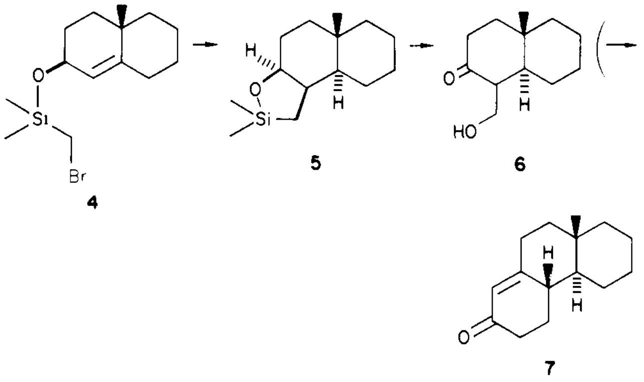
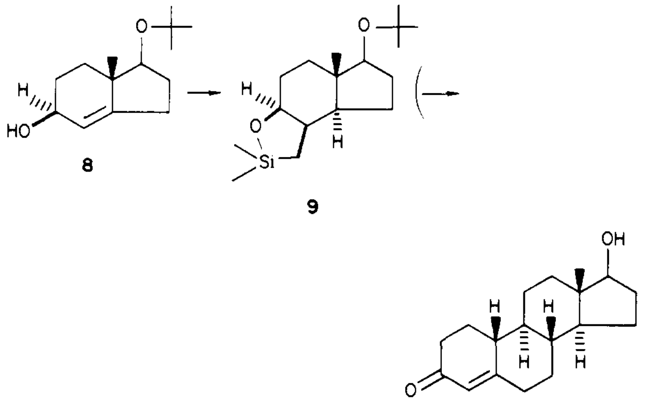
than a mixed acetal as the temporary connection. Reaction of the allylic alcohol **1** with commercially available (bromomethyl)chlorodimethylsilane (1 equiv, 10% $NEt_3$ in $CH_2Cl_2$, catalytic DMAP) followed by refluxing the resulting silyl ether **4** in benzene with 1.5 equiv of tributylstannane (1/20 equiv of AIBN, 30 min) produced, in about 65% yield, the cyclic siloxane **5**. This was essentially one isomer. The angular methyl at $\delta$ 1.02 in the decalin system again indicated a trans junction. This was rigorously established by removal of the silicon (KF-DMF, 30% $H_2O_2$),[6] oxidation of the resulting diol (NaOCl, acetic acid)[7] to the ketol **6**, acetylation, and annulation, using ethyl acetoacetate,[8,9] to give the known tricyclic enone **7**, mp 120–122 °C, identical (mp of mixture, spectra) with an authentic sample.[8]



The allylic alcohol **8** provides an even more impressive example of this method of stereocontrol. The same sequence of steps just described transformed **8** into **9** (NMR $\delta$ 0.89).[10] The stereochemistry was easily established as that of a *trans*-hydrindane by conversion, as above, using the proper analogue of ethyl acetoacetate,[9] into 19-nortestosterone, identical with an authentic sample.



The overall process just described thus achieves the operational equivalent of the net trans addition of a functionalized alkane to the double bond of cyclic allyl alcohols so that when a ring junction stereochemistry is generated (cf. **1** and **8**) the junction hydrogen is introduced trans to the original hydroxyl function of the allylic system. Further work is planned to test the generality of the method.

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**Registry No. 1**, 31654-83-8; **2**, 93756-51-5; **3**, 93756-52-6; **5**, 93756-53-7; **7**, 719-18-6; **8**, 93756-54-8; **9**, 93756-55-9; $Bu_3SnH$, 688-73-3; $BrCH_2SiClMe_2$, 16532-02-8; 2-[(2-bromo-1-ethoxyethyl)oxy]-4a-methyl-2,3,4,4a,5,6,7,8-octahydronaphthalene, 93756-50-4.

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(5) Removable connection to an allyl alcohol via a silyl ether is conceptually very similar to our previously used mixed acetal connection but differs in that it introduces a one-rather than a two-carbon functional chain at the $\alpha$-carbon of the allylic alcohol double bond, via the carbon-silicon cleavage method of ref 6. Experiments on the silyl ether connection, using (bromomethyl)dimethylchlorosilane with allylic alcohols, were carried out in 1983 by Dr. Pawel Fludzinski in our laboratory. For a recent illustration of the silyl variation of the acetal cyclization, see: Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298.

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(10) The yield (unoptimized) of pure **9** was only 36%, but we could find no evidence of the presence of any *cis*-hydrindane in the crude cyclization product.

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# An Organothorium-Nickel Phosphido Complex with a Short Th-Ni Distance. The Structure of $Th(\eta^5\text{-}C_5(CH_3)_5)_2(\mu\text{-}PPh_2)_2Ni(CO)_2$

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Two different transition metals brought into close proximity in a bimetallic complex may display chemistry unique from that found in the individual separated fragments.[2–4] Heterobimetallic centers have been formed and stabilized in such altered environments by construction of metal–metal bonds, ligand bridges, or a combination of both structural features. In this regard, phosphido ligands have been found in some instances to provide particularly stable bridge anchors which retard fragmentation of the bimetallic unit.[5] On the other hand, bridging phosphido ligands can also participate in interesting complex reactions.[6]

In our efforts to expand the chemistry of phosphido ligands to the actinides, we have recently prepared and structurally characterized a phosphido complex of thorium, $ThCp^*_2(PPh_2)_2$ (**1**).[7,8] Further, we have investigated the reactivity of this species with a variety of transition-metal complexes and now report the synthesis and structure of a nickel–carbonyl derivative. Most im-

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(7) Abbreviations used in the text include $Cp^* = \eta^5\text{-}C_5(CH_3)_5$, THF = tetrahydrofuran, COD = 1,5-cyclooctadiene, Ph = phenyl.

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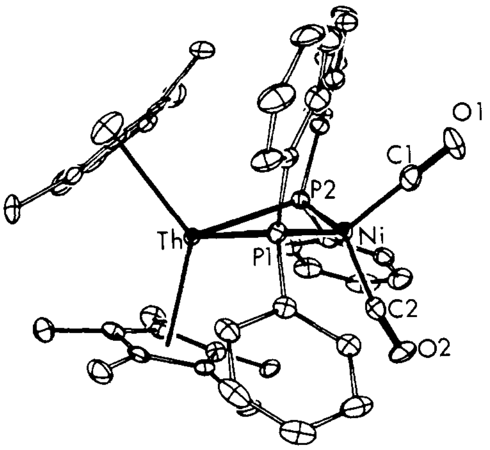

**Figure 1.** Overall geometry of the $Cp^*_2Th(PPh_2)_2Ni(CO)_2$ molecule (ORTEPII diagram, 30% thermal ellipsoids).

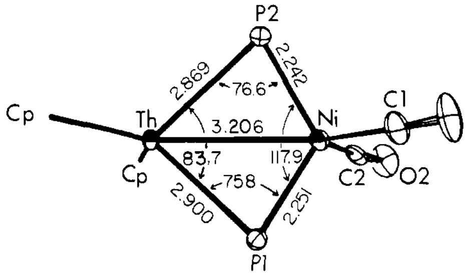

**Figure 2.** Geometry of the $Th(\mu\text{-}P)_2Ni$ core with distances shown in angstroms and angles in degrees.

portantly, the structural data for this complex present the intriguing possibility of a bonding interaction between the thorium and nickel atoms, the first such interaction between an actinide and a transition metal of which we are aware.

One equivalent each of **1** and $Ni(COD)_2$ in THF react under a CO atmosphere over a period of 2 days producing an orange microcrystalline solid[9] formulated as $Cp^*_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2$ (**2**). The solution IR spectrum of **2** exhibits two carbonyl stretching frequencies at 1988 and 1944 $cm^{-1}$, which are slightly lower than those observed ($\nu(CO)$ = 2010, 1955 $cm^{-1}$) for $Ni(CO)_2(PPh_3)_2$[10] and are consistent with the presence of a $Ni(CO)_2L_2$ fragment. In addition, a downfield chemical shift of $\delta$ 177 was observed in the $^{31}P\ \{^1H\}$ NMR spectrum, a value that is downfield of the resonance in **1**, $\delta$ 143.[8] In closely related phosphido-bridged transition-metal complexes, the $^{31}P$ chemical shift for $\mu$-$PPh_2$ ligands bridging two metals linked by a metal–metal bond often appears downfield ($\delta$ 300 to 50) whereas upfield resonances ($\delta$ 50 to −300) are commonly observed for compounds without a metal–metal bond.[11] Exceptions to these correlations have appeared,[5b,12] and structural assignments cannot be based solely on these data where an adequate data base is lacking. Because of the lack of other examples of phosphido bridged thorium–transition-metal complexes, the comparison of $^{31}P$ NMR chemical shift data for a series of closely related actinide–transition-metal binuclear systems is not possible at this time, although our continuing effort toward preparation of other related systems is in progress. It will be interesting to see if similar correlations exist for the actinide–transition-metal complexes.

The molecular structure[13] of $Cp^*_2Th(\mu\text{-}PPh_2)_2Ni(CO)_2$ is shown in Figure 1. There is no crystallographic symmetry imposed on the molecule. A view depicting important metrical parameters in the core of the mlecule is shown in Figure 2. The two thorium–phosphorus distances are shorter than those of 3.17 (3) Å found recently in a *thorium–phosphine*[16] complex, although they are nearly equivalent to the average Th–P distance of 2.866 (7) Å in **1**.[8] In contrast, the observed nickel–phosphorus bond lengths are within the range previously found for nickel–phosphine complexes.[17]

The most salient feature of the structure concerns the nature of the interaction between the thorium and nickel atoms, the distance between which is 3.206 (2) Å. We consider the appropriate radius for thorium to lie between 1.8 and 2.0 Å, on the basis of the 3.59-Å separation in the metal,[18] 3.8–4.1-Å Th–Th distances in two binary hydrides,[19] and the 4.007-Å distance in $[ThCp^*_2H(\mu\text{-}H)]_2$.[20] Note that subtraction of the covalent radius of phosphorus (1.10 Å) from the observed Th–P distance yields a value of ~1.8 Å. The structures of several binuclear nickel complexes[21] have revealed nickel–nickel separations of 2.3–2.4 Å, suggesting a covalent radius of about 1.18 Å. The nonbonding nickel–nickel separation of 3.36 Å in $[CpNiPPh_2]_2$[22] is far greater. If one assumes the distances in $[ThCp^*_2H(\mu\text{-}H)]_2$ and $[CpNiPPh_2]_2$ represent nonbonded metal–metal contacts then the present complex **2** possesses a Th–Ni distance that is ca. 0.5 Å less than the expected nonbonded distance.

The angles at the phosphorus atoms subtended by the metals are acute, with Th–P(1)–Ni = 75.8 (1)° and Th–P(2)–Ni = 76.6 (1)°. Similar values are observed in transition-metal complexes containing phosphido-bridged metal–metal bonds,[5b,23] but drastically larger values occur in phosphido-bridged systems without a metal–metal interaction, viz., Ni–P–Ni = 102.3 (2)° in $[CpNiPPh_2]_2$[22] and Fe–P–Mn = 106.4° in $Cp(CO)Fe(\mu\text{-}PPh_2)(\mu\text{-}CH_3CO)Mn(CO)_4$.[5b] There are no previously reported structures with M–P–M angles in the range 75–85° that lack a clearly defined M–M bond. In systems with no metal–metal bond, the (nonbonded) P–P contacts are short, as in $[CpNiPPh_2]_2$ where P···P = 2.70 (1) Å. In **2** the phosphorus–phosphorus separation is 3.850 (5) Å. The deviation from an ideal tetrahedral geometry about the nickel atom is also significant. While the phosphorus–nickel–carbonyl and carbonyl–nickel–carbonyl angles remain

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[9] $^1H$ NMR (300 MHz, $C_6D_6$) $\delta$ 8.0–7.0 (m), 1.72 (s); $^{31}P\{^1H\}$ NMR (121.5 MHz, $C_6D_6$) $\delta$ +177 (downfield of 85% $H_3PO_4$); IR (toluene soln) 1988 (vs), 1944 (vs), 1581 (m), 750 (m), 735 (m), 725 (m), 695 (m) $cm^{-1}$; UV-vis (toluene) 480 nm (1630 $cm^{-1}$ $M^{-1}$).

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[13] $Cp^*_2Th(PPh_2)_2Ni(CO)_2$ crystallizes in the space group $P2_1/c$ with $a$ = 11.903 (2) Å, $b$ = 11.283 (2) Å, $c$ = 34.353 (6) Å, $\beta$ = 90.08 (1)°, $V$ = 4613.8 Å$^3$, and $\rho$(calcd) = 1.42 g $cm^{-3}$ for $Z$ = 4 and $M_r$ = 986.4. Intensity data were collected at −65 (1) °C with use of an Enraf-Nonius CAD4 diffraometer. The structure was solved via MULTAN80[14] and difference Fourier techniques. Full-matrix least-squares refinement[15] utilizing 5711 absorption ($\mu$ = 38.4 $cm^{-1}$) corrected data (using $\tau$ scans on an axial reflection) for which $I > 2.0\sigma(I)$ and $1.0 \leq \theta \leq 25°$ (Mo K$\alpha$ radiation) resulted in a final $R_F$ = 4.5%. The model contained anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atoms of the four phenyl groups fixed in idealized positions ($B_{iso}$ = 4.5 Å$^2$), and a correction for secondary extinction (470 parameters). Since $\beta$ is close to 90°, symmetry-related reflections were compared to confirm monoclinic symmetry.

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close to the expected tetrahedral value (range 104.5–109.8°), the P(1)–Ni–P(2) angle is severely enlarged, at 117.9 (2)°. The corresponding P(1)–Th–P(2) angle is still acute [83.7 (1)°]; in fact, this value represents a decrease over the P–Th–P angle is **1**.[8] The closest contact between a methyl carbon on the Cp* ring and a phenyl carbon is 3.27 (2) Å compared to the closest methyl carbon contact between Cp* rings of 3.28 (2) Å.

If one considers the Th-phosphido bonding to be principally ionic in character, the P–Th–P angle may vary over a considerable range with only an insignificant cost in energy. Indeed the H–Th–H angle in $[ThCp^*{}_2H(\mu\text{-}H)]_2$ is only 58 (1)°.[20] For the present complex if one imagines a structure in which the $ThP_2Ni$ core is planar, the metal–phosphorus distances remain fixed at the observed values and the Th–Ni distance is increased to 3.7 Å, the calculated internal angles would be P–Th–P = 74.9°, Th–P–Ni = 91°, and P–Ni–P = 103.2°. Since the P–Th–P angle is less than the observed angle we would expect C–C contacts between Cp* and the phenyl rings to increase slightly for the hypothetical model. We conclude, therefore, that there are no structural constraints in the present structure which dictate a short Th–Ni distance, other than a direct metal–metal interaction. Nonetheless, the extent of this interaction obviously remains an open question. The problem is currently being pursued at Los Alamos via theoretical calculations, attempts to oxidize or reduce the complex, spectroscopic and magnetic measurements, and attempts to prepare a monobridged Th–Ni phosphido species.

**Acknowledgment.** This work was performed under the auspices of the U.S. Department of Energy and in part under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy.

**Supplementary Material Available:** ORTEP projection and tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors for $Cp^*{}_2Th(PPh_2)_2Ni(CO)_2$ (4 pages). Ordering information is given on any current masthead page.

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# Aldol Reactions of Transition-Metal Carbene Complexes

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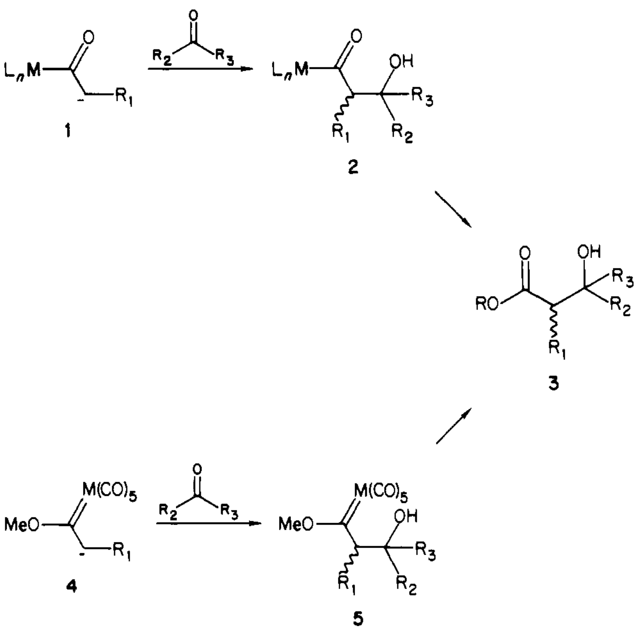
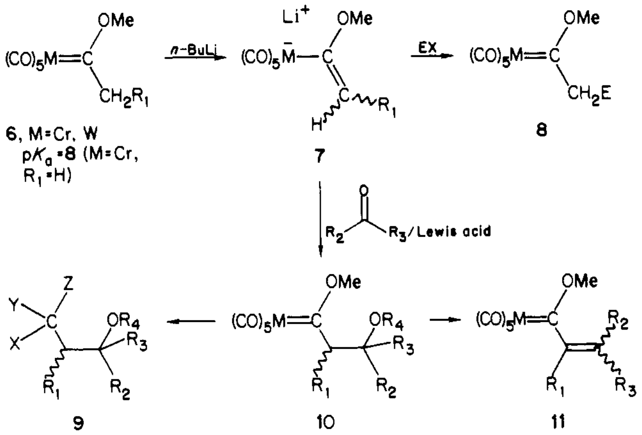
The enolate anions of metal acyl complexes are known to condense with carbonyl compounds to give $\beta$-hydroxy acyl complexes of the type **2**.[1,2] These complexes can serve as synthons for esters in the aldol reaction since oxidative cleavage of the metal gives rise to $\beta$-hydroxy esters. We report here the first examples of the reactions of "enolate" anions of transition-metal carbene complexes[3] with carbonyl compounds to give aldol products of the type **5** and an initial look at the stereoselectivity of these condensations and at methods for the removal of the metal from these complexes (Scheme I).

Scheme I



Scheme II



It is well established[3] that heteroatom-stabilized carbene complexes activate $\alpha$-hydrogens and give anions of the type **4** upon deprotonation. The methyl group in complex **6a** ($R_1$ = H, M = Cr) displays tremendous thermodynamic acidity[4] (pKa = 8) and as might be anticipated the conjugate base of complex **6a** was found to be relatively unreactive with all but the most reactive of electrophiles.[3f,g,5,6] The anions **7** do not react with ketones or most aldehydes. Reactions have only been reported with three nonenolizable aldehydes from which the $\alpha,\beta$-unsaturated complexes **11** were isolated in 20–50% yield.[6] The aldol complexes **10** were never observed from these reactions, which was attributed to an intramolecular prototropic shift which is rapid due to the greater acidity of protons $\alpha$ to the carbene carbon in **10** ($R_4$ = Li) than the proton of a hydroxyl group (Scheme II).

The inherent unreactivity of the anion **7** can be overcome by preactivating the carbonyl compound with a Lewis acid (Table I), which gives rise to the $\beta$-hydroxy carbene complex **10** ($R_4$ = H) as the exclusive product, a result that can be attributed to the much greater bond strengths of the boron and titanium bonds to

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