# Actinide-Mediated Catalysis

Probing the Reactivity of the Actinides Using Catalysis

Goals:

Determine Fundamental Chemistry of Transuranic (TRU) Elements

- Simple, well-defined systems
- Compare reactivity to well studied analogs

Benjamin P. Warner

Actinides, Catalysis, and Separations Science Group

# Actinide-Mediated Catalysis

Outline:

Why should we care about reactions of transuranic elements?

What is involved in performing transuranic chemistry?

Studies of metal-ligand coordination reactions

Reactivity studies

Combinatorial approach

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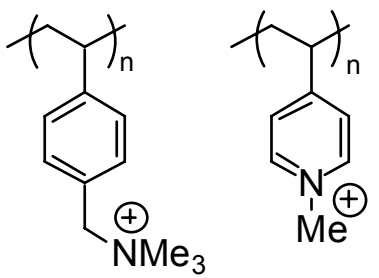
# Actinide-Mediated Catalysis

Plutonium and other actinides contact organic materials.

Processing: *Phosphates, Amides, Ketones, Ammonium Salts*

Waste Forms: *Carbohydrates, Halocarbons, Hydrocarbons, Siloxanes*

Health Effects: *Phosphates, Amides* (DM Taylor, *J. Alloys and Comp*. **271-273**, *1998*, 6-10.)

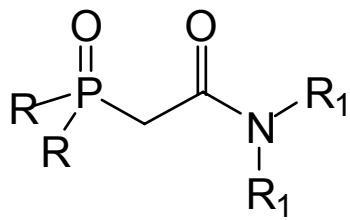


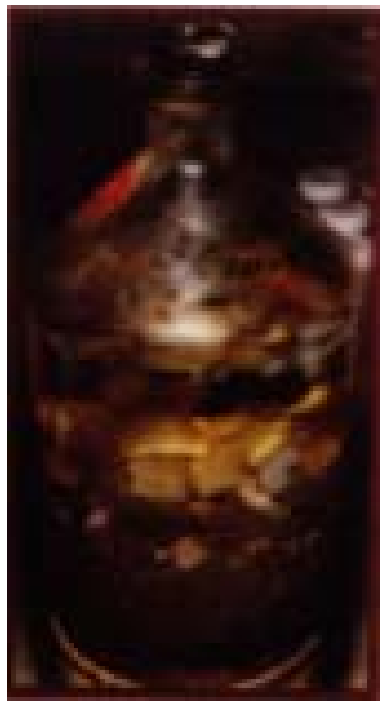




ion exchange

chelation



combustibles

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# Actinide-Mediated Catalysis

Radiolysis generates small molecule reagents, i.e. $H_2$ and $H_2O_2$

Plutonium radiolysis of water can generate 1 mol % $H_2O_2$ per day

Radiation damage is significant

Chemical activity has been shown to be significant:

Claycamp and Luo, *Radiation Research*, **137**, *1994*, 114-117.

- Pu(III) is 4.8x more active than Fe(III) in catalyzing ascorbate oxidation by $H_2O_2$
- Pu(III) is comparable to Fe(III) in inducing DNA oxidative stress

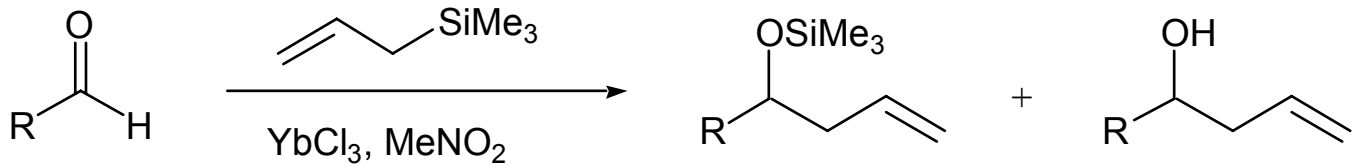
(measured by 8-oxoguanine formation and thymine glycol formation)

Questions:

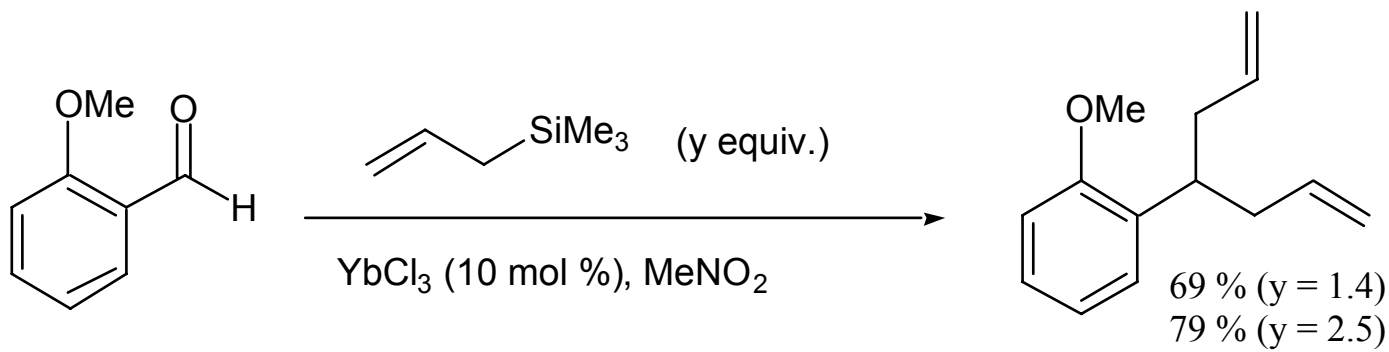
- *What is the reactivity of Pu ?*
- *How can it be understood in relation to other elements ?*
- *What are the chemical effects v. the radiological effects ?*

# Actinide-Mediated Catalysis

Simple f-element compounds are known to be catalysts



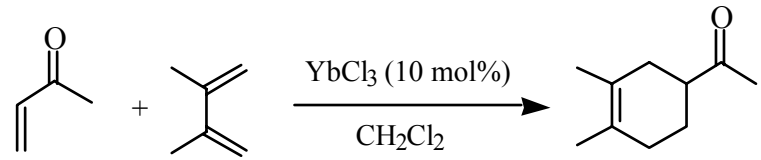

| R | | Yield (%) | |
|---|---|---|---|
| Ph | 62 | | 10 |
| 4-$NO_2C_6H_4$ | 90 | | 0 |
| *c*-$C_6H_{11}$ | 68 | | 13 |
| COOEt | 36 | | 41 |

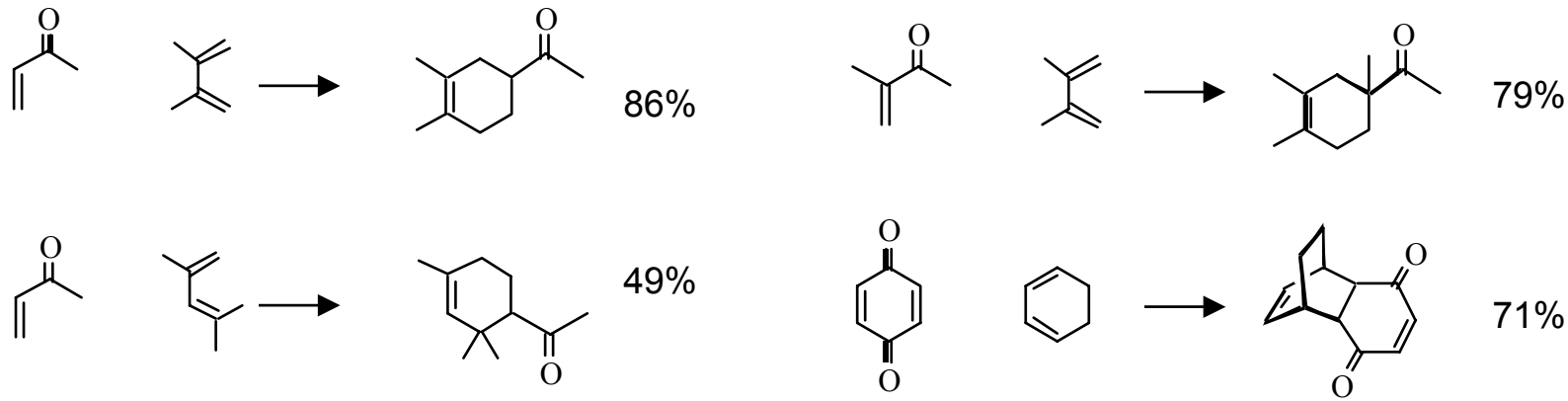


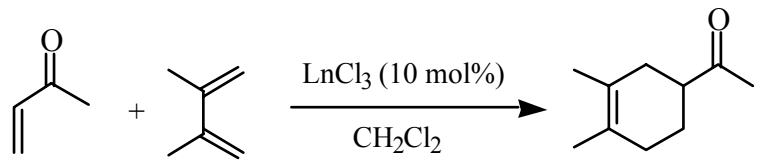

X.G. Fang, J.G. Watkin, B.P. Warner, *Tetrahedron Lett.* **41**, *2000*, 447-449.

# Actinide-Mediated Catalysis

## Simple f-element compounds are known to be catalysts




| $LnCl_3$ | $PrCl_3$ | $GdCl_3$ | $DyCl_3$ | $ErCl_3$ | $LuCl_3$ |
|---|---|---|---|---|---|
| Yield (%) | 1 | 2 | 42 | 54 | 62 |

X.G. Fang, J.G. Watkin, B.P. Warner, *Synthetic Communication*. **30**, *2000*, 2669-2676.

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# Actinide-Mediated Catalysis

Simple f-element compounds are known to be catalysts

Oxidation:


GJ Hutchings, CS Heneghan, ID Hudson, SH Taylor, *Nature*, **384**, *1996*, 341-342.

Hydrolysis:


Catalyst = $UO_2(NO_3)_2$, $k_{cat/uncat}$=6700, $pK_a$ $UO_2(NO_3)_2$ = 4.2-6.1

RA Moss, K Bracken, J Zhang, *Chem. Comm.*, *1997*, 563-564.

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# Actinide-Mediated Catalysis

## Handling Plutonium: *A Non-Trivial Exercise*

- Inert Atmosphere (He) Negative Pressure Glovebox
- Liquid Nitrogen and Solvent Traps for Distillation Inside Box
- Sample Removal Port for NMR Tubes
- Spectroscopy Well for IR, UV-Vis
- U□V-Vis Fiber Optic
- Electrochemical Feeds
- Chilling Block

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# Actinide-Mediated Catalysis

Ann Schake, Lonny Morgan, and an RCT remove organo-plutonium NMR samples.

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# Actinide-Mediated Catalysis

## Preparation of Starting Materials

$$An^0 + 3/2\ I_2 \xrightarrow{THF} AnI_3(THF)_4 \quad (An=U, Np, Pu)$$

$$An^0 + 2\ Br_2 \xrightarrow{MeCN} AnBr_4(MeCN)_4 \quad (An=Th, U, Pu)$$

$$AnI_3(THF)_4 + 3\ KN(SiMe_3)_2 \xrightarrow{THF} An(N(SiMe_3)_2)_3$$

$$An[N(SiMe_3)_2] + 3.1\ ArOH \xrightarrow{hexane} An(OAr)_3 \quad (Ar=2,6\text{-}{}^tBu_2Ph)$$

Other Starting Materials: $Cs_2PuCl_6$, $ThCl_4$, $UCl_4$

LR Avens, SG Bott, DL Clark, AP Sattelberger, JG Watkin, BD Zwick *Inorg. Chem.*, **1994**, *33*, 2248.
BD Zwick, AP Sattelberger, LR Avens, *Transuranium Organometallic Elements: The Next Generation*; American Chemical Society: Washington D. C., 1992, pp. 239-246.

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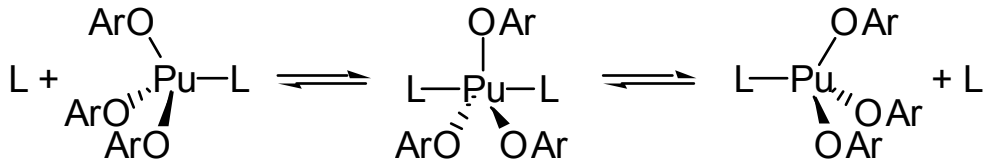
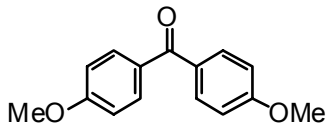
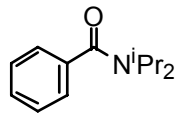
# Actinide-Mediated Catalysis

## Self-Exchange Reactions: Associative Process




$Ph_3PO$




| | | | |
|---|---|---|---|
| $\Delta H^{\neq}$ | 5.8 kCal/mol | 3.8 kCal/mol | 14.7 kCal/mol |
| $\Delta S^{\neq}$ | -22.5 eu | -26.4 eu | -2.3 eu |
| $\Delta G^{\neq}$ | 11.9 kCal/mol | 11.8 kCal/mol | 15.5 kCal/mol |

## Binding Affinities: Mirrors Process Data

$$(ArO)_3Pu + L \underset{}{\overset{K_a}{\rightleftharpoons}} (ArO)_3Pu—L$$

| | | | |
|---|---|---|---|
| $K_a$ | 9 | 214 | 190 |

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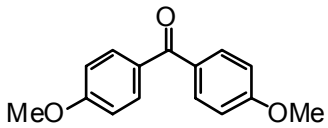
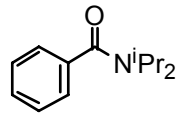
# Actinide-Mediated Catalysis

## IR Frequencies for bound and free ligands

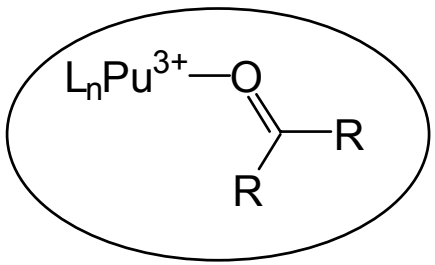


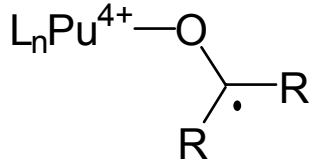

$Ph_3PO$

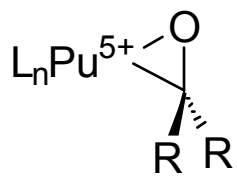



| | | | |
|---|---|---|---|
| ν-free | 1642 $cm^{-1}$ | 1192 $cm^{-1}$ | 1627 $cm^{-1}$ |
| ν-bound | 1580 $cm^{-1}$ | 1149 $cm^{-1}$ | 1564 $cm^{-1}$ |
| Δν-free | 62 $cm^{-1}$ | 43 $cm^{-1}$ | 63 $cm^{-1}$ |

## Red shift in the C=O or P=O frequency

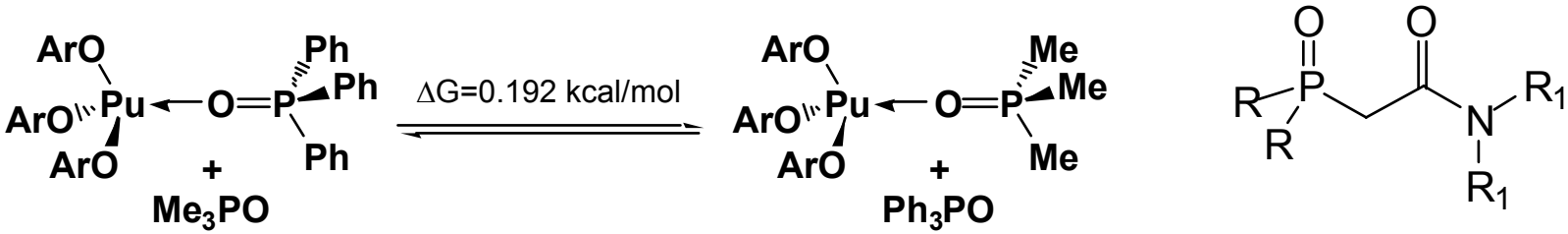


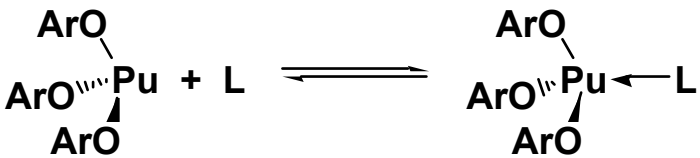



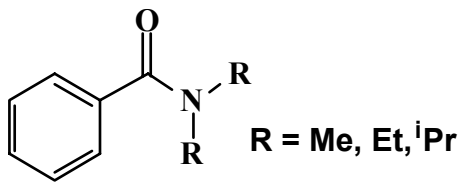
# Actinide-Mediated Catalysis

## Elucidating the “Anomalous Aryl Strengthening Effect”

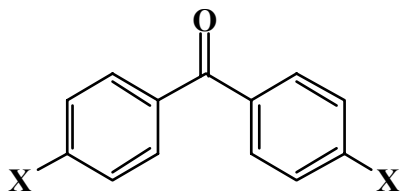



## Determining Steric and Electronic Effects on Ligation




R = Me, Et, $^{i}$Pr




X = Me, OMe, H, Cl

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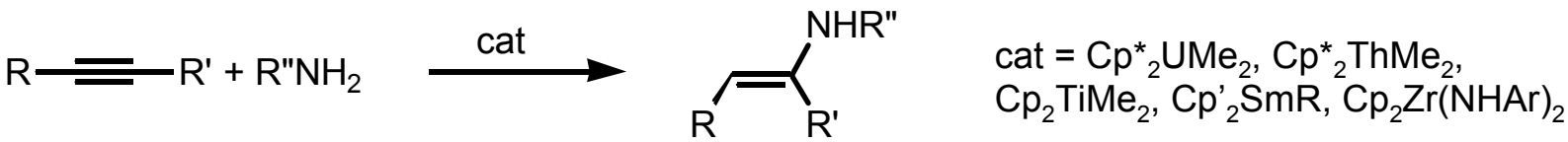
# Actinide-Mediated Catalysis

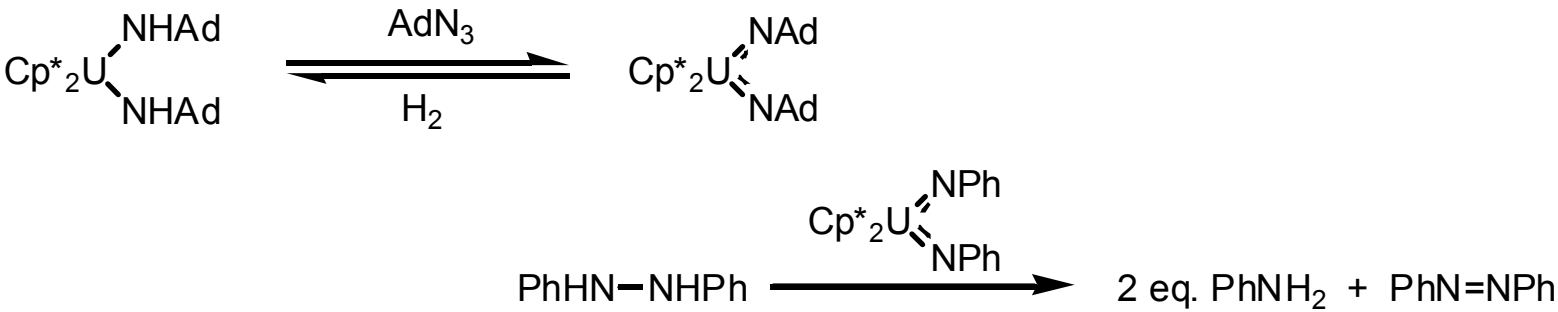
## Initial Examination of TRU Catalysis

What analogies can be drawn between actinides, transition metals, lanthanides

$Cp^*_2U$ (IV) acts like group IV and/or lanthanides - Eisen, Marks, Doye, Bergman




Uranium (VI) allows unique reactivity - Burns

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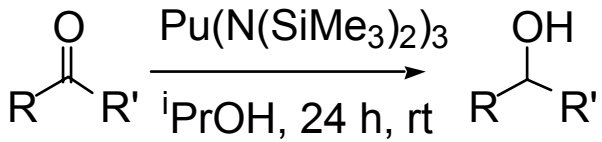
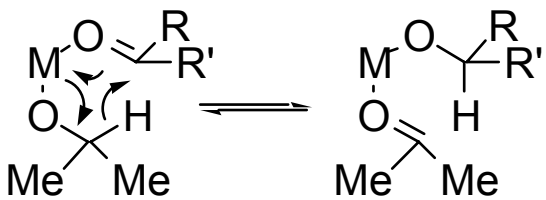
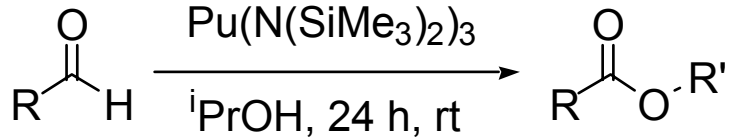
# Actinide-Mediated Catalysis

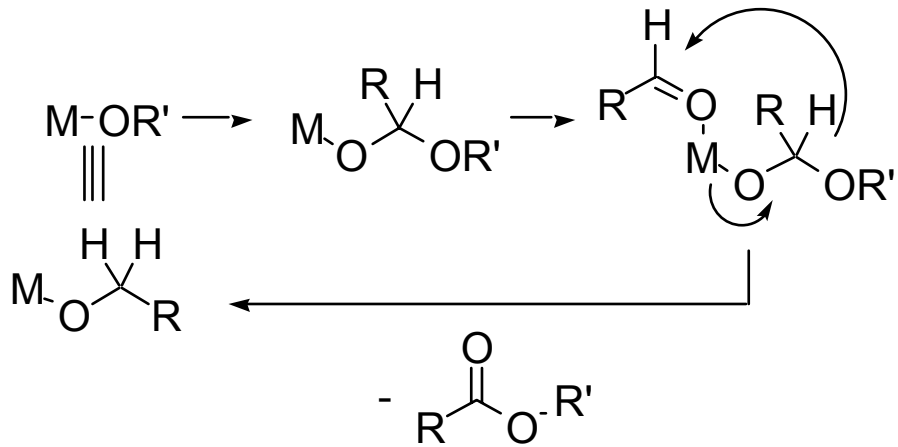
## An-Catalyzed Meerwein-Ponndorf-Verley Reduction

Pu(III) catalzes MPV and Tischenko Reactions - similar to Lanthanides

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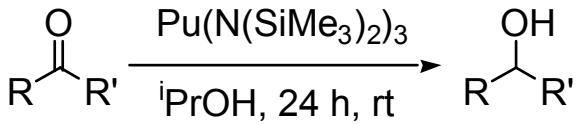
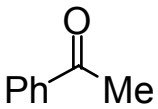
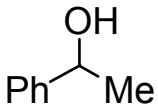
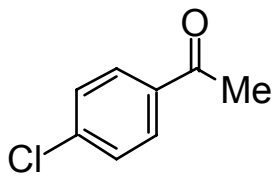
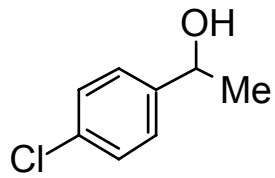
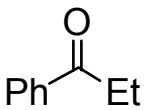
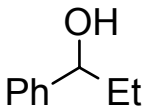
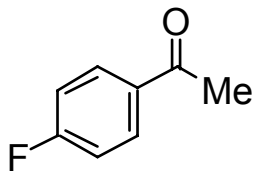
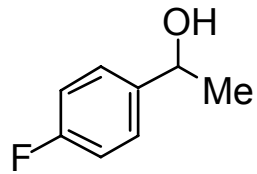
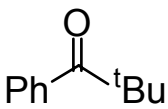
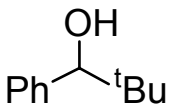
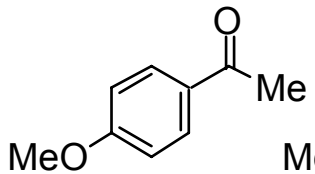
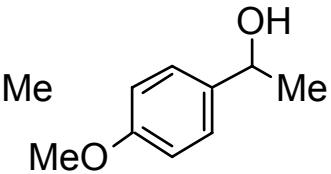
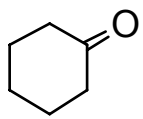
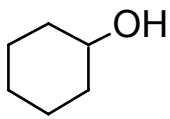
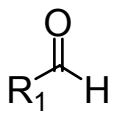
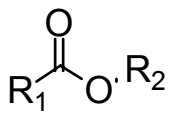
# Actinide-Mediated Catalysis

## Pu(III)-Catalyzed Meerwein-Ponndorf-Verley Reduction




| Substrate | Product | Conversion | Substrate | Product | Conversion |
|---|---|---|---|---|---|
|  |  | 91% |  |  | 92% |
|  |  | 93% |  |  | 88% |
|  |  | 88% |  |  | 57% |
|  |  | 100% | | | |
|  |  | $R_1$=4-MeOPh, $R_2$=$^i$Pr, 4-MeOPh<br>$R_1$=Cy, $R_2$=$^i$Pr, Cy | | | |

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# Actinide-Mediated Catalysis

## An-Catalyzed Meerwein-Ponndorf-Verley Reduction

- Th(IV), U(IV) do not catalyze MPV - similar to Zr
- U(III) does not catalyze MPV - U(III) is oxidized by *iso*-propanol and ketones

$$U[N(SiMe_3)_2]_3 + \text{xs } {}^{i}PrOH \longrightarrow \text{“}U(O^{i}Pr)_4\text{“}$$

(although $UI_2(iPrOH)_4^+ I^-$)

- Np(III) does not catalyze MPV - Np(III) is oxidized by ketones, but not by *iso*-propanol

| | | | |
|---|---|---|---|
| U(III)/U(IV) | -.631 V | | |
| Np(III)/Np(IV) | +.155 V | Np(III)/Np(V) | +.447 |
| Pu(III)/Pu(IV) | +.982 V | | |

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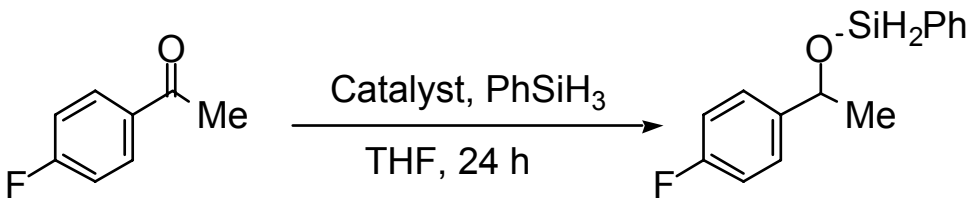
# Actinide-Mediated Catalysis

## Actinides Catalyze Ketone Hydrosilation...

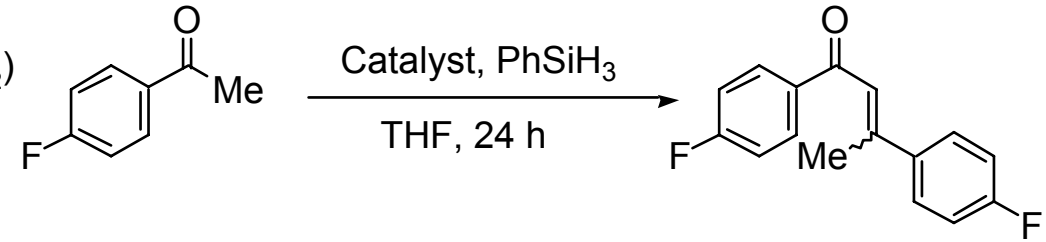



Catalyst = $Pu(N(SiMe_3)_2)_3$ + 3 iPrOH,

$\overline{An(N(SiMe_3)_2)_2(N(SiMe_2CH_2)}$ + >4 iPrOH,

## ...but the Catalyst is Difficult to Generate...

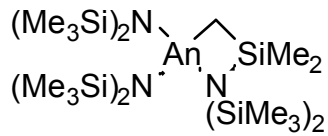
Catalyst = $\overline{An(N(SiMe_3)_2)_2(N(SiMe_2CH_2)}$ + <4 iPrOH,




## …and Uranium is Still Oxidized.

$U(N(SiMe_3)_2)_3$ + 3 iPrOH + ketone appears identical to $\overline{U(N(SiMe_3)_2)_2(N(SiMe_2CH_2)}$ + 4 iPrOH + ketone

$\overline{An(N(SiMe_3)_2)_2(N(SiMe_2CH_2)}$ =

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# Actinide-Mediated Catalysis

## Conclusions:

Pu mediates catalytic reactions

Pu(III) similar to Ln(III), An(IV) similar to Group IV

Carbonyl ligands bind to Pu(III) through simple Lewis acid-base coordination, but ketones and alcohols oxidize U(III) to U(IV), and ketones oxidize Np(III)

Associative ligand self-exchange process despite large ancillary ligands

Binding affinities of three ligands mirror those of comparable ligands in acidic-aqueous Pu(III) process chemistry

Autoradiography used to examine combinatorial Pu reaction

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# Actinide-Mediated Catalysis

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