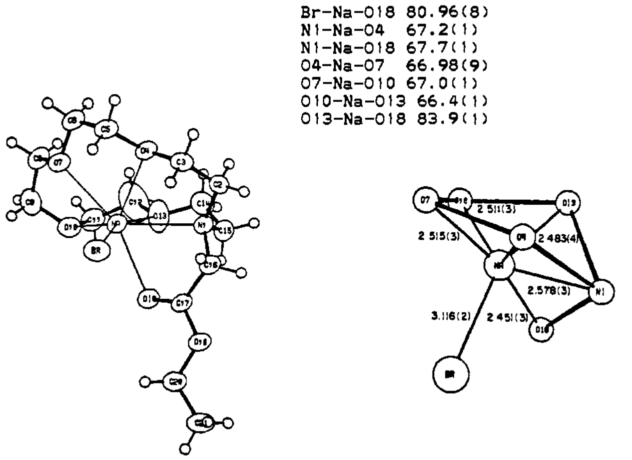
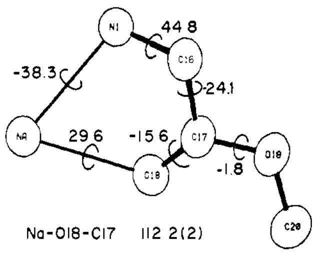


Figure 1. Perspective (left) and skeletal (right) drawings of 1·NaBr.

Distances and angles are given in a table as supplementary material. Values associated with C12 and O13 are not reliable because of thermal motion or disorder associated with these atoms. Values for the other atoms in the macrocycle are typical for macrocyclic polyethers. Values for the amino ester moiety are also typical for this fragment[9] except for C16–C17, which is slightly longer.

The structure fragment shown below depicts the interaction of the amino ester moiety with the sodium ion. The angle Na–O18–C17 is close to that expected to give maximum overlap of the carbonyl oxygen lone-pair electrons with the metal. The metal ion resides slightly (0.647 (2) Å) out of the plane defined by the four atoms (C16, C17, O18, O19) of the ester group. The N1–C16–C17–O18 torsion angle is in the range (-28.4° to 15.0°) observed for uncomplexed aminoethanoate esters.[9] In fact, the more frequent value is closer to 0°. This suggests that the position of O18 with respect to the macroring is similar in the uncomplexed and complexed states.



Structural studies of the crystalline state complement the solution binding studies.[11] In fact, the structure reported here suggests why **1** is better than a corresponding ether lariat, *N*-(2-methoxyethyl)-1-aza-4,7,10,13-tetraoxacyclopentadecane (**2**) at binding sodium ion.[12] The reason is that ester carbonyl oxygen is a better donor than ether oxygen. A recent report[13] of donor ability of various solvents toward sodium ion states that solvents with oxygen are better donors than those with nitrogen, i.e., O=PN > O=CN > O=CO > —O— > —N—. This order parallels solvent polarity and the expected electron density on oxygen for these functional groups. The strong ligation between the ester carbonyl oxygen and the sodium ion in this structure and the larger binding constant for **1** compared to **2** support the general hypothesis that ester carbonyl oxygen is a better donor than ether oxygen toward sodium ion.

The structural studies and the solvent donicities study help to illuminate nitrogen's role in lariat ethers. The improved binding observed[8b,c] for N-pivot lariat ethers compared to their C-pivot analogues should be attributed to the greater flexibility of ligands attached to nitrogen and not to the complexing ability of nitrogen. The ease of synthesis and the multitude of possibilities for modification of the side arm offer considerable advantages for N-pivot lariat ethers as specific metal ion complexing agents.

Acknowledgment. G.W.G. thanks the NIH for Grants GM-29150 and GM-31846 and W. R. Grace & Co., Inc., for their kind support of this work.

Registry No. 1, 92669-55-1; [NaBr·**1**], 92669-56-2.

Supplementary Material Available: Crystal data, table of distances and angles, positional parameters, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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[9] A search of the Cambridge Crystallographic Data Files[10] for the fragment $NCH_2C(O)OC$ produced eight structures matching the moeity. In two cases the nitrogen was part of a porphyrin; the others were amides. Bond distances and angles for the fragment were averaged for the eight structures. The parameter for the mean fragment that did not fall within 0.01 Å or 1.0° of the values in Table I was the C–C distance, mean value, 1.50 (1) Å (contact R. D. G. for further details).

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Uranium–Carbon Multiple-Bond Chemistry. 4.[1] Addition of Coordinated Carbon Monoxide across a Uranium–Carbon Multiple Bond

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An extensive chemistry is developing around the uranium–carbon multiple bond in $Cp_3U{=}CHPMePhR$ **1a**, R = Me, **1b**, R = Ph, where Cp = η-$C_5H_5^-$, Me = CH_3, and Ph = C_6H_5.[1-5] This includes the insertion of polar, unsaturated molecules[1,4] and a reaction with $[CpFe(CO)_2]_2$ in which the attachment of a CHPMePhR ligand from **1** to a terminal carbonyl in $[CpFe(CO)_2]_2$ is accompanied by coupling of this terminal carbonyl with a bridging carbonyl to form an η^1:η^3-allyl group bonded to two iron atoms.[5] We proposed[5] that the first step in the formation of this allyl involves the insertion of the terminal carbonyl into the uranium–carbon multiple bond. In order to gain further insight into this and related reactions we have investigated the interactions of **1** with several complexes that contain only terminally bonded carbonyls and report here that a terminal carbonyl in $CpMn(CO)_3$ does, in fact, insert into the uranium–carbon bond in **1a**.

After 3 days at ambient temperature, an equimolar mixture of **1a** and $CpMn(CO)_3$ in THF under dinitrogen produces a red-brown solution from which crystals of **2** can be obtained in 60% yield after addition of an equal volume of a 1:1 toluene/pentane solution. The ^1H NMR spectrum of **2** contains[6] peaks

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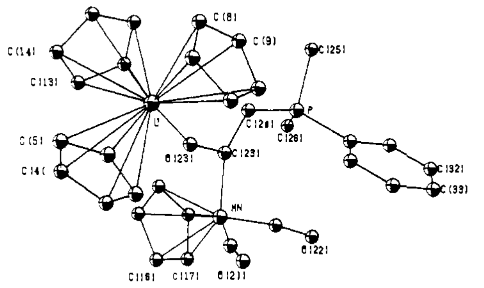


Figure 1. ORTEP drawing of Cp(OC)$_2$MnC(OUCp$_3$)=CHPMePh (**2A**). The numbering system for **2B** can be obtained by adding 50 to the values in the figure.

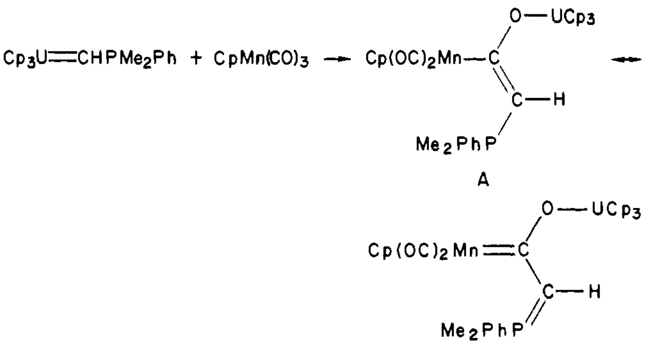
Table I. Selected Bond Distances and Angles for Cp(OC)$_2$MnC(OUCp$_3$)CHPMe$_2$Ph

molecule **2A**		molecule **2B**	
	Distances (Å)		
U(1)-O(23)	2.13 (2)	U(51)-O(73)	2.14 (2)
Mn(1)-C(23)	2.02 (4)	Mn(51)-C(73)	1.98 (3)
P(1)-C(24)	1.77 (3)	P(51)-C(74)	1.72 (4)
O(23)-C(23)	1.36 (4)	O(73)-C(73)	1.38 (4)
C(23)-C(24)	1.36 (5)	C(73)-C(74)	1.46 (5)
	Bond Angles (deg)		
U(1)-O(23)-C(23)	158 (2)	U(51)-O(73)-C(73)	163 (2)
Mn(1)-C(23)-O(23)	112 (2)	Mn(51)-C(73)-O(73)	113 (2)
Mn(1)-C(23)-C(24)	137 (3)	Mn(51)-C(73)-C(74)	138 (3)
O(23)-C(23)-C(24)	111 (3)	O(73)-C(73)-C(74)	109 (3)
P(1)-C(24)-C(23)	123 (3)	P(51)-C(74)-C(73)	122 (3)

characteristic of the CHPMe$_2$Ph moiety, Cp$_3$U, and CpMn. IR bands[6] indicated the presence of terminal carbonyl ligands. To identify **2** more completely an X-ray crystal structure was undertaken.[7]

Crystals of **2** belong to the space group *Pba*2, with unit cell parameters a = 22.423 (5) Å, b = 35.328 (7) Å, c = 8.648 (3) Å, V = 6851 (3) Å^3, and Z = 8. Space group selection, based on systematic absences, is ambiguous between *Pba*2 and *Pbam*. Attempts to solve the structure in the centrosymmetric space group *Pbam* required the U, Mn, and P atoms to lie on a crystallographic mirror plane and led to unreasonably short interatomic contacts between molecules. However, refinement in *Pba*2 resulted in a successful structural solution. Two independent, but structurally very similar, molecules, **2A** and **2B**, a toluene molecule, and a disordered THF molecule are present in the asymmetric unit. An ORTEP drawing of **2A** is shown in Figure 1, selected bond distances and angles for **2A** and **2B** are summarized in Table I, crystal data collection is summarized in Table II (supplementary material), and a complete listing of bond distances and angles for both **2A** and **2B** appears in Tables III and IV (supplementary material), respectively.

In the reaction of **1a** with CpMn(CO)$_3$ a carbonyl group in CpMn(CO)$_3$ has added across the uranium-carbon bond in **1b**. Two limiting resonance forms, **A**, an enolate, and **B**, a Fischer carbene complex, can be written to describe the bonding in **2**. Crystal structures are available for the formally similar complexes, (OC)$_5$CrC(OSiMe$_3$)=CHPMe$_3$ (**3**)[8] and (MeC$_5$H$_5$)(OC)$_2$MnC(OMe)=CHPMe$_3$ (**4**).[9] The bonding in **3** and **4** has been described[8,9] in terms of a resonance form analogous to **A**, where the metal-carbon bond has less double-bond character than in Fischer carbene complexes. Likewise, the Mn-C(23), in **2A**, and Mn-C(73), in **2B**, bond distances lie between the values of 1.87 and 1.89 Å expected[10] for Mn=C double bonds and 2.15 Å estimated[11] for a Mn—C single bond. In contrast, the metal-carbon multiple bond in Cp$_2$W=C(H)OZr(H)(C$_5$Me$_5$), a compound that forms by insertion of coordinated CO into a Zr-H single bond, is short when compared to other compounds that contain tungsten-carbon double bonds.[12]



As expected for resonance form **A**, Mn, P, and O are coplanar with C(23)-C(24) or C(73)-C(74). The orientation of this plane about the Mn-C bond is gauche to both carbonyls and the Cp group. This is not the usual configuration for Fischer carbene complexes, where orbital overlap favors an orientation that eclipses the Cp group[13,14] but is consistent with a single Mn-C bond where the conformation is determined largely by steric effects. Other bond distances and angles are also consistent with **A**. However, due to the large standard deviations in the metrical parameters, a delocalized combination of **A** and **B** cannot be ruled out.

The geometry about the uranium is normal. In accord with our observations of multiple-bond character in bonds between multiple electron pair donor atoms and U(IV),[1] we expect that the uranium-oxygen bond in **2** may possess multiple-bond character. The U—O distance is, indeed, quite short, 2.13 (1) Å, which is shorter than the U=N bond in Cp$_3$U=NPh$_2$, 2.29 (1) Å,[15] and only a little longer than the U≡N bond in Cp$_3$U≡NCMeCHPMePh$_2$, 2.06 (1) Å.[1] As expected for a multiply bonded U-O linkage, the U-O-C angle is large, 160 (1)°, the same as that observed for the uranium-nitrogen triple-bonded system, 161 (1)°.[1] This geometry is similar to that observed for other uranium alkoxides.[16]

The reactivity of the uranium-carbon multiple bond with coordinated carbon monoxide is extraordinary. Other metal compounds that contain metal-carbon multiple bonds are not known to react with the CO moiety in metal carbonyl complexes. In fact, most of the Fischer carbene complexes contain both a metal-carbon multiple bond and coordinated carbon monoxide ligands.[17-20] In both the reaction of CpMn(CO)$_3$ and [CpFe-

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(6) ^{1}H NMR (THF-d_8, 100 MHz) δ 32.5 (PCH, d, 1 H, J_{PCH} = 28 Hz), 10.4 (Ph, ortho, m, 2 H), 8.34 (meta, m, 2 H), 7.30 (para, m, 1 H), 4.86 (CpMn, s, 5 H), 4.58 (MeP, d, 6 H, J_{PCH} = 27 Hz), -10.86 (Cp$_3$U, s, 15 H). IR (Nujol mull on KBr plates) 1800-2100, 2005 (w), 1940 (m), 1900 (s), 1820 cm^{-1} (s). Anal. Calcd for U$_2$Mn$_2$P$_2$C$_{75}$H$_{80}$O$_7$: C, 51.73; H, 4.63. Found: C, 51.72; H, 3.84.

(7) A single crystal was mounted in a glass capillary and sealed under nitrogen. X-ray data were collected by use of a Syntex P$\bar{1}$ diffractometer. The structure was solved with SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976, using Patterson methods to locate the uranium, followed by refinements and Fourier maps to locate the remaining atoms. The carbon atoms in the Cp groups and those in the phenyl rings were refined as rigid bodies by use of the standard parameters contained in SHELX-76.

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$(CO)_2]_2$[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.

Acknowledgment. The support of this work by the National Science Foundation, Grant CHE82-10244 (J.W.G. and R.E.C.), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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 $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2 \cdot C_7H_8 \cdot C_4H_8O$; Table VI, positional and thermal parameters for isotropically refined atoms of $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2 \cdot C_7H_8 \cdot C_4H_8O$; Table VII, observed and calculated structure factors for $[Cp(OC)_2MnC(OUCp_3)CHPMe_2Ph]_2 \cdot C_7H_8 \cdot C_4H_8O$ (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}.

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

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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