Communication

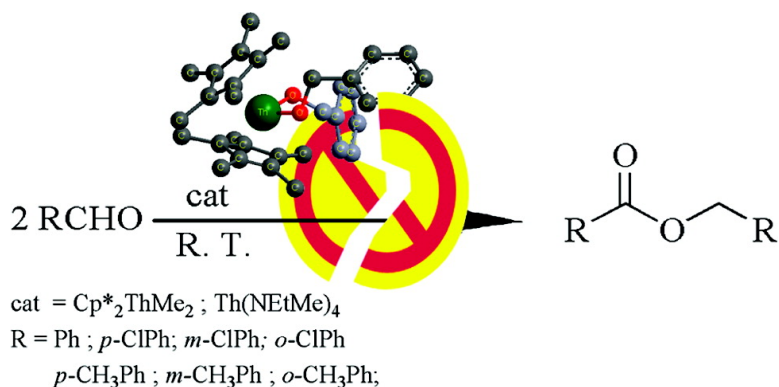# Organoactinides Promote the Tishchenko Reaction: The Myth of Inactive Actinide–Alkoxo Complexes

Tamer Andrea, Eyal Barnea, and Moris S. Eisen

$$2 \; RCHO \xrightarrow[\text{R. T.}]{\text{cat}} R \overset{O}{\underset{}{\|}} O \; R$$

cat = Cp*$_2$ThMe$_2$; Th(NEtMe)$_4$
R = Ph ; *p*-ClPh; *m*-ClPh; *o*-ClPh
   p-CH$_3$Ph ; *m*-CH$_3$Ph ; *o*-CH$_3$Ph;

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Organoactinides Promote the Tishchenko Reaction: The Myth of Inactive Actinide−Alkoxo Complexes

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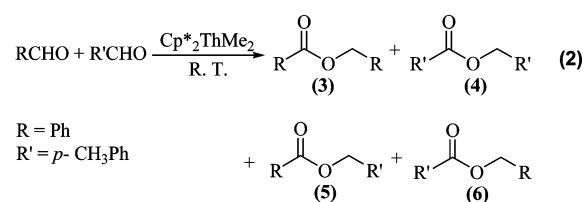
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Neutral and cationic organoactinide complexes have been extensively studied in the past decade as catalysts for several organic transformations.[1,2] Polymerization of alkenes,[3,4] oligomerization,[5,6] intermolecular hydroamination,[7−9] and hydrosilylation of terminal alkynes,[10] and 1,1-insertion of isonitriles into terminal alkynes[11] comprise some of these processes. However, because of the high oxophilicity of the actinide complexes, all the substrates containing oxygen atoms were excluded because of the expected low activity of these complexes owing to the predictable oxygen−actinide interaction. Lin et al. have demonstrated this guideline in actinide chemistry, based on the extremely low activity of actinide complexes containing alkoxy ligands in the catalytic hydrogenation of olefins.[12]

In our attempts to discover new catalytic reactions for actinide-based complexes, Barnea et al. reported their surprising activity toward the polymerization of cyclic mono- and diesters.[13] This discovery arouses the conceptual question about the activity of actinide−alkoxo complexes. To expand the scope of the actinides in catalysis, we have pursued the Tishchenko reaction (dimerization of aldehydes to give the corresponding esters (eq 1)).[14,15] Herein we report the catalytic Tishchenko reaction between two similar (eq 1) or different (eq 2) aldehydes to give the symmetric (**3** and **4**) or asymmetric (**5** and **6**) esters, correspondingly. To show the generality of the process, and to be able to propose a suitable mechanistic pathway, we have studied two organoactinide complexes $Cp^*_2ThMe_2$ (**1**) ($Cp^* = C_5Me_5$)[16] and $Th(NEtMe)_4$ (**2**),[7,17,18] in addition to kinetic and thermodynamic studies using complex **1**.

$$2\ RCHO \xrightarrow[\text{R. T.}]{\text{cat}} R\overset{O}{\underset{(3)}{C}}{}_{O}R \qquad (1)$$

cat = $Cp^*_2ThMe_2$ (**1**); $Th(NEtMe)_4$ (**2**)
R = Ph ; *p*-ClPh; *m*-ClPh; *o*-ClPh; *p*-CH₃Ph ; *m*-CH₃Ph ; *o*-CH₃Ph;

$$RCHO + R'CHO \xrightarrow[\text{R. T.}]{Cp^*_2ThMe_2} \underset{(3)}{R\overset{O}{C}OR} + \underset{(4)}{R'\overset{O}{C}OR'} \qquad (2)$$

R = Ph
R' = *p*-CH₃Ph
$$+ \underset{(5)}{R\overset{O}{C}OR'} + \underset{(6)}{R'\overset{O}{C}OR}$$

The two organoactinide complexes were found to be highly to moderately active (yields 85−65%) in the catalytic dimerization of benzaldehyde and gave the corresponding ester with no side products. Table 1 shows the data for the dimerization of benzaldehyde and other substituted benzaldehydes. Interestingly, the activity is dependent on the proximity of the substituents on the phenyl group to the metal center. For the different tolualdehydes, the ortho compound has a lower activity as compared to *p*-tolualdehyde (entries 6−8, 11−13). A different behavior was observed with the chloride substitution, in which the same yields

Table 1. Product Distribution for the Dimerization of Aldehydes by Thorium Complexes **1** and **2**[a]

entry	cat	R	cat/RCHO	3[c] %
1	**1**	H	1:100	65
2	**1**	*p*-ClPh[b]	1:100	60
3	**1**	*m*-ClPh[b]	1:100	57
4	**1**	*o*-ClPh[b]	1:100	50
6	**1**	*p*-CH₃Ph	1:100	25
7	**1**	*m*-CH₃Ph	1:100	20
8	**1**	*o*-CH₃Ph	1:100	10
9	**2**	H	1:100	85
10	**2**	*p*-ClPh[b]	1:100	85
11	**2**	*p*-CH₃Ph	1:100	82
12	**2**	*m*-CH₃Ph	1:100	75
13	**2**	*o*-CH₃Ph	1:100	55

entry	cat	R, R′	cat/RCHO/R′CHO	3[c] %	4[c] %	5[c] %	6[c] %
14	**1**	H, *p*-CH₃Ph	1:100:100	15	4	6	6
15	**1**	H, *p*-CH₃Ph	1:100:50	25	2	5	5
16	**1**	H, *p*-CH₃Ph	1:50:100	9	6	6	6

[a] The reactions were performed in benzene as solvent, at room temperature for 48 h. cat = catalyst. [b] Time of reaction = 24 h. [c] The yields were determined from the integration of ¹H NMR spectra and GC−MS.

were obtained for the para- and ortho-substituted compounds but lower yields were obtained for the corresponding meta substitution (entry 2−4).

When mixed experiments were performed by reacting benzaldehyde and *p*-tolualdehyde, the four possible esters were obtained. As expected, the *p*-tolualdehyde (less reactive) was involved in the catalytic process in a lower extent and the ester **3** was always obtained as the major product (entry 15). The ratio between the four different products can be controlled, to some extent, by manipulating the ratio between the reactants.

To suggest a plausible mechanism for the reaction and learn about the aldehyde, catalyst, and temperature influence on the reaction rate, kinetic and thermodynamic measurements were performed. Kinetic studies of the $Cp^*_2ThMe_2$-catalyzed Tishchenko reaction of benzaldehyde in benzene-d_6 were carried out using in-situ ¹H NMR spectroscopy. The reaction was found to have a first-order dependence on both catalyst and aldehyde, as presented in eq 3 (see Supporting Information).

$$\nu = k[\text{catalyst}]^1[\text{aldehyde}]^1 \qquad (3)$$

Thermodynamic studies show that the energy of activation (E_a), enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) for the rate determining step are 7.16 ± 0.40 kcal/mol, 6.5 ± 0.4 kcal/mol, and -48.8 ± 0.4 eu, respectively. The high negative entropy value dictates a highly ordered transition state at the rate determining step.[1] In addition; a primary isotopic effect was observed when using α-deuterated benzaldehyde[19] with $kH/kD = 2.7$, indicating that a hydride transfer is involved in the rate determining step. Stoichiometric reactions between the actinide complexes with

Scheme 1. Plausible Mechanism for the Catalytic Tishchenko Reaction Mediated by Cp*$_2$ThMe$_2$[a]
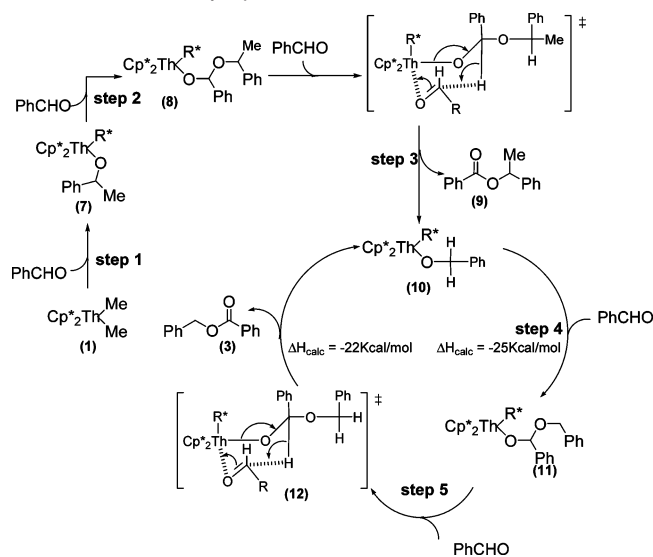
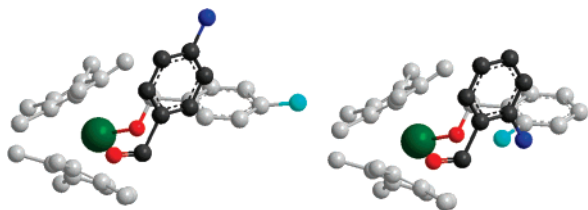[a] We use R* instead of PhCH(CH$_3$)O$^-$ or PhCH$_2$O$^-$ for clarity.

Figure 1. Illustration showing the higher steric interference between the two methyls on the ortho positions (blue and light blue atoms, right molecule) compared to para postition (left). Only one benzylalkoxo substitution is shown for clarity.

benzaldehyde yield the 2-phenetylbenzoate (**9**) (step 1−3 in Scheme 1), demonstrating that an aldehyde is able to insert into complex **1** producing the active alkoxo species.

Based on the kinetic and thermodynamic data a plausible mechanism for the Tishchenko reaction is presented in Scheme 1. In the first step of the reaction, the precatalyst **1** reacts with 2 equiv of the aldehyde to give the alkoxo complex **7**, via a four-center transition state. The first step is thermodynamically favorable because of the oxophilic nature of thorium ($\Delta H_{calcd} = -68$ kcal/mol).[20,21] A second insertion of an aldehyde into the thorium−alkoxide bond produces complex **8**. The following metathesis of complex **8** with an additional aldehyde releases the ester **9** producing the active catalytic species **10**. The catalytic insertion of an aldehyde into a thorium−alkoxo bond takes place in step 4 to give complex **11**, and its hydride transfer reaction (step 5, rate determining step) with an additional aldehyde via a plausible six-centered chairlike transition state produces the ester **3** and regenerates the active complex **10**.

It is possible to envision a β-hydrogen elimination in steps 3 and 5 producing the same results; however, the kinetic data does not support the β-hydrogen elimination mechanism. In addition, from a thermodynamic point of view, we calculated the enthalpy of the reaction for a β-hydrogen elimination and found it to be energetically higher as compared to the six-center mechanism[20,21] ($+6$ and -47 kcal/mol, respectively, eq 4−6). Therefore, we suggest that if operative, the β-hydrogen elimination is not the main termination pathway.

The effect of the substitution on the phenyl ring can be explained by considering two parallel effects: (1) the steric "obstacle" created
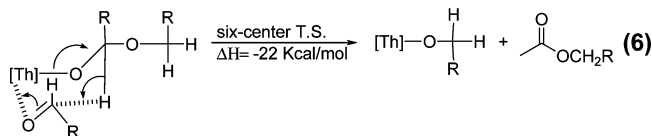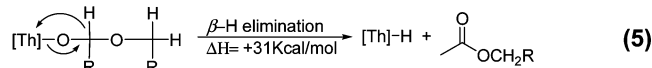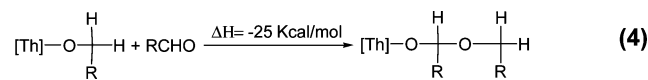
by both the chloride and the methyl groups which hinder the approaching of an aldehyde to the metal−alkoxide bond when disposed in the ortho position (See Figure 1 and Scheme 1), and (2) the electrostatic interaction between the metal and the chloride which enhances the approach of the aldehyde to the metal center and the activity.

To our knowledge, this is the first example of a catalytic coupling process of aldehydes mediated by actinide complexes. Unexpectedly the reaction proceeds via an actinide−alkoxo bond activation, which was believed to be a dead end for actinide complexes in terms of catalysis. We believe the findings here presented will inspire this new uprising field. New catalytic processes involving the activation of actinide−oxygen bonds are underway.

Supporting Information Available: Experimental section including the synthesis and ^{1}H and ^{13}C NMR analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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