formal oxidation state of the phosphorus changes from pentavalent to trivalent.

A more bulky electrophile, CPh$_3^+$, also attacks the phosphoryl oxygen of 1 to give [Cp(CO)$_2$FeP(OCPh$_3$)-(OEt)$_2$]$^+$ (3; spectroscopic data are listed in Table VIII). If the conformation of 1 is the same as that found in the solid state (i.e., the Fe–P bond does not rotate in a solution), the bulky CPh$_3^+$ does not appear to be able to approach the phosphoryl oxygen of 1 close enough to form the O–CPh$_3$ bond owing to the steric repulsion between phenyl groups of CPh$_3^+$ and the cyclopentadienyl group of 1. When 1 has the conformation in which the Cp and the phosphoryl oxygen are s-trans to each other with respect to the Fe–P bond, CPh$_3^+$ can approach close enough to form the O–CPh$_3$ bond. The formation of 3 is further support for free rotation around the Fe–P bond in 1 in solution.

H$^+$ also reacts with 1 in the same manner as the other two Lewis Acids, Me$^+$ and CPh$_3^+$. The formation of [Cp(CO)$_2$FeP(OH)(OEt)$_2$]$^+$ (4) was established from the spectroscopic data in Table VIII. The ν_{CO} (2062 and 2017 cm^{-1}) are very close to those for 2 and 3. The ^{31}P NMR resonance (146.80 ppm) is between those for 2 and 3. The ^{1}H NMR resonances due to the Cp, methylene, and methyl groups of OCH$_2$CH$_3$ group correspond to those for 2 and 3. A signal due to the hydroxy group was not detected.

Failure to observe OH is not uncommon; e.g., the ^{1}H NMR signal attributable to the EH group of [Cp(CO)$_2$FeP-(EH)(CF$_3$)$_2$]$^+$ (E = O, S, Se) prepared from Cp(CO)$_2$FeP-(E)(CF$_3$)$_2$ and a mixture of HCl and SnCl$_4$ was not detected even at −20 °C.[26]

Pyridine deprotonates 4·SO$_3$CF$_3$ to afford 1. The spectroscopic data of the resulting product in solution were identical with those of 1 in pyridine. Therefore, we conclude that 4 is relatively acidic.

Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for 1 (Tables III and IV) (4 pages); a listing of observed and calculated structure factors for 1 (Table V) (24 pages). Ordering information is given on any current masthead page.

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Reaction of Active Uranium and Thorium with Aromatic Carbonyls and Pinacols in Hydrocarbon Solvents[1]

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Highly reactive uranium and thorium metal powders have been prepared by reduction of the anhydrous metal(IV) chlorides in hydrocarbon solvents. The reduction employs the crystalline hydrocarbon-soluble reducing agent [(TMEDA)Li]$_2$[Nap] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine, Nap = naphthalene). The resulting active metal powders have been shown to be extremely reactive with oxygen-containing compounds and have been used in the reductive coupling of aromatic ketones giving tetraarylethylenes. Reactions with pinacols have given some mechanistic insight into the ketone coupling reaction. These finely divided metal powders activate very weakly acidic C–H bonds forming metal hydrides, which can be transferred to organic substrates.

Introduction

Highly dispersed and reactive metal powders have commanded a great deal of interest for their applications in catalytic and stoichiometric chemical syntheses, as well as their uses in materials science. Numerous methods exist for the preparation of these metal powders. Most of these methods for preparing metal powders involve the reduction of a metal salt or oxide by hydrogen (usually at high temperatures)[2-4] or by other chemical or electrochemical means.[3,5-10] In addition to reductive techniques, pyrolyses[3,11,12] and metal atom vaporization[13-19] have been employed. An excellent review of the preparation, reactivity,

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and physical properties of unsupported metal particles has appeared.[20]

Because of the commercial importance of uranium, a number of methods for generating finely divided chemically reactive uranium metal have been developed. Pyrophoric uranium metal powders have been prepared by thermal decomposition of uranium amalgam[21-23] or uranium hydride.[24,25] Many methods have involved reduction of uranium oxides.[26] Other methods employed are melt electrolysis[26] and potassium reduction of $(\eta^5\text{-}C_5H_5)_4U$.[27]

Since 1972, we have published many reports describing convenient methods for the generation of highly reactive metal powders and their use in organic as well as organometallic synthesis.[28-34] Most of the active metals prepared by our group have been prepared in ethereal solvents.[35] Our initial report on the preparation of active uranium (1) employed 1,2-dimethoxyethane (DME) as a solvent.[31] We have since developed a method for preparing active uranium (3) in hydrocarbon solvents which leads to much cleaner and more controllable chemistry compared to 1.[34,36]

The oxophilicity of titanium has been exploited in the well-known reductive carbonyl coupling reactions pioneered by McMurry[37-41] and others[42,43] using low-valent titanium. This reaction has been shown to occur with many other early transition metals.[44,45] The oxophilicity of the early transition metals, lanthanides, and actinides is well-known. The standard enthalpy of formation for UO_2 (-259.3 kcal/mol) and ThO_2 (-293.1 kcal/mol)[46] are among the most negative known for any MO_2 metal oxide.

Scheme I
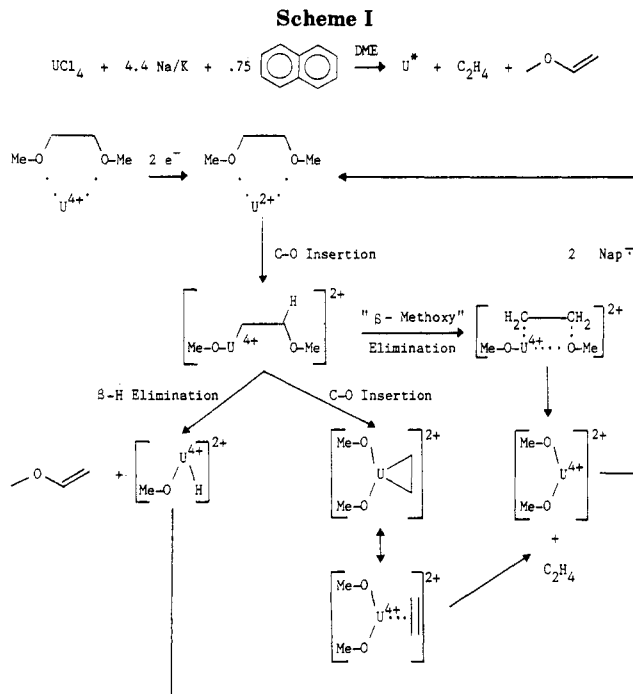
There have been no investigations of the reductive ketone coupling reaction, however, with either lanthanide or actinide metals. There are many examples of coordinated carbonyl couplings in organometallic lanthanide[47-50] and actinide[51-58] η^2-acyl complexes. The complex Cp_3U=$CHPR_3$ has been shown to reductively couple bridging and terminal carbonyl ligands of a dinuclear iron complex.[59] In certain cases, a formal trimerization[49] or tetramerization of CO can even be effected.[48,52] In none of these cases, however, has the organic fragment been removed intact from the metal center. One report has appeared where di-*n*-butyluranocene has been used in a reductive coupling reaction to give azobenzenes from nitrobenzenes.[60] In view of this coupling reaction of U(IV), the high oxophilicity of uranium, and the similarities between the chemistry of the actinides and group 4 transition metals, we have investigated the reactions of active uranium and thorium with oxygen-containing compounds.

Results and Discussion

The reduction of UCl_4 in ethereal solvents by Li, Na,

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or K does not proceed to completion due to coating of the surface of the alkali metal.[31,61] Active uranium can, however, be prepared by the reduction of UCl_4 using Na/K alloy in DME[31,61] (1). We have shown this active uranium to be very reactive with allyl iodide and benzophenone.[31] Uranocene can be prepared directly in 56% yield by reaction of 1 with cyclooctatetraene (COT) in refluxing DME for 22 h. This is the same yield reported by Streitwieser in the sealed tube reaction of a pyrophoric form of uranium (prepared under vigorous conditions by repeatedly hydrogenating uranium metal and thermally decomposing the resulting hydride) with COT at 150 °C.[24]

Active uranium prepared by Na/K reduction in DME is also an extremely active polymerization catalyst and will polymerize 100 equiv of 1,3-butadiene at -4 °C and atmospheric pressure in less than 1 h. This is much more reactive than the active uranium powder prepared by Chang et al. (via thermal decomposition of U/Hg) which polymerized 80% of 1,3-butadiene (1 atm) in 4 h at 70 °C.[62] The resulting polybutadiene prepared by our method exhibited IR bands corresponding to cis (675 cm^{-1}), vinyl (910 cm^{-1}), and trans (970 cm^{-1}) morphologies.[63]

When UCl_4 is reduced by Na/K alloy in THF (tetrahydrofuran) or DME, however, decomposition of the solvent is seen even at low temperatures. Few investigations of the reductive cleavage of DME have been reported.[64-68] When DME is used for the reduction of UCl_4, the major fragments from the solvent can be seen as gaseous components in the head space above the reaction. The active uranium (1) reacts with DME to produce primarily ethylene and methyl vinyl ether[64] (GC/MS) (Scheme I).[69] Production of these compounds can be accounted for by the insertion of a low-valent uranium species into a carbon–oxygen bond of the DME. Complexes of this type have been identified for complexes of W and Ta.[66,67] Insertion into the other C–O bond of the DME gives ethylene, whereas β-hydride elimination[70-76] gives methyl vinyl ether. If additional sodium naphthalide is added, further reduction of the solvent takes place and

more ethylene and methyl vinyl ether can be obtained. In this way, the uranium can be considered as mediating the reductive decomposition of DME into ethylene and methyl vinyl ether. Reactions of organic substrates with 1 in ethereal solvents give low yields and complicated product mixtures containing solvent fragments.[77]

In order to eliminate the reaction of active uranium with the solvent, a preparation of active uranium in an inert solvent was sought. The use of hydrocarbon solvents eliminates the problem of reactivity with oxygen functionalities. We have observed that the most highly reactive metals are obtained from soluble reducing agents. A problem exists, however, in that there are very few strong reducing agents that are soluble in nonpolar solvents. Lithium naphthalide cannot be formed in hydrocarbon solvents.

Using the method of Fujita et al.,[78] we were able to prepare a highly active form of cadmium in toluene.[32] This method works for uranium as well but is inconvenient as sonication is needed for each reaction. We have prepared and isolated the stable crystalline lithium naphthalide dianion derivative $[(TMEDA)Li]_2[Nap]$ (2) directly by sonicating a 1.6 M solution of TMEDA, Li, and naphthalene in toluene. When sonication is stopped after all of the Li has dissolved, the dianion crystallizes. This complex was prepared previously by deprotonation of 1,4-dihydronaphthalene[79] but has not been used in any synthetic chemistry. The 1,4-dihydronaphthalene that was employed is a fairly expensive and sensitive compound precluding its widespread use in synthesis. Our procedure is much less expensive and amenable to preparative scale synthesis. We routinely prepare 50–60-g quantities of this complex and have found it to be indefinitely stable at room temperature when stored in an argon-filled drybox. Complex 2 does decompose under nitrogen, however.

NMR characterization of 2 was difficult as the resonances were quite broad, presumably due to exchange between the dianion and small amounts of the paramagnetic radical anion. When the sample was cooled, these resonances sharpened until -47 °C when the complex crystallized out of solution. Even at -47 °C, the individual resonances were not resolved.

The UV/vis spectrum of complex 2 shows an absorption at 444 nm, which disappears in the presence of air. The metalation of naphthalene by potassium has been studed previously, and a visible absorption around 450 nm attributed to the naphthalene dianion.[80]

When complex 2 in benzene is quenched with water or saturated aqueous NH_4Cl, 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and naphthalene are produced (3.4:1.0:2.4). The presence of dihydronaphthalenes, especially 1,4-dihydronaphthalene, shows that a naphthalene dianion is present. After 2 equiv of complex 2 was stirred with 1 equiv of UCl_4 in benzene for 1 h, followed by quenching with water or saturated aqueous NH_4Cl, only naphthalene is observed. This shows that 2 has been

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completely consumed in reducing the UCl_4 within 1 h at room temperature.

The potential reaction of the reducing agent **2** with hydrocarbon solvents like toluene and xylenes that contain benzylic hydrogens was investigated. When a solution of **2** in toluene (prepared in situ by sonication for 13 h) was quenched with methyl iodide or dimethyl sulfate, very small amounts ($\leq 6\%$) of ethyl benzene or xylenes were observed. When a solution of **2** in benzene (prepared in situ by sonication for 13 h) was quenched with methyl iodide or dimethyl sulfate, negligible amounts ($\leq 1.5\%$) of toluene were seen. Since the sonication conditions (42 °C bath temperature; hot-spot peak temperature and pressure of about 3000 K and 300 atm, respectively, have been measured;[81] 13 h) are much more vigorous than those customarily used in the preparation of active uranium (room temperature, ≤ 1 h), it can be concluded that no reaction of complex **2** with the solvent is taking place during the reduction of UCl_4.

Unfortunately, the reactivity of active uranium prepared by this method (**3**) with acidic C–H bonds precludes its use with aliphatic ketones. Apparently, **3** reacts with the acidic α-protons of the carbonyl, generating a carbanion or equivalent which does aldol-type chemistry. Thus, acetophenone reacted with **3** to give primarily the aldol product 1,3-diphenyl-2-buten-1-one (dypnone), while cyclohexanone produced primarily 2-cyclohexylidenecyclohexanone. For this reason, only aromatic ketones will be considered in this study.

Reaction of active uranium with 2 equiv of benzophenone in refluxing xylenes gave the expected reductive coupling product tetraphenylethylene (TPE), as well as an unexpected product, 1,1,2,2-tetraphenylethane (TPA). Further reduction of tetraarylethylenes to tetraarylethanes has been observed previously in similar reductive coupling reactions of low-valent titanium.[38,82] This hydrogenation reaction has been studied by Geise.[83] The source of the extra hydrogen in these titanium reactions has been implied to be from the reducing agent when $LiAlH_4$ is used, or from the THF solvent when Mg or K are used as reducing agents.[82] This is not surprising, as $LiAlH_4$/transition-metal halide systems are well-known reducing agents for unsaturated organic compounds.[84,85] In the uranium system, however, the hydrogen source is quite different. Reaction of active uranium with TPE in a refluxing mixture of xylenes/toluene (5:3) for 4 h showed no TPA. Even when active uranium was reacted with TPE under 1 atm of H_2 in a refluxing mixture of xylenes/toluene (5:3), no TPA was seen. Reaction of active uranium with TPA under similar conditions did not produce any TPE either. This demonstrates that in our system TPA was not formed by further reduction of TPE but must be formed during the coupling step at the metal surface. In addition, the reaction of **3** (1 equiv) with benzophenone (2 equiv) in the presence of TPE (1 equiv) did not produce any appreciable additional amount of TPA. This shows that reduction of TPE by a possible hydrogen-transfer species, generated during the reaction of **3** with benzophenone, does not occur.

Active uranium reacts with diphenylmethanol (benzhydrol) to give exclusively TPA. A 60% yield of TPA was

Figure 1. Surface metallopinacols on active titanium and uranium.

Table I. Stoichiometry Effect on Reaction of Benzophenone with U*

$$U^* + 2Ph_2CO \xrightarrow[\text{8 h ref}]{\text{xylenes}} Ph_2C{=}CPh_2 + Ph_2CHCHPh_2$$

stoichiometry			% yield[a]	
UCl_4	"Li"[b]	Ph_2CO	$Ph_2C{=}CPh_2$	$Ph_2CHCHPh_2$
1	1	2	24	1
1	2	2	32	7
1	3	2	33	33
1	4	2	41	32
1	4	4	38	56
1	5	2	39	23

[a] GC Yields. [b] "Li" = 0.5[(TMEDA)Li]$_2$[Nap].

observed after 4 h in refluxing xylenes (2:1 benzhydrol/uranium). No reaction was seen at room temperature. No TPE was ever observed in this reaction. On the basis of these observations, it appears that the TPA formed in the coupling reaction of benzophenone arises from the initial reduction of benzophenone to a benzhydrol alkoxide followed by coupling of this alkoxide, rather than by further reduction of the TPE.[83,86] When 4,4'-dimethylbenzophenone is reacted with **3**, the intermediacy of 4,4'-dimethylbenzhydrol is observed.[87]

No coupling of benzophenone was observed when benzophenone was reacted with UCl_4 (unreduced) or with UCl_4 + 4TMEDA in refluxing xylenes. Clearly the coupling chemistry observed must depend on the presence of a low-valent uranium species.

By varying the stoichiometry in the reduction of UCl_4 by **2**, it can be seen that using four "Li" equivalents produces the greatest yield of coupled products (TPE + TPA) (Table I). When the UCl_4 is "over-reduced" by using five "Li" equivalents, the yield of both TPE and TPA is diminished, primarily due to the formation of large amounts of diphenylmethane (DPM). This DPM presumably arises from the action of excess reducing agent on benzophenone in the presence of uranium.

For most of the reactions in this study, a stoichiometry of two ketones per uranium has been used. This is in accord with the postulated stoichiometry of active uranium (U*) producing UO_2. When only a twofold excess of benzophenone is used, however, the combined yields of coupled products is 94%. This is in marked contrast to the titanium systems where each titanium is only capable of reacting with 1 equiv of ketone.[82] In the titanium systems, optimal yields of alkene are obtained with excess titanium, whereas we find that excess ketone produces the highest yields of alkene. This difference in M:O stoichiometry is suggestive of a different type of metallopinacol intermediate (Figure 1). Further evidence which suggests the presence of this type of intermediate is the fact that **3** reduces the α-diketone benzil to diphenylacetylene,[88] whereas active forms of titanium have been shown by two

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Table II. Temperature Effect on Reaction of Benzophenone with U*

$$U^* + 2Ph_2CO \xrightarrow[12\,h]{xylenes} Ph_2C{=\!\!=}CPh_2 + Ph_2CHCHPh_2 + Ph_2CH_2$$

temp, °C	% yield[a]		
	$Ph_2C{=}CPh_2$	$Ph_2CHCHPh_2$	Ph_2CH_2
140	34	20	30
110	30	7	34
90	35	4	14
70	53	2	8
50	7	0	0

[a] GC Yields.

authors not to effect this transformation.[40,89]

The production of the hydrogenated products TPA and DPM is very temperature-dependent. Large amounts of these compounds are formed in refluxing xylenes, whereas virtually no TPA or DPM is observed at 70 °C (Table II). This is in marked contrast to the titanium systems where low temperatures in the formation of the low-valent titanium species have been shown to promote the hydrogenation of TPE.[83] TPE can be formed quantitatively by using 3 at 70 °C with an excess of benzophenone.

In order to further probe the mechanistic course of this reaction, the possibility of a pinacolic intermediate was addressed. Metallopinacolic intermediates in reductive coupling reactions of ketones have been strongly implied by many groups on the basis of the observance of pinacols.[38,39,82] We have also observed the presence of pinacols in ketone coupling reactions that are quenched before completion. To investigate the possibility of a metallopinacolic intermediate further, the reaction of active uranium with benzopinacol was conducted. This reaction proceeded faster than the corresponding ketone reaction. In this reaction equal amounts of TPE and TPA were seen, whereas when benzophenone is reacted with 3, more TPE than TPA is seen (TPE/TPA is about 4:3). The yield of TPE is similar in the two reactions with the major difference being that more TPA is produced from the benzopinacol reaction. Benzopinacol contains two acidic hydrogens that could account for the greater yield of TPA. When benzopinacol-d_2 was reacted with 3, ≥73% (MS) of the deuterium was incorporated into TPA. This clearly shows that the benzylic hydrogens in TPA can come from a uranium hydride. Hydridic organometallic uranium species are well-known.[53,54,56,72-74,76,90-94]

The product distribution from the reaction of 3 with pinacols shows a similar temperature dependence to that of the ketone reactions, although the pinacol reactions proceed at a somewhat lower temperature. The reaction of 3 with benzopinacol at 50 °C gives only TPE, with no TPA observed.

The source of the uranium hydride in the reaction of benzophenone with 3 is not as clear however. When the reaction of benzophenone with 3 was worked up with D_2O, no deuterium incorporation in TPA or DPM was seen, nor was any seen when toluene-d_8 was used as a solvent. All of the naphthalene is recovered, and no hydrogenated or

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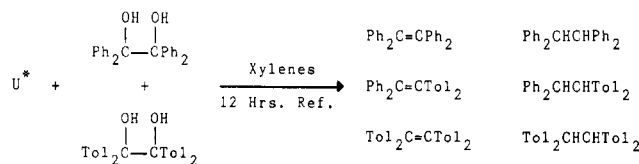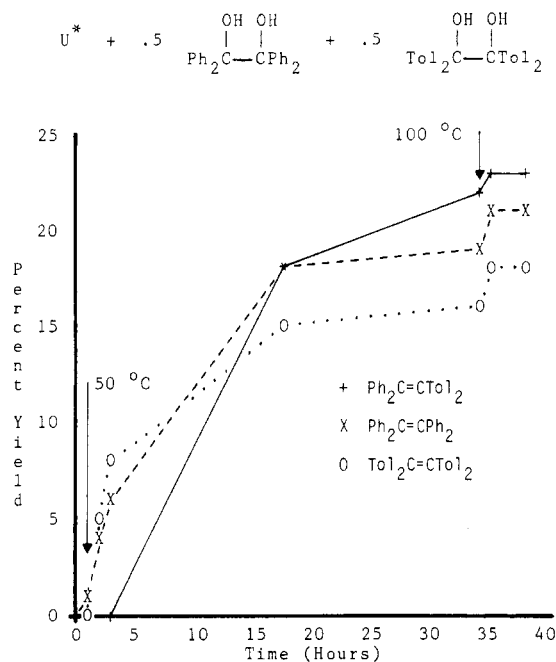

Figure 2. Product of mixed pinacol reaction with U*.

substituted naphthalenes are observed. Elemental analysis of the solid remaining after reaction of active uranium with benzophenone (following removal of the solvent and Soxhlet extraction) showed substantial amounts of nitrogen (0.52 mol of N/U) contained in the solid $LiCl/UO_x$ matrix. This suggests that TMEDA (presumably coordinated to uranium) is reacting with the low-valent uranium generating a uranium hydride. This uranium hydride could be incorporated into the reaction products TPA and DPM, just as the uranium deuteride resulting from the reaction with benzopinacol-d_2 was incorporated.

The temperature dependence of the reaction of 3 with TMEDA could account for the fact that the hydrogenated products TPA and DPM are only seen at high temperatures (vide supra). It appears that the hydrogenated products TPA and DPM arise when the benzophenone is reacted at high temperatures with 3 containing uranium hydrides. These hydrides can be formed from either substrates containing acidic hydrogens or by thermal reaction of the low-valent uranium species with coordinated TMEDA.

The inherent chemistry described for the reaction of 3 with benzophenone and benzopinacol is not altered by substituting the phenyl rings of the ketone or pinacol with methyl groups. Thus, the reaction of the ketone 4,4'-dimethylbenzophenone (Tol_2CO) or the pinacol 1,1,2,2-tetrakis(4-methylphenyl)ethane-1,2-diol (tetramethylbenzopinacol) (4) with active uranium gives tetrakis(4-methylphenyl)ethylene (TTE) and 1,1,2,2-tetrakis(4-methylphenyl)ethane (TTA). Reaction of a 1:1 mixture of benzophenone and Tol_2CO with 3 gives a statistical distribution of the six expected products (Figure 2).

In order to further examine the role of the pinacolic intermediate, a crossover experiment was conducted. In the reaction of a 1:1 mixture of 4 and benzopinacol with 3 in refluxing xylenes, a statistical distribution of all six coupled products was seen. The product distribution was identical with that seen from a 1:1 mixture of benzophenone and Tol_2CO.

When the reaction was conducted at 50 °C, however, the results were very different. At this temperature no hydrogenated products (TPA, 1,1'-bis(4-methylphenyl)-2,2'-diphenylethane, or TTA) were seen. Initially only TPE and TTE were formed. After 2 h at 50 °C, the formation of 1,1'-bis(4-methylphenyl)-2,2'-diphenylethylene (DPDTE) began to be observed. By 18 h at 50 °C, the rate of formation of TPE and TTE had decreased, and the formation of the mixed ethylene was predominant (Figure 3).

This surprising result shows that C–C bond cleavage of the metallopinacol is extremely facile. Exchange of surface-bound metallopinacols prior to deoxygenation appears to be a likely possibility (vide infra) (Figure 4). These results can be rationalized by surface activation of the active uranium particles. In the low-temperature reaction the product formed initially is that of the unexchanged metallopinacol. As the reaction proceeds, activation of the metal particle continues, which exposes more active sites on the surface. As the number of active sites on the surface of the metal particle grows, the probability of finding adjacent metallopinacols increases. In this way, the pro-

$$U^* + .5 \begin{array}{cc} OH & OH \\ | & | \\ Ph_2C & -CPh_2 \end{array} + .5 \begin{array}{cc} OH & OH \\ | & | \\ Tol_2C & -CTol_2 \end{array}$$
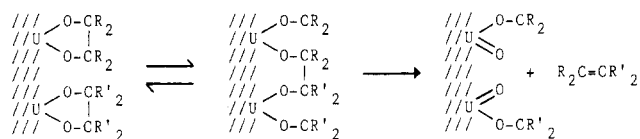
Figure 3. Mixed pinacol reaction at 50 °C.

Figure 4. Pinacol exchange on the surface of U*.

duction of the exchanged metallopinacol deoxygenation product DPDTE is dependent on surface activation of the active uranium metal particle. This accounts for the initial formation of the unexchanged products TPE and TTE until the surface is activated enough for the formation of DPDTE to be observed. At 144 °C, the reaction of the active uranium with pinacols is so fast that no induction period is observed before the formation of the exchanged deoxygenation product.

Further evidence for surface activation of active uranium by alcohols was seen in the reaction of active uranium with benzophenone in the presence of methanol. When the methanol was added along with the benzophenone to freshly prepared active uranium, TPE production could be observed even at room temperature (3 h, 13%). After 70 h at 50 °C, 38% TPE was seen. In the absence of methanol, only negligible amounts of TPE can be formed even at 50 °C.

At 50 °C, arylpinacols are deoxygenated to give tetra-arylethylenes, whereas at this temperature negligible coupling of aryl ketones is found (vide supra). When a mixture of an aryl ketone and an arylpinacol (2:1) is re-acted with active uranium, the initial product formed was found to be the one resulting from coupling of the aryl *ketone*. Once again the pinacol appears to be acting initially to activate the surface of the metal particle.

Active thorium has been prepared in a manner analogous to that of active uranium. Active thorium reacts with DME, as does active uranium 1. When benzophenone is reacted with active thorium in refluxing DME, the product mixture contains TPE and TPA in low yield (<10%), as well as many other coupled products containing solvent fragments. The reactivity of active thorium with aromatic ketones in hydrocarbon solvents is similar to that of active uranium, although the yields tend to be lower (3 days in refluxing xylenes; 11% TPE, 15% TPA) and the product

distributions are more complex. These preliminary reactions with thorium have shown 3 to be much better for the reductive coupling reactions in this study.

In addition to aromatic solvents, we have seen reactivity of active uranium prepared in 1-decene and TMEDA. The yields of TPE and TPA resulting from preparation and reaction of active uranium with benzophenone in 1-decene are only slightly lower than those in aromatic solvents, presumably due to solubility considerations. There was little difference in the proportion of TPA to TPE. It appears that decene does not serve as either a hydride source (allylic hydrogens) or a hydride sink (via hydrogenation of the double bond). The preparation and reaction of active uranium with benzophenone in TMEDA gave yields of TPE comparable to other aromatic solvents at that temperature (~20%). Negligible amounts of TPA were seen, however. The presence of a large excess of a basic solvent could serve to reduce the amount of metal hydrides present.

Conclusion

The hydrocarbon-soluble naphthalene dianion equivalent [(TMEDA)Li]$_2$[Nap] can be prepared in large amounts and used as a convenient reducing agent. This reducing agent allows active uranium and thorium to be prepared in inert hydrocarbon solvents. These active metals are extremely reactive with oxygen-containing compounds and have been shown to react with ethers, ketones, and alcohols. Active actinides also show a great propensity for formation of metal hydrides. Very weakly acidic C–H bonds in TMEDA can be activated by using these metals, with the resulting hydrides being transferred to organic functionalities. Aromatic ketones can be reductively coupled and aromatic pinacols are deoxygenated, presumably by way of a surface metallopinacolic intermediate to give tetraarylethylenes or tetraarylethanes in high yield. This reductive coupling reaction is effective without the need for a large excess of active metal, as in the titanium systems. Contrary to the active titanium systems of McMurry, active uranium and thorium are able to react with two ketones per metal atom. This implies having a mononuclear surface actinide metallopinacol, as opposed to binuclear titanium metallopinacols.

Experimental Section

$^1/_8$ in. stainless-steel column containing 3% OV-17 on Chromosorb W-AW 100/120 or Chromosorb G-NAW 100/120. Gas analysis was done on a Hewlett-Packard 5730A GC with an FID detector, using a 7 ft × $^1/_8$ in stainless-steel column containing Porapak-Q. GC data was analyzed by using a Perkin-Elmer LCI-100 laboratory computing integrator. Thin-layer chromatographic separations were performed on Merck 5775 silica gel plates. Compound identification was accomplished with a Varian EM-390, XL-200, or VXR-200 NMR spectrometer, a Perkin-Elmer 283 infrared spectrometer, and a Kratos MS-80 mass spectrometer. All NMR chemical shifts are reported in parts per million downfield from TMS. All ^{13}C spectra are reported proton decoupled. High-resolution electron-ionization mass spectra were obtained in-house with the facilities of the Midwest Center for Mass Spectrometry—a regional NSF instrumentation facility. Percent deuteration was determined by mass spectral ratio analysis of the m/z 167 cluster (TPA and DPM). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921.

Preparation of Active Uranium in DME (1). The following describes a typical preparation of active uranium in DME. In the drybox, UCl$_4$ (0.3575 g, 0.9412 mmol), Na (0.0269 g, 1.170 mmol), K (0.1177 g, 3.010 mmol), and naphthalene (0.0900 g, 0.7022 mmol) were placed in a two-neck 50-mL flask equipped with a Teflon-clad stir bar, condensor, vacuum adapter, and septum. The apparatus was removed from the drybox and connected to the argon line. Sodium–potassium alloy (NaK) was formed by heating the alkali metals with a heat gun until the K melted. The reaction flask was immersed in a cooling bath that was maintained at –60 °C. Freshly distilled DME (5.5 mL) was added and stirring started. After 2–4 days of stirring at –65 °C (when no more alloy could be seen), cooling was stopped and the active uranium was ready for use after being allowed to slowly warm to room temperature.

Reaction of 1 with 1,3-Butadiene. 1,3-Butadiene (8.2 mL, 94 mmol) was condensed into a Schlenk flask attached to an argon line and maintained with dry ice/2-propanol. The butadiene was transferred via cannula into a slurry of 1 (0.94 mmol of U) over 30–45 min by removing the dry ice/2-propanol cooling bath. The reaction flask was cooled, by using a NaCl/ice bath, and the butadiene (bp –4 °C) was kept refluxing by circulating –30 °C acetone through the condensor until the butadiene was consumed. The reaction was monitored by periodically removing head space samples with a gas-tight syringe and analyzing by GC. The slurry became very thick, with stirring barely possible after 1 h. The reaction was allowed to proceed 18 h. The uranium was removed by washing with 3 N HCl and the polymer analyzed by IR.

Preparation of [(TMEDA)Li]$_2$[Nap] (2). The following describes a typical preparation of 2. In the drybox, lithium (5.3144 g, 0.765 87 mol), cut into many small pieces, and naphthalene (49.0802 g, 0.382 914 mol) were loaded into a 500-mL three-neck flask equipped with a septum, vacuum adapter, and fritted filtration tube. This flask was removed from the drybox, immersed in the ultrasonic cleaner, and attached to the manifold. Freshly distilled TMEDA (115 mL, 0.762 mol) and freshly distilled toluene (200 mL) were added to a flask by syringe. The reaction proceeded for 4 days with sonication until all of the lithium had reacted. Upon cessation of sonication, 2 crystallized. The flask was cooled to –50 °C, and freshly distilled pentane (100 mL) was added. The solution was filtered through the sintered glass frit, and the crystals of 2 obtained were washed with cold pentane (2 × 275 mL). The majority of the pentane was removed under a flow of argon, and the crystals of 2 were transferred to another fritted tube in the drybox. This tube was attached to the vacuum line and argon passed through the crystals, from bottom to top, overnight. Yields of 2 crystals obtained were typically around 50% (50 g). A considerable amount of 2 remained in the supernatant solution, and no attempt was made to isolate more crystals from this. The crystals of 2 were stored in the argon-filled drybox and were found to be stable indefinitely. Visible absorption at 444 nm of a <0.7 mM solution (ϵ > 4000) confirms the presence of a naphthalene dianion.[80]

Preparation of Active Uranium in Hydrocarbon Solvents (3). The following describes a typical preparation of active

uranium in hydrocarbon solvents. In the drybox, UCl$_4$ (0.5020 g, 1.322 mmol) and 2 (1.0143 g, 2.7086 mmol) were placed in a two-neck 50-mL flask equipped with a Teflon-clad stir bar, vacuum adapter, and septum. On the vacuum line, freshly distilled solvent (20 mL) was added and stirring started. After 1 h of stirring at room temperature, the active uranium was ready for use.

Reaction of 3 with Ketones. To a slurry of 3 (0.5056 g (1.331 mmol) of UCl$_4$; 1.0220 g (2.7290 mmol) of 2; 20 mL of xylenes) was added, via cannula, a solution of benzophenone (0.485 60 g, 2.6649 mmol) and GC internal standard n-pentadecane (0.37 mL, 1.3 mmol) in 2 mL of freshly distilled xylenes. To the flask that contained the ketone and pentadecane was added an additional 2 mL of xylenes, and this solution was added to 3. The reaction was stirred at room temperature for 1 h, followed by refluxing overnight. The reaction was quenched with 3 N HCl and filtered, and the products were extracted with CHCl$_3$. The coupled products could be obtained by addition of hexanes to a CHCl$_3$ solution. Separation was accomplished on silica gel by using hexanes/CHCl$_3$ elution.

Reaction of 3 with Pinacols. A solution of benzopinacol (0.486 37 g, 1.3270 mmol) and GC internal standard n-pentadecane (0.37 mL, 1.3 mmol) in 10 mL of freshly distilled xylenes was warmed to dissolve (~90 °C). This solution was added to a slurry of 3 (0.5068 g (1.334 mmol) of UCl$_4$; 1.0246 g (2.7361 mmol) of 2; 20 mL of xylenes) at room temperature via cannula. The reaction was stirred at room temperature for 1 h, followed by refluxing overnight. The reaction was worked up in the same manner as the ketone reactions.

Preparation of (p-CH$_3$C$_6$H$_4$)$_2$COHCOH(p-CH$_3$C$_6$H$_4$)$_2$.[95] MgI$_2$ (1.6016 g, 5.7586 mmol), Mg powder (0.3811 g, 15.68 mmol, 70–80 mesh), and 4,4′-dimethylbenzophenone (1.9535 g, 9.2900 mmol) were loaded into a 50-mL two-neck flask which was equipped with a Teflon clad stir bar, septum, and condensor with vacuum adapter, in the drybox. Freshly distilled toluene (10 mL) and ether (5 mL) were added on the vacuum line, and stirring was started. The solution became thick and greenish with a large amount of a white precipitate. Heating was started immediately causing the white precipitate to dissolve and the solution to look somewhat purpleish. After the solution was refluxed overnight, H$_2$O (2 mL) was added. The Mg powder was dissolved in 3 N HCl and extracted with ether and toluene. The pinacol (p-CH$_3$C$_6$H$_4$)$_2$COHCOH(p-CH$_3$C$_6$H$_4$)$_2$ (1.73478 g, 4.10528 mmol, 88% yield based on 4,4′-dimethylbenzophenone) crystallized as a white solid upon addition of hexanes to the concentrated ether/toluene extract: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.27 (s, CH$_3$, 12 H), 2.95 (s, OH, 2 H), 7.05 (dd, J = 33.4, 8.4 Hz, CH, 16 H); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 20.9, 83.0, 128.0, 128.6, 136.3, 141.7; MS, m/z (relative intensity) 119.0495 (100.00, C$_8$H$_7$O), 211.1087 (6.77, ^{12}C$_{14}$^{13}CH$_{14}$O), 210.1043 (28.82, C$_{15}$H$_{14}$O), 195.0810 (10.43, C$_{14}$H$_{11}$O).

(p-CH$_3$C$_6$H$_4$)$_2$C=C(p-CH$_3$C$_6$H$_4$)$_2$: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 2.24 (s, CH$_3$, 12 H), 6.89 (s, CH, 16 H); ^{13}C NMR (CDCl$_3$, 50.309 MHz), δ 21.2, 128.3, 131.2, 153.6, 139.8, 141.3; MS, m/z (relative intensity) 389.2216 (10.57, ^{12}C$_{29}$^{13}CH$_{28}$), 388.2174 (32.29, C$_{30}$H$_{28}$).

(p-CH$_3$C$_6$H$_4$)$_2$CHOH: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.118 (dd, J = 8.3, 22.5 Hz, CH, 8 H), 5.621 (s, CH, 1 H), 2.271 (s, CH$_3$, 6 H); ^{13}C NMR (CDCl$_3$, 75 MHz) 21.0, 75.6, 126.2; MS, m/z (relative intensity) 213.1236 (0.91, ^{12}C$_{14}$^{13}CH$_{16}$), 212.1194 (5.98, C$_{15}$H$_{16}$O), 119.0490 (29.68, C$_8$H$_7$O).

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