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Mono(imidazolin-2-iminato) Actinide Complexes: Synthesis and Application in the Catalytic Dimerization of Aldehydes

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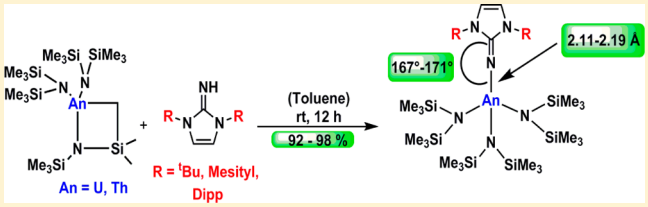
Supporting Information

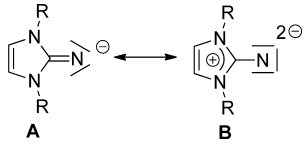
ABSTRACT: The synthesis of the mono(imidazolin-2-iminato) actinide(IV) complexes $[(Im^{R}N)An(N\{SiMe_3\}_2\}_3]$ (**3**−**8**) was accomplished by the protonolysis reaction between the respective imidazolin-2-imine ($Im^{R}NH$, R = *t*Bu, Mes, Dipp) and the actinide metallacycles $[\{(Me_3Si)N\}_2An\{\kappa^2C,N\text{-}CH_2SiMe_2N(SiMe_3)\}]$ (**1**, An = U; **2**, M = Th). The thorium and uranium complexes were obtained in high yields, and their structures were established by single-crystal X-ray diffraction analysis. The mono(imidazolin-2-iminato) actinide complexes **3**−**8** display short An−N bonds together with large An−N−C angles, indicating strong electron donation from the imidazolin-2-iminato moiety to the metal, corroborating a substantial π-character to the An−N bond. The reactivity of complexes **3**−**8** toward benzaldehyde was studied in the catalytic dimerization of aldehydes (Tishchenko reaction), displaying low to moderate catalytic activities for the uranium complexes **3**−**5** and moderate to high catalytic activities for the thorium analogues **6**−**8**, among which **8** exhibited the highest catalytic activity. In addition, actinide coordination compounds showed unprecedented reactivity toward cyclic and branched aliphatic aldehydes in the catalytic Tishchenko reaction mediated by the thorium complex $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**), exhibiting high activity even at room temperature. Moreover, complex **8** was successfully applied in the crossed Tishchenko reaction between an aromatic or polyaromatic and an aliphatic cyclic and branched aldehyde, yielding selectively the asymmetrically substituted ester in high yields (80−100%).



INTRODUCTION

The coordination chemistry of the early actinide elements thorium and uranium has reached a high level of sophistication over the past three decades.[1] The beginning of this field was marked by ubiquitous cyclopentadienyl-based ligand systems, and a large variety of uranium and thorium complexes with the general formula Cp_nAnX_{4-n} (n = 1−3; An = Th, U; X = halide, pseudo halide, alkyl) were synthesized and structurally characterized. Their stoichiometric reactivity and catalytic activity have been thoroughly investigated.[2] Due to their electronic properties, cyclopentadienyl ligands were further applied for the stabilization of unusually low oxidation states of the respective actinide complexes.[3] The state of art, however, includes a large variety of actinide complexes with unique reactivities,[4,5] e.g., with heteroatom-containing ligand systems, such as amidinates,[6] guanidinates,[7] hydrotris(3,5-dimethylpyrazolyl)borate scorpionates,[8] tris(aryl)oxide chelates,[9] larger macrocyclic systems,[10] and tetracoordinate actinide(IV) complexes with sterically demanding ligand systems.[11] Special attention has been attributed to nitrogen-containing ligands, displaying a higher An−N bond order, such as the imido,[12] ketimido,[13] and nitrido and azido[14] moieties. Similar to the ketimido systems, the imidazolin-2-iminato system represents a highly nucleophilic, strongly basic, and monoanionic nitrogen-donor ligand, which can be described by the limiting resonance structures shown in Scheme 1. Due to the ability of the imidazolium ring to stabilize a positive charge efficiently (**B**), the imidazolin-2-iminato moiety can be regarded as a $2\sigma,4\pi$-electron donor and therefore as a cyclopentadienyl analogue, in particular when coordinated to early transition metals in high oxidation states.[15] The resulting transition metal[16] and lanthanide[17] complexes are notorious for their short M−N bonds and large, almost linear M−N−C angles, suggesting a higher bond order to the M−N linkage.[18]

Scheme 1. Resonance Structures of Imidazolin-2-iminato Ligands



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Scheme 2. Synthesis of Mono(omidazolin-2-iminato) Actinide(IV) Complexes 3−8

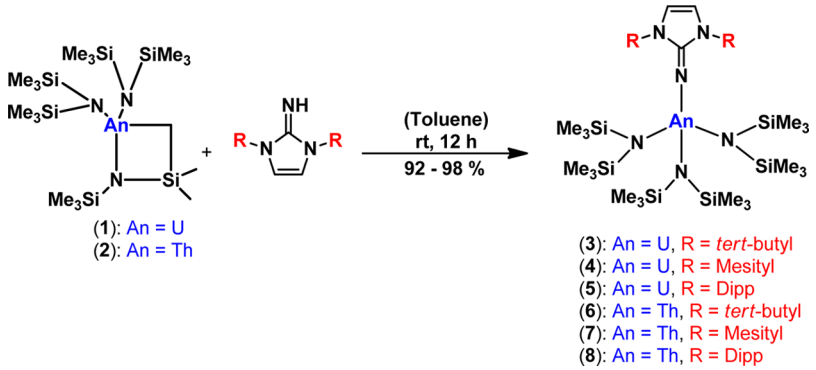

Table 1. Crystallographic Data for Complexes 3−8

	3	4	5·3C$_7$H$_8$	6	7	8·3C$_7$H$_8$
empirical formula	$C_{29}H_{74}N_6Si_6U$	$C_{39}H_{78}N_6Si_6U$	$C_{45}H_{90}N_6Si_6U\cdot 3C_7H_8$	$C_{29}H_{74}N_6Si_6Th$	$C_{39}H_{78}N_6Si_6Th$	$C_{45}H_{90}N_6Si_6Th\cdot 3C_7H_8$
formula weight/g mol^{-1}	913.51	1037.64	1398.89	907.52	1031.65	1392.20
T/K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a/Å	11.9540(4)	21.6750(8)	12.0440(2)	11.9540(4)	21.6750(8)	12.0820(4)
b/Å	19.2770(8)	12.2840(11)	14.0560(3)	19.2770(8)	12.2840(11)	14.0920(4)
c/Å	19.4130(4)	20.0070(14)	23.1880(4)	19.4130(4)	20.0070(14)	23.2090(10)
α/deg	90	90	95.5880(18)	90	90	95.8390(11)
β/deg	90	99.745(4)	92.6530(15)	90	99.745(4)	92.6290(11)
γ/deg	90	90	102.1780(8)	90	90	102.239(2)
V/Å^3	4473.5(3)	5250.1(6)	3809.91(12)	4473.5(3)	5250.1(6)	3832,5(2)
Z	4	4	2	4	4	2
ρ/g cm^{-3}	1.356	1.313	1.198	1.347	1.305	1.185
μ(Mo Kα)/mm^{-1}	3.814	3.259	2.262	3.519	3.008	2.077
Θ range for data collection/deg	2.26−25.03	0.95−24.13	0.88−24.56	2.00−24.18	1.91−24.14	0.88−25.05
F(000)	1864	2120	1408	1856	2112	1404
limiting indices	$0 \le h \le 14$	$-4 \le h \le 23$	$0 \le h \le 13$	$0 \le h \le 13$	$-24 \le h \le 24$	$0 \le h \le 14$
	$0 \le k \le 21$	$-13 \le k \le 0$	$-15 \le k \le 15$	$0 \le k \le 21$	$-13 \le k \le 0$	$-16 \le k \le 16$
	$0 \le l \le 23$	$0 \le l \le 22$	$-26 \le l \le 25$	$0 \le l \le 21$	$0 \le l \le 22$	$-27 \le l \le 27$
reflections collected/unique (R_{int})	4104/4104 (0.0802)	7372/7372 (0.0650)	11339/11339 (0.0315)	3788/3788 (0.0890)	7788/7788 (0.0968)	12969/12969 (0.0902)
% completeness to Θ	99.1	88.4	99.7	99.1	93.0	99.5
GOF on F^2	1.124	1.023	1.073	1.164	1.142	1.060
R_1, wR_2 [$I > 2\sigma(I)$]	0.0351, 0.0713	0.0350, 0.0788	0.0545, 0.1384	0.0423, 0.0608	0.0701, 0.0951	0.0849, 0.1730
R_1, wR_2 (all data)	0.0407, 0.0728	0.0522, 0.0837	0.0799, 0.1526	0.0494, 0.0622	0.1047, 0.1029	0.1691, 0.2208
largest diff peak and hole/e Å^{-3}	0.734 and −0.801	0.939 and −0.817	1.066 and −0.873	0.599 and −0.953	0.740 and −0.536	0.985 and −1.428

Recently, we reported the synthesis and structural characterization of a series of uranium(IV) imidazolin-2-iminato complexes, which were obtained by an acid−base reaction between the homoleptic tetraamido complex [U(NMeEt)$_4$] and neutral imidazolin-2-imines Im^{R}NH.[19] Despite variation of the stoichiometry of the starting materials and of the reaction conditions, the uranium(IV) complexes obtained depended on the steric encumbrance of the R substituent of the imidazolin-2-iminato ligand, corroborating a thermodynamic control of the reaction, which did not allow for the preparation of mono(imidazolin-2-iminato) actinide(IV) complexes. Moreover, an analogous reaction between [Th(NMeEt)$_4$] and the respective imidazolin-2-imine led to a myriad of products, and a single complex could not be isolated. In the present study, we report a strategy for the selective synthesis and characterization of a series of mono(imidazolin-2-iminato) thorium(IV) and uranium(IV) complexes, which were obtained in high yields by protonolysis of the actinide metallacycles [{(Me$_3$Si)N}$_2$An-{κ^2C,N-CH$_2$SiMe$_2$N(SiMe$_3$)}] (**1**, An = U; **2**, M = Th).[20] The large ionic radii and the presence of f-orbitals in the actinide series, which allow for large coordination numbers and unusual coordination geometries, gave rise to a unique reactivity in organic transformations.[21] The catalytic activity of actinide coordination compounds has been investigated in a wide range of processes, such as the polymerization of α-olefins,[22] hydrothiolation,[23] hydroalkoxylation,[23] hydrosilylation[24] and hydroamination[25] of terminal alkynes, isontrile−alkyne coupling,[26] coupling of terminal alkynes,[27] ring-opening polymer-

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3−8[a]

	3	4	5·3C$_7$H$_8$	6	7	8· 3C$_7$H$_8$
An−N1	2.329(8)	2.328(4)	2.346(6)	2.401(8)	2.370(7)	2.369(10)
An−N2	2.303(7)	2.319(4)	2.342(6)	2.347(7)	2.350(6)	2.395(8)
An−N3	2.318(7)	2.323(4)	2.313(6)	2.346(7)	2.397(8)	2.418(8)
An−N4	2.118(8)	2.143(4)	2.137(6)	2.176(8)	2.189(7)	2.197(10)
N4−C$_{ipso}$[b]	1.290(12)	1.313(6)	1.319(9)	1.292(12)	1.308(10)	1.291(14)
An−N4−C$_{ipso}$[b]	169.5(7)	169.8(4)	169.5(5)	166.9(8)	168.5(6)	170.7(7)
N1−An−N2	104.3(2)	119.53(16)	106.1(2)	105.2(3)	118.1(3)	105.2(3)
N2−An−N3	118.5(2)	107.85(15)	104.7(2)	118.8(3)	110.2(3)	106.8(3)
N3−An−N4	98.3(3)	126.74(15)	104.8(2)	100.1(3)	122.4(3)	114.4(3)
N1−An−N3	109.7(3)	101.04(15)	111.7(2)	109.6(3)	101.8(2)	111.5(3)
N1−An−N4	122.5(3)	106.81(15)	115.2(2)	118.0(3)	108.0(2)	105.2(3)
N2−An−N4	104.5(3)	96.54(15)	114.0(2)	105.8(3)	97.5(2)	113.4(3)
cone angle	83	73	69	84	71	64

[a]An: U for complexes **3**−**5**; Th for complexes **6**−**8**. [b]C$_{ipso}$: C19 for complexes **3**, **4**, **6**, **7**; C31 for complexes **5** and **8**.

ization of cyclic esters,[28,6i,19] and the Tishchenko reaction with aromatic aldehydes.[29] Despite the large scope of organic transformations mediated by actinide complexes, the examples involving oxygen-containing substrates remain scarce, which can be attributed to the high oxophilicity of the early actinides and the resulting formation of thermodynamically stable, catalytically inactive actinide−oxo species.[30] Therefore, an interesting conceptual question regards the ability to increase the catalytic activity of actinide compounds toward oxygen-containing substrates by avoiding the formation of catalytically inactive actinide−oxo species by decreasing the oxophilicity of the metal center. This approach can be in principle investigated by the coordination of strongly nucleophilic ligands, such as the imidazolin-2-iminato moiety, which might be expected to increase the electron density of the metal center and therefore decrease its oxophilicity, which should in turn lead to an increased catalytic activity toward oxygen-containing molecules, such as esters and aldehydes. We decided to investigate the reactivity of the mono(imidazolin-2-iminato) thorium(IV) complex [(Im^{Dipp}N)Th{N(SiMe$_3$)$_2$}$_3$] (**8**) toward aromatic, cyclic, and branched aliphatic aldehydes. The use of a thorium(IV) complex, bearing only one sterically encumbering imidazolin-2-iminato ligand, should ensure an enhanced catalytic activity, while enabling the substrate to enter the coordination sphere of the metal, due to the reduced steric bulk in comparison to bis- and tris(imidazolin-2-iminato) complexes.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The mono(imidazolin-2-iminato) actinide(IV) complexes **3**−**8** were obtained in high yields by treatment of a toluene solution of the actinide metallacycles **1** and **2** with a toluene solution of 1 equiv of the respective imidazolin-2-imine Im^{R}NH at room temperature (Scheme 2). Subsequent stirring of the reaction mixture for 12 h at room temperature, removal of the solvent, and recrystallization from a concentrated toluene solution at −35 °C afforded the actinide complexes **3**−**8** in high yields. Crystals suitable for X-ray crystallography were obtained from toluene solutions at −35 °C. Crystallographic data for complexes **3**−**8** are presented in Table 1; selected bond lengths and angles are assembled in Table 2.

The mono(imidazolin-2-iminato) uranium(IV) complexes [(Im^{R}N)U{N(SiMe$_3$)$_2$}$_3$] (**3**−**5**) (Figure 1−3) are obtained as orange powders in high yields of 92%, 94%, and 95% for [(Im^{Mes}N)U{N(SiMe$_3$)$_2$}$_3$] (**4**), [(Im^{tBu}N)U{N(SiMe$_3$)$_2$}$_3$] (**3**), and [(Im^{Dipp}N)U{N(SiMe$_3$)$_2$}$_3$] (**5**), respectively. X-ray measurements performed on single crystals of compounds **3**−**5** show a distorted tetrahedral coordination environment around the metal, with N−U−N angles of 98.3(3)−122.5(3)°, 96.54(15)−126.74(15)°, and 104.8(2)−111.7(2)°, for complexes **3**, **4**, and **5**, respectively. Moreover, to describe the steric

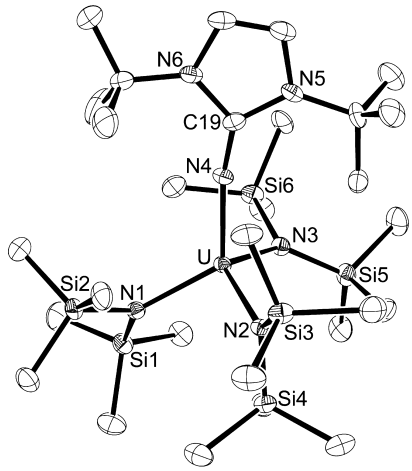

Figure 1. ORTEP drawing of [(Im^{tBu}N)U{N(SiMe$_3$)$_2$}$_3$] (**3**) with thermal displacement parameters at 20% probability. Hydrogen atoms are omitted for clarity.

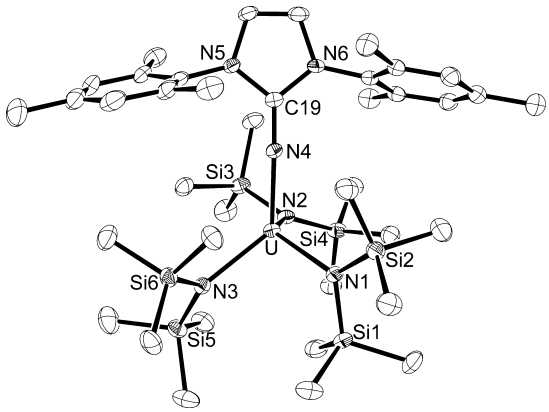

Figure 2. ORTEP drawing of [(Im^{Mes}N)U{N(SiMe$_3$)$_2$}$_3$] (**4**) with thermal displacement parameters drawn at 20% probability. Hydrogen atoms are omitted for clarity.

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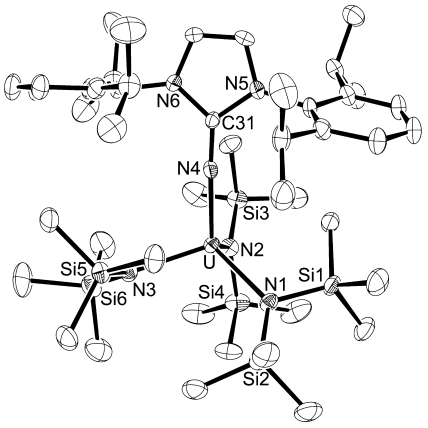

Figure 3. ORTEP drawing of $[(Im^{Dipp}N)U\{N(SiMe_3)_2\}_3]$ (**5**) with thermal displacement parameters drawn at 20% probability. Hydrogen atoms and distorted solvent molecules are omitted for clarity.

demand of phosphine ligands Tolman et al.[31] introduced the ligand cone angle, which is defined as the angle between the metal at the vertex of the cone formed by the coordinating ligands and the metal center, and the hydrogen atoms at its perimeter, which was later adapted to further ligand systems, such as cyclopentadienyl ligands by Coville et al.[32] This parameter can also be applied for the description of the steric demand of imidazolin-2-iminato systems, displaying values of 83°, 73°, and 69° for $[(Im^{tBu}N)U\{N(SiMe_3)_2\}_3]$ (**3**), $[(Im^{Mes}N)U\{N(SiMe_3)_2\}_3]$ (**4**), and $[(Im^{Dipp}N)U\{N(SiMe_3)_2\}_3]$ (**5**), respectively. The U−N4 bond distances in complexes **3**−**5** are short, with values of 2.118(9), 2.143(4), and 2.137(6) Å for **3**, **4**, and **5**, respectively, which are on average 0.20 Å shorter than the U−N_{amido} bond lengths in the respective uranium compound (Table 2). Moreover, the U−N4−C_{ipso} angles with values of 169.5(7)°, 169.8(4)°, and 169.5(5)°, for **3**, **4**, and **5**, respectively, are close to linearity, in comparison to the U−N_{amido}−Si angles, which exhibit as expected a bent geometry (Table 2). The bonding properties of imidazolin-2-iminato are comparable to those of the ketimido moiety, which is also described as a 2σ,4π-electron donor in actinide complexes.[13] The U−N4 bond lengths in the mono(imidazolin-2-iminato) uranium complexes **3**−**5** are yet slightly shorter than the U−N bond distances in uranium(IV) bis(ketimido) compounds and clearly shorter than the average U−N_{amido} bond.[12] The short U−N4 bond lengths and large U−N4−C_{ipso} angles indicate a substantial π-character of the U−N4 bond, suggesting a higher bond order of the same. To further elucidate the bonding properties of the imidazolin-2-iminato moiety, the N4−C_{ipso} bond distances in complexes **3**−**5** are compared with the respective bond distances for lanthanide and group IV mono(imidazolin-2-iminato) complexes, which have been investigated in previous studies.[16−18] Whereas the uranium(IV) complexes **3**−**5** display N4−C_{ipso} bond lengths of 1.290(12), 1.313(6), and 1.319(9) Å for compounds **3**, **4**, and **5**, respectively, the rare earth complexes exhibit N−C_{ipso} bond distances of 1.251(4), 1.266(5), 1.271(10), and 1.254(14) Å, for $[(Im^{Dipp}N)LuCl_2]\cdot 3THF$, $[(Im^{Dipp}N)GdCl_2]\cdot 3THF$, $[(Im^{Dipp}N)YbCl_2]\cdot 3THF$,[33] and for $[(Im^{Dipp}N)SmCl_2]\cdot 3THF$[33] respectively, showing a slight elongation of the N−C_{ipso} bond in uranium complexes **3**−**5**, further sustaining a higher U−N bond order. For group IV metals a comparison of the N4−C_{ipso} bond distances in the uranium compounds **3**−**5** with the respective bonds in titanium(IV) mono(imidazolin-2-iminato) complexes, showed slightly longer N−C_{ipso} bond distances for the titanium(IV) compounds with values of 1.331(3), 1.348(4), and 1.330(6) Å, for $[(Im^{tBu}N)TiCl_3]$,[16a] $[(Im^{Mes}N)TiCl_3]$,[16e] and $[(Im^{Dipp}N)TiCl_3]$,[16e] respectively, indicating a more covalent bond in the respective mono(imidazolin) titanium(IV) complexes than in the respective lanthanide or actinide complexes.

The mono(imidazolin-2-iminato) thorium(IV) complexes **6**−**8** (Figure 4−6) were crystallized in a similar fashion from

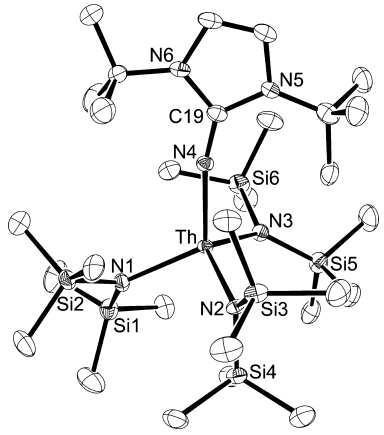

Figure 4. ORTEP drawing of $[(Im^{tBu}N)Th\{N(SiMe_3)_2\}_3]$ (**6**) with thermal displacement parameters drawn at 20% probability. Hydrogen atoms are omitted for clarity.

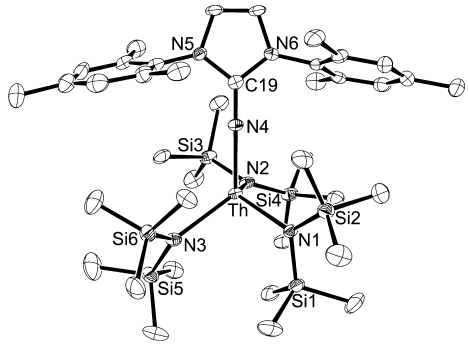

Figure 5. ORTEP drawing of $[(Im^{Mes}N)Th\{N(SiMe_3)_2\}_3]$ (**7**) with thermal displacement parameters drawn at 20% probability. Hydrogen atoms are omitted for clarity.

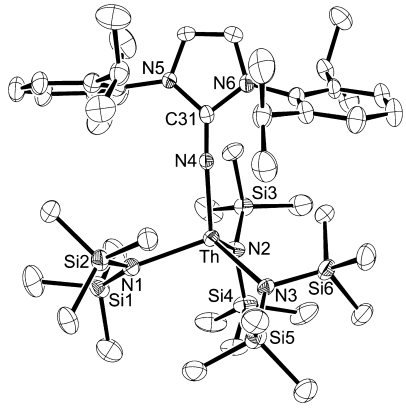

Figure 6. ORTEP drawing of $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) with thermal displacement parameters drawn at 20% probability. Hydrogen atoms and distorted solvent molecules are omitted for clarity.

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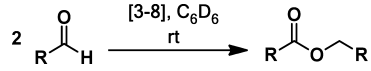
concentrated toluene solutions at −35 °C. However, the crystals of the thorium complexes showed a notorious instability, decomposing at room temperature when submerged into parathon-*N* oil, which is commonly used for single-crystal X-ray measurements of air sensitive compounds.To determine the crystal structures of the thorium(IV) complexes **6**−**8**, the single-crystalline material was submerged in cold (−35 °C) perfluoropolyalkylether oil, the vessel was immediately submerged in liquid nitrogen, and the single crystals were fished from the vessel at −78 °C and rapidly mounted on the diffractometer. Especially, single crystals of complex **8** showed an exceedingly high instability, losing their transparency within seconds, when submerged in cold parathion-*N* oil, or within a few minutes, when submerged in cold (−35 °C) perfluoropolyalkylether oil. The thorium complexes $[(Im^{tBu}N)Th\{N(SiMe_3)_2\}_3]$ (**6**), $[(Im^{Mes}N)Th\{N(SiMe_3)_2\}_3]$ (**7**), and $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) are isostructural with the uranium analogues **3**−**5**, crystallizing in the same crystallographic space groups, and exhibiting similar imidazolin-2-iminato cone angles of 84°, 71°, and 64°, for complexes **6**, **7**, and **8**, respectively (Table 2). The coordination around the thorium center is distorted tetrahedral, and the N−Th−N bond angles are comparable to the N−U−N bond angles in complexes **3**−**5**, displaying values of 100.1(3)−118.8(3)°, 101.8(8)−118.1(3)°, and 105.2(3)−114.4(3)°, for compounds **6**, **7**, and **8**, respectively. The Th−N4−C_{ipso} angles are close to linearity, displaying values similar to the U−N4−C_{ipso} values, in the isostructural complexes **3**−**5**, with values of 166.9(8), 168.5(6), and 170.7(7)°, for complexes **6**, **7**, and **8**, respectively. The Th−N4 bond distances are slightly elongated in comparison to the U−N4 distances (*vide supra*), exhibiting values of 2.176(8), 2.189(7), and 2.197(14) Å for $[(Im^{tBu}N)Th\{N(SiMe_3)_2\}_3]$ (**6**), $[(Im^{tBu}N)Th\{N(SiMe_3)_2\}_3]$ (**7**), and $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**), respectively. The difference of approximately 0.06 Å between the Th−N and U−N bond lengths is in good agreement with the predicted value of 0.05 Å.[34] The Th−N4 bond lengths are on average 0.10 Å shorter than the Th−N bond distances in thorium bis(ketimido) complexes, and on average 0.20 Å shorter than Th−N_{amido} bonds.[13,34] The short Th−N4 bond lengths and the large Th−N−C angles indicate a substantial π-character of the Th−N bond, comparable to the respective U−N bond (*vide supra*). The N4−C_{ipso} bond lengths in the mono(imidazolin-2-iminato) thorium complexes **6**−**8** are comparable to the uranium analogs, displaying values of 1.292(12), 1.308(10), and 1.291(14) Å, for compounds **6**, **7**, and **8**, respectively, indicating similar interactions in the actinide complexes **3**−**8**. Furthermore, a comparison of the An−N_{amido} bond distances in complexes **3**−**8**, which range between 2.303(7) and 2.346(6) Å, for the uranium complexes **3**−**6**, and 2.346(7) and 2.418(8) Å, for the respective thorium compounds **6**−**8**, are slightly elongated (0.05−0.1 Å) as compared to those of various uranium(IV) and thorium(IV) bis(trimethylsilyl) amido complexes,[5n,35] which can be attributed to the steric demand of the imidazolin-2-iminato ligand.

Catalytic Tishchenko Reaction. The dimerization of two aldehydes to yield the respective ester via a hydride shift, in which one of the aldehyde monomers acts as a hydride donor and the other as a hydride acceptor (disproportionation), is known as the Tishchenko reaction (Scheme 3).[36] Despite the large number of studies carried out with main group,[37] transition metal,[38] and lanthanide[39] catalysts, the tolerance of the respective metal complexes toward functional groups and

Scheme 3. General Reaction Scheme for Metal-Catalyzed Dimerization of Aldehydes



hydrogen atoms in the β-position reduces the scope of accessible esters and represents a major impediment for the use of the Tishchenko reaction in organic synthesis.[37−39] In addition, when two different aldehydes are reacted in the crossed Tishchenko reaction, the selectivity toward the mixed ester still remains a major challenge and can only be achieved in particular cases.[40] In a previous study, we have reported the reactivity of $Cp^*_2ThMe_2$ toward aromatic aldehydes, showing a high catalytic activity and a tolerance toward several functional groups.[29] Herein, we investigated the reactivity of the mono(imidazolin-2-iminato) actinide(IV) complexes **3**−**8** toward aldehydes, addressing the fundamental question whether postmetallocene actinide catalysts display a reactivity not only toward aromatic aldehydes but also toward cyclic and branched aliphatic aldehydes, as well as in the crossed Tishchenko reaction. To determine the catalyst with the highest activity, we carried out catalytic studies using benzaldehyde as the substrate and complexes **3**−**8** as precatalysts. Although the uranium complexes **3**−**5** displayed moderate to low activities (Table 3), the thorium analogues **6**−**8** displayed higher catalytic activities, with $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) showing the highest catalytic activity among the mono(imidazolin-2-iminato) complexes **3**−**8**; hence, it was applied for all further catalytic studies. Despite the notorious instability displayed by single crystals of complex **8**, when submerged in parathion-*N* oil, or perfluoropolyalkylether oil, the thorium compound **8** is stable in solution and can therefore be applied for catalytic studies, even at elevated temperatures (90 °C for weeks). The reactivity of a metal coordination complex depends on the availability of the metal center for coordination to the incoming substrate moiety. To further explore the difference in activity of the actinide compounds **3**−**8**, the steric encumbrance around the respective actinide center was investigated using space filling models (Figure 7). The cavities, built by the carbon atoms of the R-substituents of the imidazolin-2-iminato ligand and the carbon atoms of the

Table 3. Catalytic Dimerization of Benzaldehyde Mediated by Complexes 3−8[a]

	Yield (%)			
complex	6 h	12 h	24 h	48 h
3	0	3	8	12
4	0	0	5	9
5	0	6	12	37
6	2	7	15	26
7	0	5	11	19
8	21	61	100	
9[b,29]	13		41	65
10[c,29]	21		61	85
11[d,29]	58		96	

[a]Reaction conditions: 4.48 μmol of catalyst; cat/PhCHO 1/100; 500 μL of C_6D_6; room temperature (rt). [b]Catalyst: $[Cp^*_2Th(CH_3)_2]$ (10 μmol); cat/PhCHO 1/100, rt. [c]Catalyst: $[Th(NMeEt)_4]$ (10 μmol); cat/PhCHO 1/100, rt. [d]Catalyst: *ansa*-$[Me_2SiCp''_2Th(CH_3)_2]$ (10 μmol); cat/PhCHO 1/100, rt.

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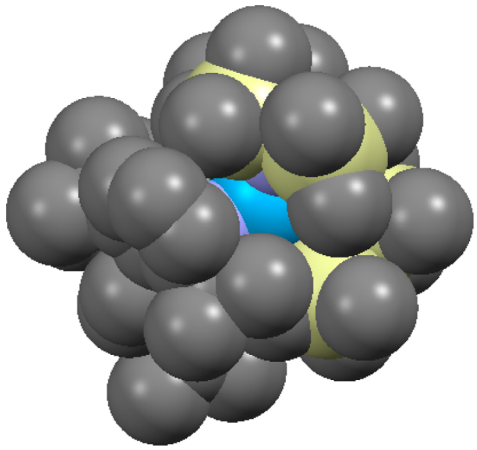


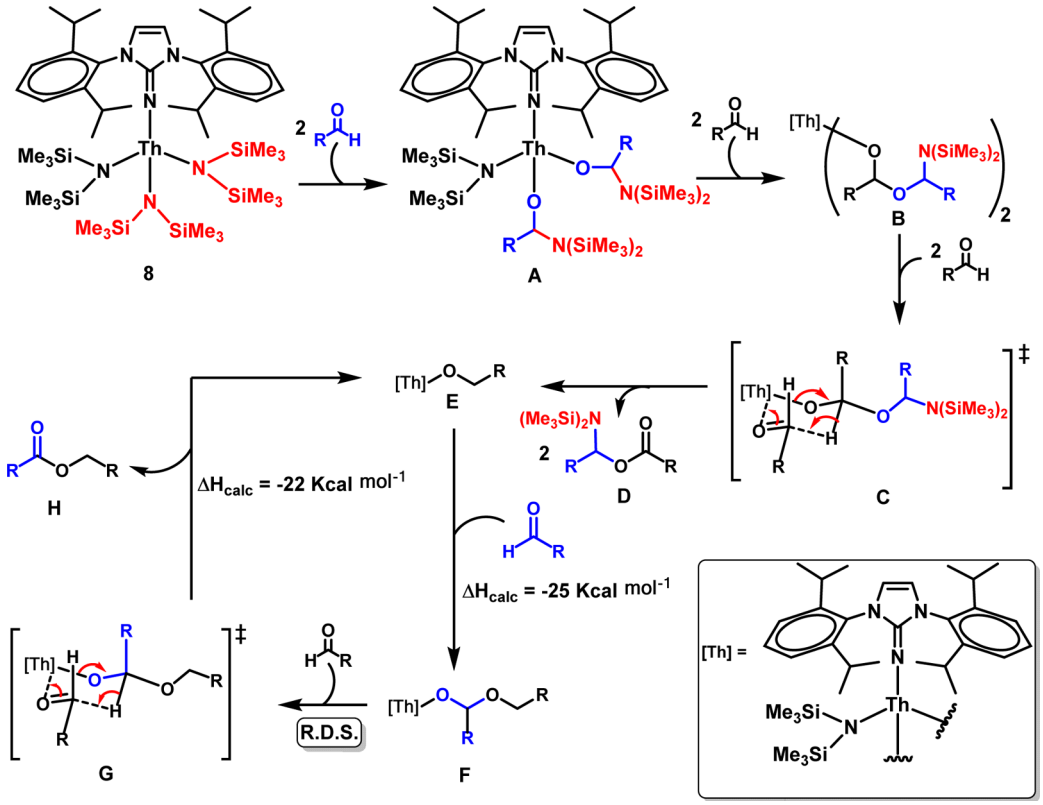
Figure 7. Space filling model of $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) showing the large cavity of ~5.7 Å. Color code: Th, green; N, blue; Si, yellow; C, gray. Hydrogen atoms are omitted for clarity.

bis(trimethylsilyl)amido ligands, display values between 3.6 and 4.5 Å for complexes **3**–**7**; the complex $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) exhibits a larger cavity (~5.7 Å), which is in agreement with the higher activity displayed by this compound.

Recently, we reported the catalytic performance of the homoleptic amido complex $[Th(NMeEt)_4]$ (**10**), as well as of $[Cp^*_2Th(CH_3)_2]$ (**9**) and the *ansa*-bridged thorium(IV) complex *ansa*-$[Me_2SiCp_2''(CH_3)_2]$ (**11**) (Cp'' = $C_5(CH_3)_4$), toward aromatic aldehydes, among which the *ansa*-bridged thorium complex displayed the highest catalytic activity (Table 3, entries 9–11).[29] The catalytic activity of the mono(imidazolin-2-iminato) thorium complex **8** toward benzaldehyde is higher than the activity observed for $[Th(NMeEt)_4]$ (**10**) and $[Cp^*_2Th(CH_3)_2]$ (**9**) and comparable to the activity exhibited by *ansa*-$[Me_2SiCp''_2Th(CH_3)_2]$ (**11**). However, in contrast to the previously reported actinide complexes, which catalyzed neither the Tishchenko reaction of aliphatic aldehydes nor the selective crossed Tishchenko reaction, the mono(imidazolin-2-iminato) thorium complex **8**, showed an unprecedented high activity toward cyclic and branched aliphatic aldehydes, as well as in the crossed Tishchenko reaction (*vide infra*).

Important reactions that need to be performed in catalytic studies are poisoning experiments. The basic idea is to find out what percentage of the precatalyst is active in the reaction. Hence, poisoning experiments with isopropanol showed that all catalyst **8** is active in the catalytic process, and experiments with stoichiometric amounts of $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) and benzaldehyde showed that two aldehyde units can insert into the Th–$N(SiMe_3)_2$ bonds, leading to the formation of 2 equiv of $N(SiMe_3)_2$ α-substituted ester (**D**), which was characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and mass spectroscopy. A plausible mechanism for the Tishchenko reaction, mediated by complex **8**, is presented in Scheme 4. After the insertion of an aldehyde unit into the Th–$N(SiMe_3)_2$ bond, the thorium alkoxo species **A** is obtained, which undergoes a second aldehyde insertion into the Th–O bond forming the intermediate complex **B**. Complex **B** will react with an additional aldehyde via a six-centered transition state (**C**), leading to the active thorium–oxo catalyst **E** through the elimination of 1 equivalent of the $N(SiMe_3)_2$ α-substituted ester (**D**) per trimethylsilylamido ligand. A subsequent insertion of an incoming aldehyde unit into the Th–O bond of complex **E** forms the intermediate complex **F**, which reacts

Scheme 4. Proposed Mechanism for the Tishchenko Reaction Mediated by Complex 8[29,41]



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with another aldehyde via a six-membered transition state (**G**) to yield the ester **H** and regenerating the catalytically active thorium−oxo species **E**. To trap the intermediates of the catalytic cycle shown in Figure 4, experiments with stoichiometric amounts of benzaldehyde were performed, and the intermediates were characterized by ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy. The addition of 2 equiv of benzaldehyde to complex **8**, led to the quantitative formation of the thorium intermediate **A** (R = Ph), which after treatment with an additional 2 equiv of benzaldehyde yielded the thorium−alkoxo species **B** (R = Ph). Subsequent addition of 2 equiv of benzaldehyde to the reaction mixture led to the elimination of 2 equiv of the $N(SiMe_3)_2$ α-substituted ester **D** (R = Ph), with formation of complex **E** (R = Ph). The reactivity of complex **8** was investigated with a variety of substrates (Table 4), including substituted aromatic, polyaromatic, cyclic, and branched aliphatic aldehydes, exhibiting a higher catalytic activity toward cyclic and branched aliphatic aldehydes than for their aromatic counterparts. Therefore, we carried out crossed Tishchenko experiments (Scheme 5) with two different aldehydes, one of which was an aromatic or polyaromatic aldehyde, and the other one being a cyclic or branched aliphatic aldehyde (Table 5). When the reaction was performed with an equimolar ratio of both aldehydes, the symmetrically and asymmetrically substituted esters were obtained in similar amounts, and no selectivity toward the formation of either one or the other ester was observed. However, when an excess of the aromatic aldehyde was applied, the asymmetrically substituted ester is obtained as the major product and only small amounts of the homocoupled esters are observed.

Table 4. Catalytic Tishchenko Reaction Mediated by Complex 8

		yield (%) RCH_2OCOR		
entry[a]	RCHO	6 h	12 h	24 h
1	Ph	21	61	100
2	1-naphthyl	0	10	32
3	2-naphthyl	0	24	61
4	4-NO_2−Ph	39	77	100
5	cyclohexyl	84	100	
6	cyclopentyl	82	100	
7	isopropyl	94	100	
8	*o*-Ph$(CHO)_2$	100		

[a]Reaction conditions: 4.48 μmol of catalyst **8**; cat/RCHO 1/100; 500 μL of C_6D_6; rt.

The mono(imidazolin-2-iminato) thorium(IV) complex $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) displayed a high activity in the dimerization of cyclic and branched aliphatic aldehydes (Table 4, entries 5−7) to yield the respective symmetrically substituted ester with 100% conversion after 12 h. Monosubstituted aromatic esters were obtained in moderate to high yields after the Tishchenko reaction with the respective aromatic aldehyde proceeds for 24 h at room temperature (Table 4, entries 1−5). Furthermore, the intramolecular Tishchenko reaction (Scheme 6) was performed with phthalaldehyde, displaying a full conversion to phthalide after 6 h.

When complex **8** is reacted with two different aldehydes, one of them bearing an aromatic or polyaromatic substituent (RCHO), the other a cyclic or branched aliphatic substituent (R^1CHO), four possible products can be obtained (Scheme 5). When a ratio of 1:1 between RCHO and R^1CHO is used, unexpectedly the asymmetrically substituted ester (RCH_2OCOR^1) is the first product observed after a reaction time of 2 h, together with trace amounts of $R^1CH_2OCOR^1$. Longer reaction times lead to the formation of the symmetrically substituted esters RCH_2OCOR and $R^1CH_2OCOR^1$, as well as traces of R^1CH_2OCOR, after a reaction time 24 h, with a ratio of 25:5:33:35 for RCH_2OCOR^1, R^1CH_2OCOR, RCH_2OCOR, and $R^1CH_2OCOR^1$, respectively. The formation of the asymmetrically substituted ester RCH_2OCOR^1 suggests that the benzylic thorium alkoxo species **E** (Scheme 4) reacts preferentially with an aliphatic aldehyde, which will react again favorably with another aromatic aldehyde (after hydride transfer), closing the catalytic cycle. After the reaction proceeds, the amount of the symmetrically substituted esters increases, suggesting a competition between the aldehydes in the reaction mixture. To control the catalytic reaction toward the selective formation of the asymmetrically substituted ester, we applied an excess of the aromatic aldehyde (RCHO) (RCHO:R^1CHO 200:50) to avoid the competition reactions, resulting in the formation of symmetrically substituted esters. Owing to the better hydride-donor ability of aliphatic aldehydes than of aldehydes bearing electron withdrawing groups (e.g., R = aryl), which are considered to be better hydride acceptors,[40,42] we were able to control the reaction toward the formation of the asymmetrically substituted ester. This result indicates that the hydride transfer is the rate-determining step (rds) in the catalytic cycle. When all the aliphatic aldehyde (R^1CHO) is consumed after 1.5 h (>95% yield of the asymmetric ester is obtained), the excess of the aromatic aldehyde yields the symmetrically substituted ester RCH_2OCOR, until full conversion is reached after 24 h.

CONCLUSIONS

The synthesis of mono(imidazolin-2-iminato) actinide(IV) complexes $[(Im^RN)An\{N(SiMe_3)_2\}_3]$ was performed by the protonolysis reaction of the actinide metallacycles **1** and **2** with the respective neutral imidazolin-2-imines (Im^RNH) to afford complexes **3**−**8** in high yields. Due to the higher reactivity of the An−CH_2 bond in comparison to the An−N bonds in the actinide metallacycles **1** and **2**, the monosubstituted imidazolin-2-iminato actinide complexes could be obtained selectively, without a dependence on the steric encumbrance of the respective imidazolin-2-iminato ligand. The mono(imidazolin-2-iminato) actinide complexes **3**−**8** were characterized by X-ray crystallography, displaying very short An−N bonds and close to linear An−N−C bond angles, suggesting a substantial π-character to the An−N bond. The reactivity of complexes **3**−**8** in the catalytic Tishchenko reaction was investigated, displaying low to moderate activities for the uranium complexes **3**−**5** and moderate to high activities for the thorium complexes **6**−**8**. The

Scheme 5. Crossed Tishchenko Reaction Catalyzed by 8

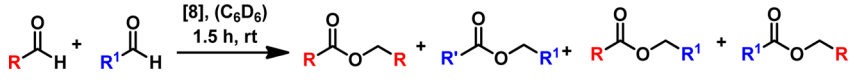

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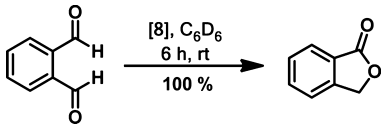
Table 5. Crossed Tishchenko Reaction Mediated by Complex 8[a]

			yield (%)			
entry	RCHO	R^1CHO	RCH_2OCOR	$R^1CH_2OCOR^1$	RCH_2OCOR^1	R^1CH_2OCOR
1	Ph	C_6H_{11}			92	8
2	Ph	C_5H_9		12	84	
3	Ph	isopropyl		20	80	
4	1-naphthyl	C_6H_{11}	5		100	
5	2-naphthyl	C_6H_{11}	5		88	12

[a]Reaction conditions: 4.48 μmol of catalyst **8**; cat/RCHO 1/200; cat/R^1CHO 1/50; 750 μL of C_6D_6; rt; yield was determined by ^{1}H NMR spectroscopy of the crude reaction mixture after 1.5 h. The yield is based on the moles of the aromatic aldehyde.

Scheme 6. Catalytic Lactonization of Phthalaldehyde Mediated by Complex 8



mono(imidazolin-2-iminato) thorium(IV) complex $[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) exhibited the highest catalytic activity, and its reactivity toward aromatic, polyaromatic, cyclic, and branched aliphatic was studied, displaying a moderate to high activity toward aromatic and polyaromatic aldehydes and a very high catalytic activity in the dimerization of cyclic and branched aliphatic aldehydes. The reactivity of **8** was further studied in the crossed Tishchenko reaction, affording quantitative yield of the asymmetrically substituted ester, with only small amounts of the homocoupled aldehydes.

EXPERIMENTAL SECTION

General Considerations. All manipulations of air sensitive materials were performed with rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high vacuum line (10^{-5} Torr), or in nitrogen filled MBraun and Vacuum Atmospheres gloveboxes with a medium capacity recirculator (1−2 ppm oxygen). Argon and nitrogen were purified by passage through an MnO oxygen removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze−pump−thaw cycles prior to use (hexane, toluene, benzene-d_6, toluene-d_8). $Im^{Dipp}NH$, $Im^{Mes}NH$, $Im^{tBu}NH$[15], and the metallacycles **1** and **2**[20e] were synthesized according to published literature procedures. Benzaldehyde, cyclohexanecarbaldehyde, cyclopentanecarbaldehyde, isobutyraldehyde, and 1-naphthaldehyde (Sigma-Aldrich) were distilled over sodium bicarbonate and stored in a glovebox prior to use. 2-Naphthaldehyde and phthalaldehyde (Sigma-Aldrich) were dried for 12 h on a high vacuum line (10^{-5} Torr) and stored in a glovebox prior to use. NMR spectra were recorded on Avance 300 and Avance 400 Bruker spectrometers. Chemical shifts for ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR measurements are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. Elemental analyses were carried out by the microanalysis laboratory at the Hebrew University of Jerusalem. MS experiments were performed at 200 °C (source temperature) on a Maxis Impact (Bruker) mass spectrometer with an APCI solid probe method. For X-ray crystallographic measurements, the single-crystalline material was immersed in perfluoropolyalkylether oil and was quickly fished with a glass rod and mounted on a Kappa CCD diffractometer under a cold stream of nitrogen. Data collection was performed using monochromated Mo Kα radiation using φ and ω scans to cover the Ewald sphere.[43] Accurate cell parameters were obtained with the amount of indicated reflections (Table 1).[44] The structure was solved by SHELXS-97 direct methods[45] and refined by the SHELXL-97 program package.[46] The atoms were refined anisotropically. Hydrogen atoms were included using the riding model. The software used for creating space filling models was Mercury 3.1.[47]

General Procedure for the Synthesis of Mono(imidazolin-2-minato) Actinide(IV) Complexes. A solution of the actinide metallacycle **1** or **2** (500 mg) in toluene (10 mL) was treated with a toluene solution of the respective imidazolin-2-imine Im^RNH (1.0 equiv in 10 mL) at room temperature. The reaction mixture was stirred for 12 h at room temperature, and the solvent was subsequently removed under vacuum to afford crude **3**−**8**. The crude products **3**−**8** were recrystallized from a concentrated toluene solution at −35 °C to yield **3**−**8** as crystalline materials.

$[(Im^{tBu}N)U\{N(SiMe_3)_2\}_3]$ (**3**): yield 94% (598 mg, 0.65 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.01 (s, 54 H, $Si(CH_3)_3$), 1.01 (s, 18 H, $C(CH_3)_2$), 2.11 (2 H, CH); ^{13}C NMR (75.5 MHz, C_6D_6) δ 2.63 ($Si(CH_3)_3$), 27.96 ($C(CH_3)_3$), 33.51 ($C(CH_3)_3$), 59.21 (CH), 148.2 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −10.14. Anal. Calcd for $C_{29}H_{74}N_6Si_6U$: C, 38.13; H, 8.17; N, 9.20. Found: C, 38.47; H, 8.23; N, 9.29.

$[(Im^{Mes}N)U\{N(SiMe_3)_2\}_3]$ (**4**): yield 92% (665 mg, 0.64 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ −13.17 (s, 54 H, $Si(CH_3)_3$), −3.87 (s, 6 H, *para*-CH_3), 6.19 (s, 4 H, H_{ar}), 17.30 (s, 12 H, *ortho*-CH_3), 27.75 (s, 2 H, CH); ^{13}C NMR (75.5 MHz, C_6D_6) δ 2.63 ($Si(CH_3)_3$), 19.24 (CH_3), 32.72 (CH_3), 57.32 (CH), 131.68 (C_{ar}—H), 151.81 (C_{ar}—C), 158.91 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −11.74. Anal. Calcd for $C_{39}H_{78}N_6Si_6U$: C, 45.14; H, 7.58; N, 8.10. Found: C, 44.87; H, 7.63; N, 7.98.

$[(Im^{Dipp}N)U\{N(SiMe_3)_2\}_3]$ (**5**): yield 95% (742 mg, 0.66 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ −9.01 (s, 54 H, $Si(CH_3)_3$, −4.96 (s, 12 H $CH(CH_3)_2$), 1.28 (s, 12 H, $CH(CH_3)_2$), 7.15−7.92 (m, 6 H, H_{ar}), 25.77 (s, 4 H, $CH(CH_3)_2$), 26.46 (s, 2 H, CH); ^{13}C NMR (75.5 MHz, C_6D_6) δ 2.69 ($Si(CH_3)_3$), 18.87 ($CH(CH_3)_2$), 24.00 ($CH(CH_3)_2$), 28.95 ($CH(CH_3)_2$), 33.64 ($CH(CH_3)_2$), 37.93 ($CH(CH_3)_2$), 59.27 (CH), 132.97 (C_{ar}—H), 158.41 (C_{ar}—C), 163.78 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −11.03. Anal. Calcd for $C_{45}H_{90}N_6Si_6U$: C, 48.14; H, 8.09; N, 7.49. Found: C, 48.60; H, 8.15; N, 7.43.

$[(Im^{tBu}N)Th\{N(SiMe_3)_2\}_3]$ (**6**): yield 95% (605 mg, 0.67 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.50 (s, 54 H, $Si(CH_3)_3$), 1.48 (s, 18 H, $C(CH_3)_2$), 5.86 (s, 2 H, CH); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.90 ($Si(CH_3)_3$), 30.96 ($C(CH_3)_3$), 56.06 ($C(CH_3)_3$), 108.63 (CH), 145.35 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −9.89. Anal. Calcd for $C_{29}H_{74}N_6Si_6Th$: C, 38.38; H, 8.22; N, 9.26. Found: C, 38.56; H, 8.27; N, 9.33.

$[(Im^{Mes}N)Th\{N(SiMe_3)_2\}_3]$ (**7**): yield 94% (681 mg, 0.66 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.38 (s, 54 H, $Si(CH_3)_3$), 2.18 (s, 6 H, *para*-CH_3), 2.30 (s, 12 H, *ortho*-CH_3), 5.50 (s, 2 H, CH), 6.76 (s, 4 H, H_{ar}); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.63 ($Si(CH_3)_3$), 20.25 (CH_3), 21.10 (CH_3), 112.33 (CH), 136.90 (C_{ar}—H), 138.63 (C_{ar}—C), 145.23 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −10.12. Anal. Calcd for $C_{39}H_{78}N_6Si_6Th$: C, 45.41; H, 7.62; N, 8.15. Found: C, 45.71; H, 7.66; N, 8.19.

$[(Im^{Dipp}N)Th\{N(SiMe_3)_2\}_3]$ (**8**) yield 98% (768 mg, 0.69 mmol); ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.40 (s, 54 H, $Si(CH_3)_3$, 1.10 (d, J = 6.71 Hz, 12 H $CH(CH_3)_2$), 1.45 (d, J = 6.71 Hz, 12 H, $CH(CH_3)_2$), 3.31 (m, 4 H, $CH(CH_3)_2$), 5.75 (s, 2 H, CH), 7.14−7.16 (m, 6 H, H_{ar}); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.99 ($Si(CH_3)_3$), 23.79

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($CH(CH_3)_2$), 25.81 ($CH(CH_3)_2$), 28.66 ($CH(CH_3)_2$), 115.49 (CH), 125.13 (C_{ar}—H), 136.37 (C_{ar}—C), 147.61 (C_{ipso}═N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −9.79. Anal. Calcd for $C_{45}H_{90}N_6S_{i6}Th$: C, 48.44; H, 8.13; N, 7.53. Found: C, 48.94; H, 8.19; N, 7.46.

General Procedure for the Catalytic Tishchenko Reaction. A sealable J. Young NMR tube was loaded with 5.00 mg (4.48 μmol) of complex **3**−**8** from a stock solution in C_6D_6 inside the glovebox. The respective aldehyde (0.448 mmol, 100 equiv) was added, and the reaction was immediately diluted to 500 μL with C_6D_6. Solid aldehydes were dissolved in 300 μL of C_6D_6 before being added to the solution of the precatalyst. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 24 h, the tube was opened to air, and the reaction was quenched with methanol. The products were identified by ^{1}H NMR spectroscopy and MS analysis, and the chemical shifts were compared with previously reported literature data.[29,48−55]

Esterification of Benzaldehyde. The esterification of benzaldehyde (46.0 μL, 0.448 mmol) was carried out following the general procedure described above. Benzylbenzoate[29] was obtained in 100% yield after 24 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 5.17 (s, 2 H, CH_2), 7.06−7.28 (m, 8 H, H_{ar}), 8.09 (d, J = 7.66 Hz, H_{ar}). MS: m/z 213.11 (M^+), 92.09 ($PhCH_2^+$).

Esterification of 1-Naphthylaldehyde. The esterification of 1-naphthylaldehyde (61.0 μL, 0.448 mmol) was carried out following the general procedure described above. 1-Naphthylmethyl 1-naphthoate[48] was obtained in 32% yield, after a reaction time of 24 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 5.89 (s, 2 H, CH_2), 7.39−7.98 (m, 14 H, H_{ar}). MS: m/z 312.13 (M^+), 141.07 ($ArCH_2^+$).

Esterification of 2-Naphthylaldehyde. The esterification of 2-naphthylaldehyde (70.0 mg, 0.448 mmol) was carried out following the general procedure described above. 2-Naphthylmethyl 2-naphthoate[48] was obtained in 61% yield after a reaction time of 24 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 5.63 (s, 2 H, CH_2), 7.36−8.31 (m, 14 H, H_{ar}). MS: m/z 312.16 (M^+), 141.09 ($ArCH_2^+$).

Esterification of 4-Nitrobenzaldehyde. The esterification of 4-nitrobenzaldehyde (68.0 mg, 0.448 mmol) was carried out following the general procedure described above. 4′-(Nitrobenzyl)-4-nitrobenzoate[29] was obtained in 100% yield after a reaction time of 24 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 4.78 (s, 2 H, CH_2), 6.76−6.79 (m, 2 H, H_{ar}), 7.27−7.35 (m, 2 H, H_{ar}), 7.56−7.73 (m, 4 H, H_{ar}). MS: m/z: 303.23 (M^+), 137.9 ($ArCH_2^+$).

Esterification of Cyclohexanecarbaldehyde. The esterification of cyclohexanecarbaldehyde (54.0 μL, 0.448 mmol) was carried out following the general procedure described above. Cyclohexylmethyl cyclohexanecarboxylate[49] was obtained in 100% yield after a reaction time of 12 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 0.90−2.34 (m, 22 H, CH_2), 3.85 (d, J = 6.87 Hz, 2 H, CH_2). MS: m/z 225.18 (M^+), 98.15 ($ChexCH_2^+$).

Esterification of Cyclopentanecarbaldehyde. The esterification of cyclopentanecarbaldehyde (48.0 μL, 0.448 mmol) was carried out following the general procedure described above. Cyclopentylmethyl cyclopentanecarboxylate[50] was obtained in 100% yield after a reaction time of 12 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.02−2.67 (m, 18 H, CH_2), 3.89 (d, J = 7.3 Hz, 2 H, CH_2). MS: m/z 197.16 (M^+), 97.09 ($CpentCO^+$).

Esterification of Isobutyraldehyde. The esterification of isobutyraldehyde (41.0 μL, 0.448 mmol) was carried out following the general procedure described above. Isobutylisobutyrate[51] was obtained in 100% yield after a reaction time of 12 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 0.87 (d, J = 6.37 Hz, 6 H, CH_3), 1.07 (d, J = 6.56 Hz, 6 H, CH_3), 2.45−2.55 (m, 2 H, CH), 3.79 (d, J = 6.71 Hz, 2 H, CH_2). MS: m/z 145.11(M^+).

Lactonization of Phthalaldehyde. The lactonization of phthalaldehyde (60.0 mg, 0.448 mmol) was carried out following the general procedure described above. Phthalide[52] was obtained in 100% yield after a reaction time of 6 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 5.21 (s, 2 H, CH_2), 7.48−7.55 (m, 1 H, H_{ar}), 7.71−7.76 (m, 1 H, H_{ar}), 7.81−7.89 (m, 1 H, H_{ar}), 8.10 (d, J = 7.59 Hz, 1 H, H_{ar}). MS: m/z 134.95 (M^+).

General Procedure for the Catalytic Crossed Tishchenko Reaction. A sealable J. Young NMR tube was loaded with 5.00 mg (4.48 μmol) of complex **8** from a stock solution in C_6D_6 inside the glovebox. The respective aromatic aldehyde (0.896 mmol, 200 equiv) and aliphatic aldehyde (0.224 mmol, 50 equiv) were added, and the reaction was immediately diluted to 750 μL with C_6D_6. Solid aldehydes were dissolved in 300 μL of C_6D_6 before being added to the catalyst solution. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 24 h, the tube was opened to air and the reaction quenched with methanol. The products were identified by ^{1}H NMR spectroscopy and MS analysis, and the values were compared to previous literature.

Cross-Esterification of Benzaldehyde with Cyclohexanecarbaldehyde. Tthe cross-esterification of benzaldehyde (93.0 μL, 0.896 mmol) and cyclohexanecarbaldehyde (27.0 μL, 0.224 mmol) was carried out following the general procedure described above. Benzylcyclohexanecarboxylate[53] was obtained in 92% yield after a reaction time of 1.5 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.10−1.87 (m, 10 H, CH_2), 2.29 (m, 1 H, CH), 5.09 (s, 2 H, CH_2), 7.20−7.37 (m, 5 H, H_{ar}). MS: m/z 219.14 (M^+).

Cross-Esterification of Benzaldehyde with Cyclopentanecarbaldehyde. The cross-esterification of benzaldehyde (93.0 μL, 0.896 mmol) and cyclopentanecarbaldehyde (24.0 μL, 0.224 mmol) was carried out following the general procedure described above. Benzylcyclopentanecarboxylate was obtained in 84% yield after a reaction time of 1.5 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.51−1.93 (m, 8 H, CH_2), 2.73 (m, 1 H, CH), 5.11 (s, 2 H, CH_2), 7.26−7.38 (m, 5 H, H_{ar}). MS: m/z 205.13 (M^+).

Cross-Esterification of Benzaldehyde with Isobutyraldehyde. The cross-esterification of benzaldehyde (93.0 μL, 0.896 mmol) and isobutyraldehyde (20.0 μL, 0.224 mmol) was carried out following the general procedure described above. Benzylisobutyrate[54] was obtained in 80% yield after a reaction time of 1.5 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.17 (d, J = 7.30 Hz, 6 H, CH_3), 2.51−2.53 (m, 1 H, CH), 5.10 (s, 2 H, CH_2), 7.25−7.38 (m, 5 H, H_{ar}). MS: m/z 179.17 (M^+), 73.08 ($CH(CH_3)_2CO^+$).

Cross-Esterification of 1-Naphthaldehyde with Cyclohexanecarbaldehyde. The cross-esterification of benzaldehyde (112.0 μL, 0.896 mmol) and cyclohexanecarbaldehyde (27.0 μL, 0.224 mmol) was carried out following the general procedure described above. 1-Naphthylmethylcyclohexanecarboxylate[55] was obtained in 100% yield after a reaction time of 1.5 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.21−2.04 (m, 10 H, CH_2), 2.43 (m, 1 H, CH), 5.63 (s, 2 H, CH_2), 7.40−7.90 (m, 6 H, H_{ar}), 8.04 (d, J = 8.6 Hz, 1 H, H_{ar}) MS: m/z 269.38 (M^+).

Cross-Esterification of 2-Naphthaldehyde with Cyclohexanecarbaldehyde. The cross-esterification of benzaldehyde (140.0 mg, 0.896 mmol) and cyclohexanecarbaldehyde (27.0 μL, 0.224 mmol) was carried out following the general procedure described above. 2-Naphthylmethylcyclohexanecarboxylate[55] was obtained in 88% yield after a reaction time of 1.5 h. ^{1}H NMR (300.00 MHz, C_6D_6): δ 1.25−2.01 (m, 10 H, CH_2), 2.40 (m, 1 H, CH), 5.29 (s, 2 H, CH_2), 7.46−7.81 (m, 7 H, H_{ar}). MS: m/z 269.33 (M^+).

Intermediate Trapping Experiments. A sealable J. Young NMR tube was loaded with 50.0 mg (44.8 μmol) of complex **8** and dissolved in 1.0 mL of C_6D_6 inside the glovebox. Benzaldehyde (10 μL, 89.6 μmol, 2.1 equiv) and the solution of catalyst **8** were added inside the glovebox. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After full consumption of the benzaldehyde after 30 min to give complex **A**, benzaldehyde (10 μL, 89.6 μmol, 2.1 equiv) was added to the reaction mixture inside the glovebox and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. Complex **B** was obtained after 30 min. Then, benzaldehyde (10 μL, 89.6 μmol, 2.1 equiv) was added to the reaction mixture, yielding complex **E** and ester **D** after 30 min.

$[(Im^{Dipp}N)Th\{OCHN(SiMe_3)_2\}_2\{N(SiMe_3)_2\}]$ (**A**): ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.13 (s, 36 H, $Si(CH_3)_3$), 0.41 (s, 18 H, $Si(CH_3)_3$), 1.11 (d, J = 6.44 Hz, 12 H, $CH(CH_3)_2$), 1.47 (d, J = 6.44 Hz, 12 H, $CH(CH_3)_2$), 3.33−3.36 (m, 4 H, $CH(CH_3)_3$), 5.78 (s, 2 H, CH), 5.90 (s, 2 H, $CH(N(SiMe_3)_2)$, 7.00−7.11 (m, 10 H, H_{ar}), 7.14−

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7.55 (m, 6 H, H_{ar}); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.15 ($Si(CH_3)_3$), 5.98 ($Si(CH_3)_3$), 23.81 ($CH(CH_3)_2$), 25.80 ($CH(CH_3)_2$), 28.71 ($CH(CH_3)_2$), 68.90 ($CH(N(Si(CH_3)_3)$), 115.79 (CH), 124.49−137.17 (C_{ar}), 148.10 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −32.81 ($Si(CH_3)_3$), −9.81 ($Si(CH_3)_3$).

[(Im^{Dipp}N)Th{$OCHPhOCH_2Ph$}$_2${$N(SiMe_3)_2$}] (**B**): ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.41 (s, 18 H, $Si(CH_3)_3$), 1.13 (d, J = 6.90 Hz, 12 H, $CH(CH_3)_2$), 1.44 (d, J = 6.90 Hz, 12 H, $CH(CH_3)_2$), 3.31−3.36 (m, 4 H, $CH(CH_3)_2$), 4.20 (s, 2 H, OCHPh), 5.19 (s, 4 H, OCH_2Ph), 7.11−7.70 (m, 26 H, Har); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.90 ($Si(CH_3)_3$), 23.81 ($CH(CH_3)_2$), 25.80 ($CH(CH_3)_2$), 28.67 ($CH(CH_3)_2$), 61.12 (OCH_2Ph), 79.23 (OCHPh), 115.79 (CH), 124.79−137.51 (C_{ar}), 147.72 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −9.82.

[(Im^{Dipp}N)Th{OCH_2Ph}$_2${$N(SiMe_3)_2$}] (**E**): ^{1}H NMR (300.0 MHz, C_6D_6) δ 0.41 (s, 18 H, $Si(CH_3)_3$), 1.14 (d, J = 6.85 Hz, 12 H, $CH(CH_3)_2$), 1.44 (d, J = 6.85 Hz, $CH(CH_3)_2$), 3.32−3.36 (m, 4 H, $CH(CH_3)_2$), 5.21 (s, 4 H, OCH_2Ph), 5.79 (s, 2 H, CH), 7.14−7.68 (m, 16 H, H_{ar}); ^{13}C NMR (75.5 MHz, C_6D_6) δ 5.91 ($Si(CH_3)_3$), 23.80 ($CH(CH_3)_2$), 25.79 ($CH(CH_3)_2$), 28.67 ($CH(CH_3)_2$), 55.71 (CH_2Ph), 116.00 (CH), 125.16−136.54 (C_{ar}), 147.55 (C_{ipso}=N); ^{29}Si NMR (59.6 MHz, C_6D_6) δ −9.81.

General Procedure for Reactions with Stoichiometric Amounts of Aldehydes. A sealable J. Young NMR tube was loaded with 50.0 mg (44.8 μmol) of complex **8** from a stock solution in C_6D_6 inside the glovebox. The respective aldehyde (0.228 mmol, 6.20 equiv) was added, and the reaction was immediately diluted to 1000 μL with C_6D_6. Solid aldehydes were dissolved in 300 μL of C_6D_6 before being added to the solution of the precatalyst. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 3 h, the tube was opened to air, and the reaction was quenched with methanol. The products (**D1**−**D8**) were characterized by ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy and MS analysis.

Stoichiometric Reaction with Benzaldehyde. The stoichiometric reaction with benzaldehyde (24 μL, 0.228 mmol) was carried out following the general procedure described above. ((Bis(trimethylsilyl)amino)phenyl)methyl 2-benzoate (**D1**) was obtained in 95% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.10 (s, 18 H, $Si(CH_3)_3$), 6.15 (s, 1 H, CH), 7.29−7.41 (m, 10 H, H_{ar}). ^{13}C NMR (75.5 MHz, C_6D_6): δ 3.15 ($Si(CH_3)_3$), 82.3 ($CHN(Si(CH_3)_3)_2$), 125.3−132.5 (C_{ar}), 169.4 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −1.76. MS: m/z 372.2 (M^+).

Stoichiometric Reaction with 1-Naphthylaldehyde. The stoichiometric reaction with 1-naphthylaldehyde (31 μL, 0.228 mmol) was carried out following the general procedure described above. (Bis(trimethylsilyl)amino)(naphthalen-1-yl)methyl 1-naphthanoate (**D2**) was obtained in 92% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.05 (s, 18 H, $Si(CH_3)_3$), 6.98 (s, 1 H, CH), 7.31−7.43 (m, 8 H, H_{ar}), 7.50−7.57 (m, 6 H, H_{ar}). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.68 ($Si(CH_3)_3$), 84.2 ($CHN(Si(CH_3)_3)_2$), 121.9−134.5 (C_{ar}), 166.5 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −1.98. MS: m/z 472.4 (M^+).

Stoichiometric Reaction with 2-Naphthylaldehyde. The stoichiometric reaction with 2-naphthylaldehyde (36.0 mg, 0.228 mmol) was carried out following the general procedure described above. (Bis(trimethylsilyl)amino)(naphthalene-2-yl)methyl 2-naphthoate (**D3**) was obtained in 93% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.05 (s, 18 H, $Si(CH_3)_3$), 7.07 (s, 1 H, CH), 7.47−7.51 (m, 14 H, H_{ar}). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.79 ($Si(CH_3)_3$), 87.5 ($CHN(Si(CH_3)_3)_2$), 124.9−135.8 (C_{ar}), 166.5 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −2.03. MS: m/z 472.3 (M^+).

Stoichiometric Reaction with 4-Nitrobenzaldehyde. The stoichiometric reaction with 4-nitrobenzaldehyde (35.0 mg, 0.228 mmol) was carried out following the general procedure described above. (Bis(trimethylsilyl)amino)(4-nitrophenyl)methyl 4-nitrobenzoate (**D4**) was obtained in 98% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.15 (s, 18 H, $Si(CH_3)_3$), 7.02 (s, 1 H, CH), 7.57−7.67 (m, 8 H, H_{ar}). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.59 ($Si(CH_3)_3$), 86.7 ($CHN(Si(CH_3)_3)_2$), 125.4−155.3 (C_{ar}), 166.1 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −2.36. MS: m/z 462.2 (M^+).

Stoichiometric Reaction with Cyclohexanecarbaldehyde. The stoichiometric reaction with cyclohexanecarbaldehyde (28 μL, 0.228 mmol) was carried out following the general procedure described above. (Bis(trimethylsilyl)amino)(cyclohexyl)methyl cyclohexanecarboxylate (**D5**) was obtained in 99% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.04 (s, 18 H, $Si(CH_3)_3$), 1.39−1.60 (m, 20 H, CH_2), 1.67−1.84 (m, 2 H, CH), 5.69 (s, 1 H, CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.99 ($Si(CH_3)_3$), 23.5−49.1 (CH_2), 81.5 ($CHN(Si(CH_3)_3)_2$), 175.8 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −0.97. MS: m/z 384.3 (M^+).

Stoichiometric Reaction with Cyclopentanecarbaldehyde. The stoichiometric reaction with cyclopentanecarbaldehyde (24 μL, 0.228 mmol) was carried out following the general procedure described above. (Bis(trimethylsilyl)amino)(cyclopentyl)methyl cyclopentanecarboxylate (**D6**) was obtained in 99% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.04 (s, 18 H, $Si(CH_3)_3$), 1.84−2.01 (m, 18 H, CH_2), 2.17−2.59 (m, 2 H, CH), 5.26 (s, 1 H, CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ 6.21 ($Si(CH_3)_3$), 25.4−45.1 (CH_2), 83.5 ($CHN(Si(CH_3)_3)_2$), 171.6 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −0.89. MS: m/z 356.3 (M^+).

Stoichiometric Reaction with Isobutyraldehyde. The stoichiometric reaction with isobutyraldehyde (21 μL, 0.228 mmol) was carried out following the general procedure described above. 1-(Bis(trimethylsilyl)amino-2-methylpropyl isobutyrate (**D7**) was obtained in 97% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.05 (s, 18 H, $Si(CH_3)_3$), 1.01 (d, J = 6.56 Hz, 6 H, $CH(CH_3)_2$), 1.03 (d, J = 6.56 Hz, 6 H, $CH(CH_3)_2$), 2.26−2.33 (m, 2 H, $CH(CH_3)_2$), 5.81 (s, 1 H, CH). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.13 ($Si(CH_3)_3$), 15.17 ($CH(CH_3)_2$), 17.59 ($CH(CH_3)_2$), 34.7 ($CH(CH_3)_2$), 89.1 (CH), 174.3 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −0.92. MS: m/z 304.3 (M^+).

Stoichiometric Reaction with Phthalaldehyde. The stoichiometric reaction with phthalaldehyde (16 mg, 0.114 mmol) was carried out following the general procedure described above. 3-(Bis(trimethylsilyl)amino)isobenzofuran-1(3*H*)-one (**D8**) was obtained in 99% yield after a reaction time of 3 h. ^{1}H NMR (300.0 MHz, C_6D_6): δ 0.06 (s, 18 H, $Si(CH_3)_3$), 5.93 (s, 1 H, CH), 7.09−7.11 (m, 2 H, H_{ar}), 7.62−7.64 (m, 2 H, H_{ar}). ^{13}C NMR (75.5 MHz, C_6D_6): δ 5.15 ($Si(CH_3)_3$), 91.24 (CH), 121.3−138.4 (C_{ar}), 168.3 (C=O). ^{29}Si NMR (59.6 MHz, C_6D_6): δ −1.31. MS: m/z 294.1 (M^+).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and crystallographic information for complexes **3**−**8** are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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