO)_{10}$.

When $Mn_2(CO)_{10}$ is photolyzed in an alkane matrix at 77 K, the sole process discernible is the photoejection of CO.[4] This is probably so because the alternative route results only in the im-

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(1) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.
(2) (a) Hughey, J. L., IV; Anderson, C. P.; Meyer, T. L. *J. Organomet. Chem.* **1977**, *125*, C49. (b) Fox, A.; Poë, A. *J. Am. Chem. Soc.* **1980**, *102*, 2497. (c) Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.
(3) Yesaka, M.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.
(4) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934.