noesters with tri-*n*-butyltin hydride to give aldehydes, although **1'h** is less reactive compared with (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones (**1**).

The palladium-catalyzed carbonylative addition of terminal acetylene (eq 2) and the reduction of **1** by *n*-Bu$_3$SnH (eq 3) can be carried out successively without isolation of **1**.[16] This one-pot transformation from acetylene to **2** is synthetically equivalent to regio- and stereoselective selenoformylation of acetylene (Scheme I).

The present investigation provides the first example of transition-metal-catalyzed reduction of selenoesters with tin hydride to aldehydes: (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones are converted into (*Z*)-3-(arylseleno)-2-alkenals with excellent chemoselectivity and site selectivity in high yields under moderate reaction conditions. This paper also reveals the utility of transition-metal catalysts in synthetic reactions using chalcogen compounds.[17]

Acknowledgment. This research was supported by a Grant-in-Aid for Developmental Scientific Research (No. 03555183) from the Ministry of Education, Science, and Culture of Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining mass spectra with a JEOL JMS-DX303 instrument and elemental analyses.

Supplementary Material Available: Text giving experimental details and analytical and spectroscopic data for the compounds formed (4 pages). Ordering information is given on any current masthead page.

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(16) For example, in a 50 mL stainless steel autoclave were placed 1-octyne (1.0 mmol), (PhSe)$_2$ (1.0 mmol), Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol), and benzene (0.5 mL). After the mixture was stirred for 18 h at 80 °C under pressurized CO (20 kg/cm^2), CO was purged and benzene (15 mL) was added to the reaction mixture. Then *n*-Bu$_3$SnH (1.0 mmol) was added over a period of 5 min under a flow of argon. The reaction mixture was filtered through Celite and concentrated in vacuo. The formation of **2a** was confirmed by ^{1}H NMR spectroscopy (86%, *E*:*Z* = 11:89).

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Organometallic Molecule–Inorganic Surface Coordination and Catalytic Chemistry. Facile and Selective Alkane Activation by Supported Tetraallylthorium

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Summary: The adsorption of Th(η^3-allyl)$_4$ on dehydroxylated alumina yields an active catalyst for the exchange of alkane and cycloalkane C–H bonds with D$_2$. C–H reactivities fall in the order primary > secondary > tertiary and less sterically hindered > more sterically hindered.

Although significant advances have been made in the activation of C–H bonds by f-element/early-transition-element[1,2] and middle-/late-transition-element[1,3] complexes, closing cycles which effect the catalytic intermolecular activation of relatively inert alkane molecules with favorable rates and selectivities remains a major challenge. For organo-f-element/early-transition-element complexes, key questions concern whether catalytic processes may be insurmountably constrained by intrinsic electronic, steric, or other factors (e.g., inactivating side reactions) or whether activities higher than heretofore observed[1,2] are possible. We have recently shown that adsorption of organothorium complexes on Lewis acidic surfaces such as dehydroxylated alumina (DA) affords highly electrophilic molecular surface species[4] which are active olefin hydrogenation and polymerization catalysts.[5,6] Activity scales approximately as catalyst precursor coordinative unsaturation, with Th(η^3-allyl)$_4$/DA mediating traditionally demanding arene hydrogenation at rates rivaling those of supported platinum metal catalysts.[7] We now report that Th(η^3-al-

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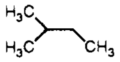
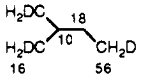
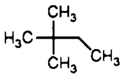
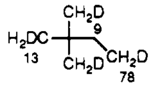
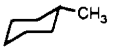
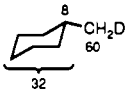
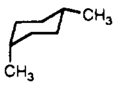
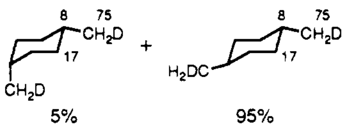
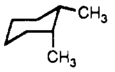
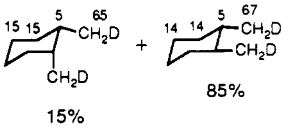
Table I. Kinetic and Product Structure/Label Distribution Data for Th(η^3-allyl)$_4$/DA-Catalyzed Alkane C–H → C–D Functionalization[a]

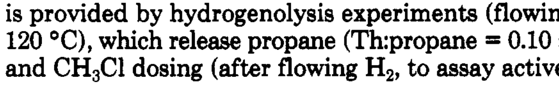
entry no.	substrate	N_t (h^{-1})[b]	deuterium distribn in product (%)[c]
1	$CH_3CH_2CH_2CH_2CH_3$	778	$CH_2DCHDCHDCHDCH_2D$ 58 32 10
2		879	
3		825	
4	C_6H_{12}	1285	$C_6H_{12-x}D_x$[d]
5		1113	
6		884	
7		834	

[a] At 90 °C, 50 psi D_2; Th:substrate ≈ 1:1000; D_2:substrate ≈ 100:1. [b] Substrate C–H bonds converted/(catalyst active site/h). [c] From $^{13}C\{^1H\}$, ^{13}C, and $^2H\{^1H\}$ NMR spectroscopy; estimated uncertainty ±5%. [d] Different isotopomers cannot be resolved by NMR spectroscopy.

lyl)$_4$/DA also catalyzes the rapid and selective deuteration of linear and cyclic alkanes. The C–H activation data (rates, regiochemistry), poisoning, and spectroscopoic measurements, as well as data on concurrent skeletal rearrangements, provide preliminary information on mechanism and active site structure.

Th(η^3-allyl)$_4$[8] was adsorbed (~0.20 molecule/nm^2 by ICP) on DA from pentane solution using the rigorously anaerobic techniques described elsewhere.[5] Slurries of this catalyst were rapidly stirred in neat alkane (Th:substrate = 1:1000) under a D_2 atmosphere (50 psi; D_2:substrate ≈ 100:1) at 90 °C.[9] Product analysis by $^{13}C\{^1H\}$, ^{13}C, and $^2H\{^1H\}$ NMR as well as by GC-MS (Table I) reveals rapid C–H/C–D exchange. Indeed, turnover frequencies are comparable to, or exceed those, of conventional group 9 heterogeneous alkane activation catalysts.[10] C–H functionalization occurs with substantial selectivity and in an order which does not parallel C–H bond dissociation enthalpies:[11] primary > secondary > tertiary and sterically less hindered > sterically more hindered. NMR and GC-MS as a function of conversion reveal stepwise single C–H exchanges, with no evidence for preferential multiple exchange processes[12] (e.g., nonstatistical amounts of RD_2 species are below the detection limit). Interestingly, entries 6 and 7 in Table I also reveal concurrent isomerization of the *cis*-dimethylcyclohexanes to cis–trans mixtures[13] during C–H/C–D exchange. Control experiments indicate that neat DA exhibits negligible catalytic activity for any of the aforementioned transformations under the present reaction conditions.[14]

Previous CPMAS NMR studies showed that the adsorption chemistry of organoactinides on DA involves the transfer of alkyl anions to Lewis acid sites on the surface with formation of electrophilic organoactinide cations.[4] Although the present adsorbate coverages are too low for surface NMR studies, it is reasonable to postulate similar chemistry (e.g., eq 1). Progressive dosing of a working catalyst with measured quantities of H_2O effects a monotonic decrease in N_t (poisoning[5b–d]), assays active Th–R/Th–H functionalities, and indicates that the upper limit of Th(η^3-allyl)$_4$/DA sites which are catalytically significant is 8 ± 1% (a common state of affairs in heterogeneous catalysis[4]). Corroborative information on Th(η^3-allyl)$_4$/DA is provided by hydrogenolysis experiments (flowing H_2 at 120 °C), which release propane (Th:propane = 0.10 ± 0.02), and CH_3Cl dosing (after flowing H_2, to assay active Th–H



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[9] In a typical experiment, a 60-mL Griffin–Worden quartz medium-pressure reactor having a two-port head and connected to a 500-mL metal gas ballast tank was flamed under high vacuum and charged in the glovebox with 50 mg of Th(η^3-C_3H_5)$_4$/DA (2.0 × 10^{-6} mol of Th). A magnetic stirbar was next introduced and the apparatus removed from the glovebox and attached to a high-vacuum line. After thorough evacuation (10^{-6} Torr), 1.0 mL (7.5 × 10^{-3} mol) of freshly distilled (from Na/K) 2,2-dimethylbutane was transferred under vacuum onto the supported organoactinide at −78 °C. The reactor was then warmed to room temperature and pressurized to 50 psi of D_2 (passed through activated SiO_2 at 77 K). The reactor was immersed in a thermostated oil bath maintained at 90 ± 0.1 °C and stirred rapidly at a rate sufficient to avoid mass-transfer effects (800 rpm).[7b] Products were isolated by vacuum transfer subsequent to 77 K quenching.

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[13] (a) Estimated[13b] 90 °C cis ⇌ trans equilibrium constants for entries 6 and 7 are 14.1 (33.6) and 13.4 (31.8), respectively, at 90 (25) °C. (b) Thermodynamic data: Kalsi, P. S. *Stereochemistry, Conformation, and Mechanism*; Wiley: New York, 1990; Chapter 4.

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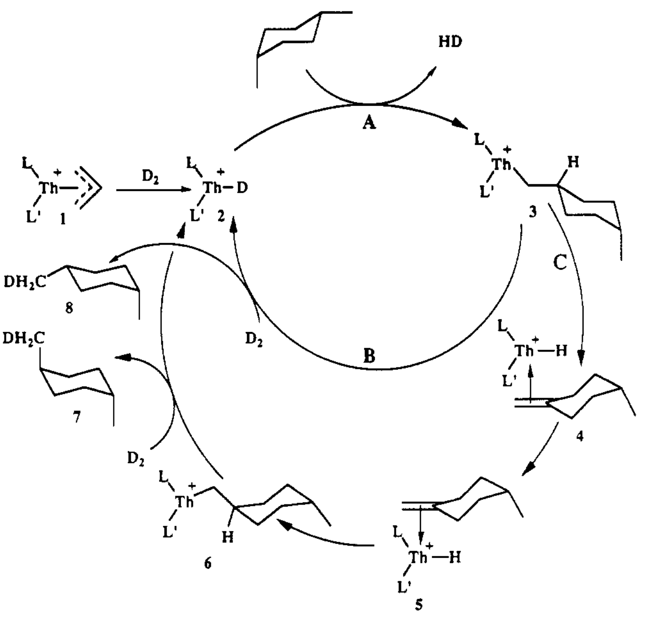
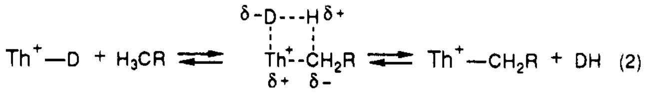
Scheme I. Possible Scenario for the Th(η^3-allyl)$_4$/DA-Catalyzed C–H Activation and Isomerization of Alkanes



functionalities), which yields Th:methane = 0.08 ± 0.02. Since replacement of a single Th–R functionality by Th–O– or Th–Cl is expected to radically alter active site reactivity,[4,5] these results suggest that the chemical probes are sampling the same sites/functionalities and that the active sites possess a single reactive metal–ligand σ bond (e.g., (L)(L')Th^+–R). It is also found that benzene is an inhibitor of alkane activation in that C–H/C–D exchange is not observed until conversion to $C_6H_6D_6$[7] is complete. In accord with the difficult reduction of Th(IV),[16] quantitative EPR spin counting experiments indicate that detectable Th(III)[16a] is $\leq 10^{-5}\%$ of the Th(η^3-allyl)$_4$/DA sites, while XPS using a load-lock sample inlet chamber reveals only (≥95%) Th(IV)[17] $4f_{7/2}$ and $4f_{5/2}$ signals at 338 and 349 eV, respectively.

A reasonable mechanistic scenario for alkane activation (Scheme I) invokes the microscopic reverse of Th–hydrocarbyl hydrogenolysis:[18] presumably endothermic[19] Th–C bond formation and HD elimination via a "four-center", heterolytic "σ-bond metathesis" pathway (e.g., eq 2; A,



$$\mathrm{Th^{+}{-}D + H_3CR \rightleftharpoons \begin{matrix} {}^{\delta-}D\cdots H^{\delta+} \\ \vdots \qquad \vdots \\ Th^{+}\cdots CH_2R \\ \delta+ \quad \delta- \end{matrix} \rightleftharpoons Th^{+}{-}CH_2R + DH} \qquad (2)$$

Scheme I)[20] followed by deuterolysis (B; the microscopic reverse).[18] Cycloalkane skeletal isomerization could then occur via β-H elimination (C) and readdition of Th^+–H[5b,21] to the opposite face of the olefin. This process (5 → 6) would involve rapid olefin dissociation–readdition, although a concerted, "tumbling" process in which the olefin remains weakly bound, e.g., by a C–H "agostic" interaction, cannot be ruled out. Interestingly, the isotopic labeling experiments (Table I) reveal little D incorporation at the dimethylcyclohexane tertiary carbon centers and negligible differences in the D label distribution of the isomerized and unisomerized hydrocarbons. These results argue that the abstracted H atom must be readded[21] on a time scale more rapid than the exchange of Th–H with D_2 (which homogeneous[20] and heterogeneous[18b] precedent suggests is rapid). Moreover, these results argue in accord with the chemical probes (vide supra) either that ancillary ligands L and L' in Scheme I non-D in identity (e.g., η^3-allyl or oxide) or that such Th–D functionalities are chemically/stereochemically inequivalent to those formed via β-H abstraction and hence cannot compete for olefin addition.[23,24] The aforementioned apparent steric sensitivity of the C–H functionalization process (Table I) also argues that the functioning catalyst center is surrounded by significant ligational bulk (it is not "naked" ThH_3^+).

In summary, these results demonstrate that supported organo-f-element catalysts are competent for the rapid and selective activation of alkane and cycloalkane C–H bonds. While the active sites are likely to be electrophilic and coordinatively unsaturated, the present data also suggest non-negligible ancillary ligation having steric and stereochemical consequences.

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(23) Similar arguments apply if the β-H elimination/isomerization involves an endocyclic C–H functionality.

(24) A reviewer has suggested that dimethylcyclohexane isomerization may occur via an unprecedented β-carbocationic Th-hydrocarbyl arising from β-H^- transfer to Th in C (Scheme I). The present data do not rigorously exclude this possibility; however, we note the absence of classical carbocation rearrangement patterns (e.g., methyl shifts) among the products in Table I. Regardless of how the β-H transfer is depicted, the results indicate the resulting Th–H does not exchange with D prior to readdition to the hydrocarbon fragment.