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# Selective Actinide-Catalyzed Tandem Proton-Transfer Esterification of Aldehydes with Alcohols for the Production of Asymmetric Esters

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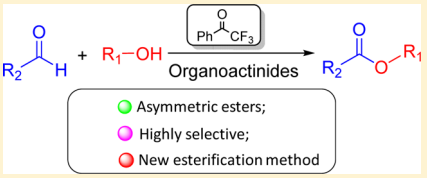
Supporting Information

**ABSTRACT:** Actinide-catalyzed tandem proton-transfer esterification between aldehydes and alcohols is presented herein for the first time. It represents a novel convenient and external-oxidant-free methodology in the preparation of asymmetric ester compounds. Various kinds of aldehydes and alcohols can be applied to this reaction, affording the corresponding ester product in moderate to high yields. A plausible mechanism was proposed on the basis of the kinetic, stoichiometric, and deuterium-labeling studies.




Exploring new esterification strategies is a very challenging endeavor in modern synthetic chemistry. In addition to being routinely obtained from nucleophilic substitution reactions between carboxylic acids and alcohols, esters can also be prepared by other methodologies, such as oxidative esterification,[1−7] the Tishchenko reaction,[8−12] dehydrogenative coupling,[13−15] etc., in which aldehydes are employed as an alternative to carboxylic acids. However, challenges remain in these processes. For example, the Tishchenko reaction is not adequate for the synthesis of unsymmetrical esters[16,17] and in the oxidative esterification, an external oxidant is indispensable, which will potentially oxidize alcohols to aldehydes and afterward result in selectivity-controlling issues and byproduct formation. Therefore, developing a more convenient external-oxidant-free esterification methodology, which is also capable of giving rise to unsymmetrical esters, is highly demanding.

The past few decades have witnessed tremendous advances in the design and application of organoactinide catalysts.[18−27] In the forefront of research is the catalytic transformation of oxygenated substrates, due to the high oxophilicity of the actinides, forming thermodynamically stable actinide−oxo species in the presence of oxygen-containing compounds.[26,28,29] To date, a very limited number of processes involve oxygen-containing substrates, such as hydroalkoxylation,[30,31] the Tishchenko reaction,[32−34] small-molecule activation,[35] cyclic ester polymerization,[36−38] and the catalytic formation of hydrogen from water.[39] We have recently disclosed that imidazolin-2-iminato actinide precursors are able to react with an aldehyde, $R_2CHO$, generating the actinide alkoxide moieties An-$OCH_2R_2$, able to serve as an effective active species to afford the corresponding symmetric esters.[40] Inspired by that work, we envisage that, if the actinide precursor is able to undergo first a rapid alcoholysis in the presence of alcohols $R_1OH$,[30,31] the resulting analogous actinide alkoxide species, An-$OR_1$, could also react with an aldehyde to furnish the asymmetric ester compound $R_2COOR_1$ selectively. Moreover, it is of note that the actinide alkoxide species, generated from the esterification cycle, is different from that produced from the alcoholysis step; therefore, an additional proton-transfer step is required in order to complete the cycle (vide infra). On the basis of these consideration, a series of direct esterification studies between aldehydes and alcohols is disclosed herein by using the metallacyclic actinide amido complexes $[(Me_3Si)_2N]_2$An-$[\kappa^2(N,C)$-$CH_2Si(CH_3)_2N(SiMe_3)]$ (An = Th (**1**), U (**2**)) and $U[N(SiMe_3)_2]_3$ (**3**) as precatalysts.

To our pleasure, the asymmetric esterification process can be smoothly catalyzed by actinide complexes **1**−**3** to generate the corresponding esters, despite the high bond energies of actinide−oxygen bonds,[41] and representative results are summarized in Table 1. Initial optimization investigations using benzaldehyde and methanol substrates revealed that the thorium(IV) amido complex **1** performed with the best activities among the three precatalysts. Catalytic reactions using the U(IV) (**2**) and U(III) (**3**) complexes gave lower yields of the corresponding ester. Increasing the amount of PhCHO enhanced the yield of the methyl benzoate **6aa** significantly; up to 73% conversion was obtained with a 3:1 molar ratio (the initial TOF value is up to 1.25 $h^{-1}$), implying that a high concentration of aldehydes is a crucial factor in achieving the desired transformation. However, increasing the MeOH amount to 3 equiv displayed a negative effect on the ester yield, with only 6% MeOH consumption based on alcohol (42% yield based on aldehyde). Performing the reaction in toluene-*d* or benzene-*d* afforded comparable conversions, whereas in THF-*d*, some inhibition is observed.

Once the optimized conditions were established, our attention turned to an investigation of the scope capabilities and limitations. A wide variety of combinations of substrates was investigated, and the results are shown in Table 1. We observe that activated benzaldehydes with electron-withdrawing groups, such as 4-Cl, 4-$NO_2$, 3-$NO_2$, 4-CN, and 4-$CF_3$, displayed activities higher than that of benzaldehyde even at shorter times, which is the result of the relatively easier hydride transfer from the 2° carbon of the hemiacetalate to the carbonyl of the

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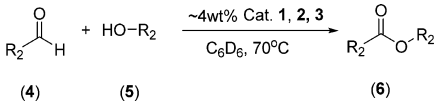
**Table 1. Catalysis of the Asymmetric Esterification of Aldehydes with Alcohols by Complexes 1−3**[a]




(4) (5) (6)

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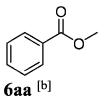
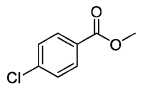
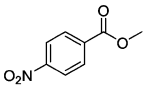
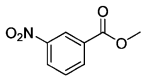
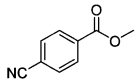
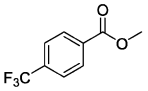
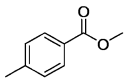
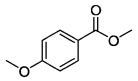
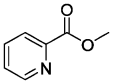
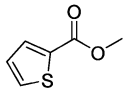
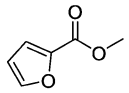
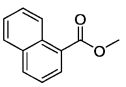
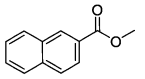
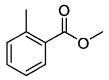
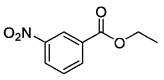
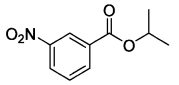
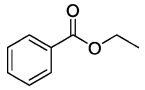
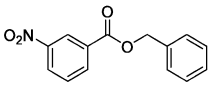
|  **6aa** [b] | 33% (Cat. **1**, [**4**]/[**5**] = 1:1)<br>58% (Cat. **1**, [**4**]/[**5**] = 2:1)<br>73% (Cat. **1**, [**4**]/[**5**] = 3:1)<br>34% (Cat. **1**, [**4**]/[**5**] = 1:2)[c]<br>42% (Cat. **1**, [**4**]/[**5**] = 1:3)[c]<br>77% (Cat. **1**, [**4**]/[**5**] = 3:1, in Toluene-*d*)<br>54% (Cat. **1**, [**4**]/[**5**] = 3:1, in THF-*d*) | 6% (Cat. **2**, [**4**]/[**5**] = 3:1)<br>3% (Cat. **2**, [**4**]/[**5**] = 1:1)<br>0% (Cat. **2**, [**4**]/[**5**] = 1:3)<br>7% (Cat. **3**, [**4**]/[**5**] = 3:1)<br>2% (Cat. **3**, [**4**]/[**5**] = 1:1)<br>1% (Cat. **3**, [**4**]/[**5**] = 1:3) |
|  **6ba**, 80% |  **6ca**, 76% [d] |  **6da**, 90% [d] |
|  **6ea**, 89% [d] |  **6fa**, 83% [d] |  **6ga**, 55% |
|  **6ha**, 6%<br>7%[e] |  **6ia**, 75% |  **6ja**, 30% |
|  **6ka**, 44% |  **6la**, 43% |  **6ma**, 79% |
|  **6na**, 13% |  **6db**, 40% |  **6dc**, 37% |
|  **6ab**, 33% |  **6dd**, 48% | |

[a]Conditions unless specified otherwise: 5.0 mg of precatalyst **1**, [**1**]/[CHO]/[OH] = 1/150/50, 700 μL of $C_6D_6$, 70 °C, 24 h. The yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture on the basis of the alcohols. [b]Different precatalysts were used. [c]The yield was determined on the basis of the aldehyde. [d]Reaction time 6 h. [e]Reaction at 110 °C in toluene-*d*.

incoming substrate in a six-membered transition fashion (vide infra). In contrast, incorporation of electron-donating groups reduced the ester yields dramatically, displaying values of 55% and 6% for 4-methyl- and 4-methoxylbenzaldehyde, respectively. Elevating the temperature to 110 °C showed negligible improvement in the ester productivities for 4-methoxylbenzaldehyde, indicative of an inherent sluggish reactivity caused by strongly electron donating substituents. For aldehyde substrates bearing heteroaromatic rings, the corresponding yields were found to be highly dependent on the nature of heteroatoms, with the best performance observed in picolinaldehyde, affording a yield (75%) comparable to that with benzaldehyde. For the other two substrates, furfural and 2-thenaldehyde, much lower conversions were obtained. These results presumably are due to the relatively stronger bidentate binding of sulfur- and oxygen-containing substrates to the thorium center. Steric hindrance of the aldehyde also plays an important role in determining the reactivities. Reacting 1-naphthaldehyde with MeOH afforded less conversion in comparison with benzaldehyde, and a further increase in the steric encumbrance by using 9-anthrylaldehyde resulted in a completely inhibited reactivity, with no ester production after 24 h. In striking contrast, the reaction of 2-naphthaldehyde with MeOH gave rise to ester yields comparable to that with benzaldehyde, indicating that substituents on the ortho position of benzaldehyde suppressed the reactivity significantly. A similar result was obtained when 2-methylbenzyldehyde was reacted with MeOH, giving rise to ester **6na** in 13% yield, which is much lower than the value obtained for its isomer **6ga**. Aliphatic aldehydes, including phenylacetaldehyde, cyclohexanecarboxaldehyde, and isobutyraldehyde, were also used to couple with MeOH; however, only the symmetric esters were obtained. In addition to methanol, ethanol, benzyl alcohol, and isopropyl alcohol were also applied in this reaction, but unfortunately, all of them lead to relatively lower ester yields in comparison with MeOH, even when using activated 3-nitrobenzaldehyde was used. The reaction of the tertiary alcohol $^t$BuOH with aldehydes gave no products, implying that the steric encumbrance of the alcohol, with similar aldehydes, also has a great influence on the efficiency of the catalytic system.

During this esterification process, two kinds of byproducts, i.e., substituted benzyl alcohols and symmetrically coupled esters, were detected, which were generated from the proton-transfer step and the Tishchenko cycle, respectively. Monitoring the progress of the reaction of PhCHO/MeOH system using $^1$H NMR spectroscopy showed that the benzyl alcohol was formed concurrently with **6aa** from the beginning of the reaction with a roughly 1:1 ratio. This result corroborates the proton-transfer step; while benzyl benzoate was not observed until a majority of MeOH was consumed, then the Tishchenko cycle turned into the predominant catalytic cycle. These observations rule out the possibility of a transesterification reaction between actinide methoxides and symmetrical benzyl benzoate to form the unsymmetrical ester product **6aa**. It is noteworthy that increasing the concentration of the alcohols will induce lower ester yields; however, it will also suppress the Tishchenko reaction completely and will generate compound **6aa** as the only product, manifesting a selective method in preparing unsymmetrical esters. Another strategy of suppressing the Tishchenko cycle was inspired by the rate discrepancy between secondary alcohols and methanol. We assume that if one special kind of ketone could participate and act as a good hydride acceptor during the six-membered-ring transition state, the produced secondary alcohols will have sluggish activities in comparison to methanol, and hence a majority of the reduced secondary alcohol will be left unreacted in the reaction medium. As a study case, the ketone α,α,α-trifluoromethylacetophenone (TFMAP) was chosen as a hydride acceptor, since the presence of the phenyl ring will increase the steric hindrance of the resulted secondary alcohol, inducing reduced reactivity, and the presence of the trifluoromethyl group will allow rapid approach of a hydride to its carbonyl moiety at the six-membered transition state (Scheme 1). With this hypothesis, a sacrificial proton transfer esterification between various kinds of aldehydes and methanol, in the presence of TFMAP, was conducted, and the representative results are summarized in Table 2. Table 2 shows that adding 1 equiv of TFMAP to the PhCHO/MeOH mixture efficiently suppresses the Tishchenko reaction, producing only 3% of the homocoupled ester after 24 h. Using 1 equiv more of TFMAP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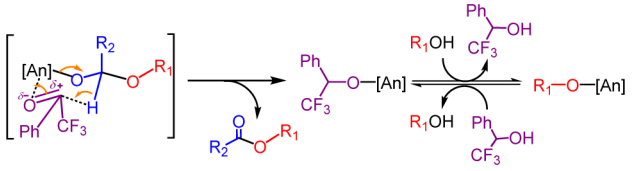
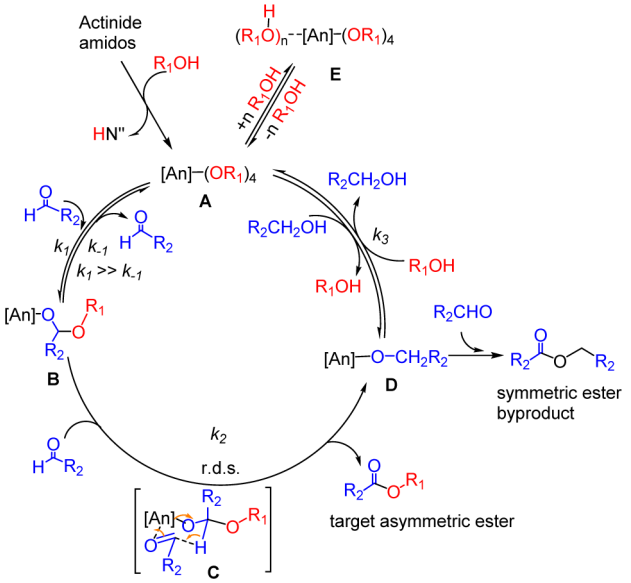
**Scheme 1. Mechanical Procedure of Hydride Transfer Using TFMAP as Acceptor**



**Scheme 2. Proposed Mechanism for Tandem Proton-Transfer Esterification**




resulted in a complete shutoff of the Tishchenko cycle, causing the reaction to proceed selectively through the proton-transfer esterification cycle and furnishing the asymmetrical ester as the sole product. Similar results were observed for 4-methylbenzaldehyde and 2-naphthaldehyde, indicating a large scope capability of the sacrificial ketone. During these studies, no cross-coupling products between aldehyde and TFMAP were detected.

To shed light on the mechanism, an in situ stoichiometric reaction between precatalyst **1** and 10 equiv of MeOH was first investigated, which led to the immediate formation of thorium methoxide species and complete displacement of the amino groups simultaneously, indicated by the disappearance of the original amido groups and the appearance of free amine hexamethyldisilazane $HN(SiMe_3)_2$ signals. To this reaction mixture was added 10 equiv of PhCHO, and the corresponding ester product **6aa** was observed. In contrast, the reaction of the precatalyst **1** with 10 equiv of PhCHO instantly gave rise to the symmetrical ester product benzyl benzoate and the $N(SiMe_3)_2$ $\alpha$-substituted ester,[42] both of which were not observed in the beginning of the catalytic process, demonstrating that methanolysis of **1** is the first rapid step during the catalytic cycle.

Kinetic studies using PhCHO, methanol, and complex **1** revealed first-order dependence on the precatalyst and aldehyde and an inverse first-order kinetics in alcohols, giving rise to the rate equation (1). The inverse first order in alcohols indicates the possibility of excess $R_1OH$ coordinating to the active species **A** (Scheme 2) and subsequent formation of the deactivated species **E**, which implies kinetic inhibition competing with the turnover-limiting step (a detailed analysis of the kinetic equation can be found in the Supporting Information).[43,44]

$$\frac{\partial p}{\partial t} = k'[\mathbf{1}][R_2CHO][R_1OH]^{-1} \quad (1)$$

Thermodynamic activation parameters were experimentally calculated from the Eyring and Arrhenius plots, displaying a moderate activation barrier ($E_a$) of 17.0(0) kcal mol$^{-1}$. The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation are 16.3(6) kcal mol$^{-1}$ and −26.2(1) eu, respectively, the latter of which being evocative of an organized transition state. Deuterium labeling experiments were performed using a benzaldehyde-*d* (PhCDO)/MeOH/**1** system, revealing a primary kinetic isotope effect ($k_{PhCHO}/k_{PhCDO} = 4.61$), which indicates that the hydride transfer from the hemiacetal intermediate to a coordinated aldehyde, during the six-membered transition state, is the rate-determining step. This rationalization is consistent with previous experimental results that using different aldehydes had a great influence on the reactivities. In contrast, a KIE ($k_{MeOH}/k_{MeOD}$) value of 1.04 was obtained when using methanol-*d* for the (MeOD)/PhCHO/**1** catalytic system, suggesting rapid alcoholysis and proton transfer steps during the catalytic cycle. The isolation of benzyl alcohol-$d_2$ and benzyl benzoate-$d_2$ during these studies again corroborated the proton transfer step.

On the basis of the above analysis, a plausible mechanism for the proton transfer esterification is presented in Scheme 2. In the first step, fast acid−base protonolysis of the actinide amido complexes, by the alcohol, gave rise to the actinide alkoxide species **A**,[44] which then inserted into the carbonyl group of an aldehyde, affording the actinide species **B**. In the presence of an additional 1 equiv of an aldehyde, hydride transfer from intermediate **B** to the carbonyl group of the incoming aldehyde, via a six-membered transition state, is operative, furnishing the unsymmetrical ester and concomitantly generating the actinide alkoxide species **D**. In the presence of excess alcohol, proton transfer takes place between **D** and the alcohol, regenerating the initial active species **A** and simultaneously releasing 1 equiv of the substituted benzyl alcohol. Upon consumption of the alcohol, at

**Table 2. Proton Transfer Esterification in the Presence of the Sacrificial Ketone TFMAP**[a]

| entry | $[R_1CHO]$ | $[R_2OH]$ | $PhCOCF_3$/MeOH | yield of $R_1COOR_2$ (%)[b] | yield of $R_1COOCH_2R_1$ (%)[c] |
|---|---|---|---|---|---|
| 1 | PhCHO | MeOH | 1/1 | 71 | 3 |
| 2 | | | 2/1 | 68 | |
| 3 | 4-MePhCHO | MeOH | 1/1 | 47 | |
| 4 | | | 2/1 | 28 | |
| 5 | 2-naphthaldehyde | MeOH | 1/1 | 65 | 2 |
| 6 | | | 2/1 | 43 | |
| 7 | PhCHO | EtOH | 1/1 | 20 | 3 |

[a]Conditions: 5 mg of catalyst, [**1**]/[CHO]/[OH] = 1/150/50, 700 $\mu$L of $C_6D_6$, 70 °C, 24 h. [b]Yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture based on MeOH. [c]Yield was based on aldehyde.



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a later stage of the reaction, the proton transfer step slows down, and the actinide alkoxide species **D** will start the Tishchenko reaction cycle, affording the homocoupled ester. In the presence of the sacrificial ketone TFMAP, because of its preferable affinity, TFMAP will outcompete with aldehydes during the coordination step to the actinide species **B**, and subsequent hydride transfer will give rise to $\alpha$-(trifluoromethyl)benzyl alcoholate actinide compounds, which then undergo proton transfer with alcohols to furnish back the active species **A** (Scheme 1).

In summary, we have demonstrated the ability of organoactinides to undergo a tandem proton-transfer esterification. This reaction can be applied to various combinations of aldehydes and alcohols. The steric and electronic properties of these two substrates play a crucial role in determining the efficiency of the catalysts. In the presence of the sacrificial ketone $\alpha,\alpha,\alpha$-trifluoromethylacetophenone, homocoupled symmetrical ester byproducts can be prevented, giving rise exclusively to unsymmetrical esters.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00101.

Experimental details, characterization data, kinetic rate laws, thermodynamic studies, and deuterium-labeling investigations (PDF)

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) Ekoue-Kovi, K.; Wolf, C. *Chem. - Eur. J.* **2008**, *14*, 6302−6315.
(2) Tang, S.; Yuan, J.; Liu, C.; Lei, A. *Dalton Trans.* **2014**, *43*, 13460−13470.
(3) Lerebours, R.; Wolf, C. *J. Am. Chem. Soc.* **2006**, *128*, 13052−13053.
(4) Maki, B. E.; Scheidt, K. A. *Org. Lett.* **2008**, *10*, 4331−4334.
(5) Finney, E. E.; Ogawa, K. A.; Boydston, A. J. *J. Am. Chem. Soc.* **2012**, *134*, 12374−12377.
(6) Whittaker, A. M.; Dong, V. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 1312−1315.
(7) Rueping, M.; Sunden, H.; Hubener, L.; Sugiono, E. *Chem. Commun.* **2012**, *48*, 2201−2203.
(8) Törmäkangas, O. P.; Koskine, A. M. P. *Recent Res. Devel. Organic Chem.* **2001**, *5*, 225−255.
(9) Berberich, H.; Roesky, P. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1569−1571.
(10) Seki, T.; Nakajo, T.; Onaka, M. *Chem. Lett.* **2006**, *35*, 824−829.
(11) Ralston, K. J.; Hulme, A. N. *Synthesis* **2012**, *44*, 2310−2324.
(12) Omura, S.; Fukuyama, T.; Murakami, Y.; Okamoto, H.; Ryu, I. *Chem. Commun.* **2009**, 6741−6743.
(13) Cheng, J.; Zhu, M.; Wang, C.; Li, J.; Jiang, X.; Wei, Y.; Tang, W.; Xue, D.; Xiao, J. *Chem. Sci.* **2016**, *7*, 4428−4434.
(14) De Sarkar, S.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2010**, *132*, 1190−1191.
(15) Grigg, R.; Mitchell, T. R. B.; Sutthivaiyakit, S. *Tetrahedron* **1981**, *37*, 4313−4319.
(16) Hoshimoto, Y.; Ohashi, M.; Ogoshi, S. *J. Am. Chem. Soc.* **2011**, *133*, 4668−4671.
(17) Curran, S. P.; Connon, S. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10866−10870.
(18) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550−567.
(19) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855−899.
(20) Arnold, P. L. *Chem. Commun.* **2011**, *47*, 9005−9010.
(21) Hayton, T. W. *Chem. Commun.* **2013**, *49*, 2956−2973.
(22) Evans, W. J.; Mueller, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 2678−2686.
(23) Cooper, O.; Camp, C.; Pécaut, J.; Kefalidis, C. E.; Maron, L.; Gambarelli, S.; Mazzanti, M. *J. Am. Chem. Soc.* **2014**, *136*, 6716−6723.
(24) Wang, J.; Gurevich, Y.; Botoshansky, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 9350−9351.
(25) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 10860−10861.
(26) Weiss, C. J.; Marks, T. J. *Dalton Trans.* **2010**, *39*, 6576−6588.
(27) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *Organometallics* **2010**, *29*, 6308−6320.
(28) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979−7985.
(29) Arnold, P. L.; Turner, Z. R. *Nat. Rev. Chem.* **2017**, *1*, 0002.
(30) Wobser, S. D.; Marks, T. J. *Organometallics* **2013**, *32*, 2517−2528.
(31) Batrice, R. J.; Kefalidis, C. E.; Maron, L.; Eisen, M. S. *J. Am. Chem. Soc.* **2016**, *138*, 2114−2117.
(32) Andrea, T.; Barnea, E.; Eisen, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2454−2455.
(33) Sharma, M.; Andrea, T.; Brookes, N. J.; Yates, B. F.; Eisen, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 1341−1356.
(34) Karmel, I. S. R.; Fridman, N.; Tamm, M.; Eisen, M. S. *Organometallics* **2015**, *34*, 2933−2942.
(35) Gardner, B. M.; Stewart, J. C.; Davis, A. L.; McMaster, J.; Lewis, W.; Blake, A. J.; Liddle, S. T. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 9265−9270.
(36) Karmel, I. S. R.; Fridman, N.; Eisen, M. S. *Organometallics* **2015**, *34*, 636−643.
(37) Karmel, I. S. R.; Khononov, M.; Tamm, M.; Eisen, M. S. *Catal. Sci. Technol.* **2015**, *5*, 5110−5119.
(38) Hayes, C. E.; Sarazin, Y.; Katz, M. J.; Carpentier, J.-F.; Leznoff, D. B. *Organometallics* **2013**, *32*, 1183−1192.
(39) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341−349.
(40) Karmel, I. S. R.; Fridman, N.; Tamm, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2014**, *136*, 17180−17192.
(41) Haynes, W. M. *CRC Handbook of Chemistry and Physics*, 96th ed.; CRC Press: Boca Raton, FL, 2015−2016; pp 9−69.
(42) In the actinide amido complex mediated Tishchenko reactions, an $N(SiMe_3)_2$ $\alpha$-substituted ester compound was formed in the beginning of the catalytic cycle. Please see ref 40.
(43) Dudnik, A. S.; Weidner, V. L.; Motta, A.; Delferro, M.; Marks, T. J. *Nat. Chem.* **2014**, *6*, 1100−1107.
(44) The structure of species **A** was verified using theoretical approaches. Please see ref 31.




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