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Supported Organoactinide Complexes as Heterogeneous Catalysts. A Kinetic and Mechanistic Study of Facile Arene Hydrogenation

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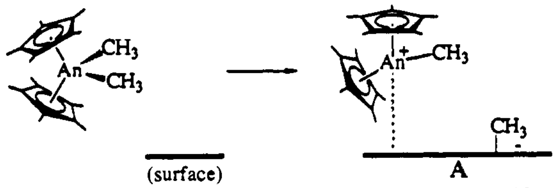
Abstract: This contribution reports a kinetic and mechanistic study of arene hydrogenation by the supported organoactinide complexes Cp′Th(benzyl)$_3$/DA (**1**/DA), Th(1,3,5-$CH_2C_6H_3Me_2$)$_4$/DA (**2**/DA), and Th(η^3-allyl)$_4$/DA (**3**/DA) where Cp′ = η^5-Me_5C_5 and DA = dehydroxylated γ-alumina. In slurry reactions (90 °C, P_{H_2} = 180 psi), the activity for benzene hydrogenation follows the order **1**/DA < **2**/DA < **3**/DA with an N_t value for **3**/DA of ~25 000 h^{-1} active site^{-1}. This approaches or exceeds most conventional platinum metal catalysts in efficacy for benzene reduction. Benzene hydrogenation by **3**/DA at 90 °C, P_{H_2} = 180 psi, follows the rate law $N_t = \nu[\text{benzene}]^0[P_{H_2}]^1$ with $N_t(H_2)/N_t(D_2) = 3.5 \pm 0.3$ and $E_a = 16.7 \pm 0.3$ kcal mol^{-1}. Partially hydrogenation products cannot be detected at partial conversions, and there is no D_2 incorporated in the unconverted benzene. D_2 is not delivered to a single benzene face, but rather a 1:3 mixture of *all-cis* and *cis,cis,trans,cis,trans* isotopomers is formed. Active site characterizations using D_2O poisoning, hydrogenolysis, and CH_3Cl dosing indicate that ≤8 ± 1% of the Th surface sites are responsible for the bulk of the benzene hydrogenation. EPR and XPS studies provide no evidence for surface Th oxidation states less than +4. As a function of arene, the relative rates of Th(η^3-C_3H_5)$_4$/DA-catalyzed hydrogenation are benzene > toluene > *p*-xylene > naphthalene, with the regiochemistry of *p*-xylene reduction similar to that for benzene. Experiments with 1:1 benzene–*p*-xylene mixtures reveal that benzene is preferentially hydrogenated with almost complete exclusion of *p*-xylene (~97:3), inferring that the benzene binding constant to the active sites is ~6.7× that of *p*-xylene. It is possible to propose a mechanism for arene hydrogenation which involves single Th(IV) sites, includes inoperativity of oxidation addition/reductive elimination sequences, and passes among established metal–ligand structures via precedented pathways.

Introduction

The absorption of early transition element and actinide hydrocarbyls on Lewis acidic surfaces (e.g., dehydroxylated alumina, $MgCl_2$, dehydroxylated SiO_2–Al_2O_3) is frequently accompanied by marked (and potentially useful) enhancements in catalytic activity for olefin conversions such as polymerization, hydrogenation, and metathesis.[1-5] Organoactinides[6] offer a number of advantageous features as probe precursor molecules for elucidating such surface reaction chemistry. These include well-defined/constrained formal metal oxidation states, a range of available precursor coordinative unsaturation levels, built-in diamagnetic/paramagnetic spectroscopic probes, and a growing data base of kinetic, mechanistic, and thermodynamic information. In earlier catalytic work, we reported that materials of the type $Cp'_2Th(CH_3)_2$/DA and $Cp'Th(CH_2C_6H_5)_3$/DA (Cp′ = η^5-Me_5C_5; DA = dehydroxylated γ-alumina) are highly active catalysts for ethylene polymerization and, per active site, rival the activities of the most active platinum metal catalysts (e.g., Rh/SiO_2) for the hydrogenation of simple olefins.[4c,d] The order of activity for the latter transformation, $Cp'Th(CH_2C_6H_5)_3$/DA > $Cp'_2Th(CH_3)_2$/DA > Cp_3ThCH_3/DA, suggests the importance of precursor coordinative unsaturation in determining ultimate adsorbate catalytic activity. Correlated ^{13}C CPMAS NMR experiments[5a,7] identify alkyl anion abstraction processes (e.g., eq 1) as a key function of the support Lewis acid sites.[8] Hydrocarbyl cations such as **A** are expected to be highly electrophilic and kinetically competent for the individual steps constituting olefin polymeri-



(1)

A

An = Th,U

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zation and hydrogenation cycles. Indeed, solution phase representations of A have recently confirmed these expectations.[9,10]

The above observations raise two intriguing issues. First, it would be of interest to learn whether supported organoactinide catalysts are active for more demanding catalytic transformations. Second, it would be of interest to evaluate the properties of organoactinide catalysts derived from precursors having greater coordinative unsaturation and/or offering the potential for more coordinatively unsaturated adsorbate structures. We report here a detailed study of the scope, regiochemistry, kinetics, and mechanism of arene hydrogenation catalyzed by a series of supported organothorium complexes. Arene hydrogenation is a particularly demanding transformation in homogeneous solution,[11-15] and in several cases the mechanism has been argued to involve oxidative addition/reductive elimination sequences at single molecular sites. Arene hydrogenation pathways catalyzed by typical heterogenous platinum metal catalysts likely involve multiple metal sites and formal shuttling between metal oxidation states (e.g., in dissociative H_2 chemisorption).[16,17] In contrast, supported organothorium complexes would appear to offer no possibility for oxidation state shuttling nor for classical metal cluster coordination effects. Nevertheless, it will be seen that supported organothorium complexes form the basis for a broad class of arene hydrogenation catalysts with $Th(\eta^3\text{-allyl})_4/DA$ rivalling the most active platinum metal catalysts in activity.

Experimental Section

All procedures were performed in Schlenk-type glassware interfaced to a high-vacuum (10^{-5}–10^{-6} Torr) line or in a nitrogen-filled Vacuum Atmosphere glovebox equipped with an efficient recirculating atmosphere purification system (typically 0.5–1.0 ppm of O_2). Argon (Matheson, prepurified) was further purified by passage through MnO/vermiculite and Davison 4A molecular sieves. Deuterium (Matheson) was purified by passing through a 77 K stainless steel column filled with silica (Davison 62) which had been heated in a helium stream at 120 °C for 1.0 h. Hydrogen (Matheson U.H.P.) was used as received. Naphthalene (Aldrich) was purified by three consecutive vacuum sublimations and was stored in a storage tube in the glovebox. $ThCl_4{\cdot}3THF$ was prepared by the recrystallization of $ThCl_4$ (Cerac) from THF at room temperature.[18] Allylmagnesium bromide (Aldrich) was used as received. Pentane (Aldrich, HPLC grade), toluene (Aldrich), benzene (Aldrich), and *p*-xylene (Aldrich) were distilled from Na/K alloy and were stored in vacuo over Na/K in bulbs on the vacuum line. Benzene-d_6 and toluene-d_8 (Cambridge Istotopes) were distilled from Na/K alloy. The compounds $Cp'Th(CH_2C_6H_5)_3$ (**1**)[19a] and $Th[1,3,5\text{-}CH_2C_6H_3Me_2]_4$ (**2**)[19b] were prepared according to established procedures. The support DA was prepared as previously described[4b,d] and was stored in vacuum-tight storage tubes under an inert nitrogen atmosphere at −20 °C.

Synthesis of $Th(\eta^3\text{-}C_3H_5)_4$ (3). In the glovebox, 700 mg (1.19 mmol) of $ThCl_4{\cdot}3THF$ was loaded into the 50-mL container of a two-sided fritted reaction vessel fritted with a Teflon valve side arm. At −78 °C, 25 mL of diethyl ether was condensed onto the white crystals, and then under an argon flush, a solution of allylmagnesium bromide (7.5 mL of a 1 M solution in diethyl ether; 7.15 mmol) was syringed onto the suspension. A yellow coloration was evident immediately upon the addition. The yellow solution was stirred at −78 °C for 1 h and then an additional 24 h at −20 °C to ensure completion of the reaction. The solvent was next removed at −20 °C in vacuo, and the resulting solids were extracted at −20 °C with 25 mL of diethyl ether. Following cold filtration, the filtrate was evaporated in vacuo at −20 °C and the residue extracted with 3 × 25 mL of toluene at −20 °C. The yellow extract was filtered and the filtrate was evaporated in vacuo at −20 °C (requiring 16 h). The resulting yellow residue was then extracted with 3 × 25 mL of pentane, the solution filtered, and the filtrate evaporated in vacuo at −20 °C. Using this procedure, no evidence of diethyl ether or THF was observed by ^1H NMR spectroscopy. Since $Th(\eta^3\text{-}C_3H_5)_4$ decomposes at 0 °C (forming a brown precipitate), it is necessary to perform all the above procedures at −20 °C. NMR samples were prepared by syringe transfer of an aliquot of a precooled solution of the complex in toluene-d_8 into a cooled J-Young NMR tube under an argon flush. ^1H NMR (400 MHz, C_7D_8 −20 °C) δ 5.993 (tt, $^3J_{syn} = 9.2$ Hz; $^3J_{anti} = 15.2$ Hz), 3.549 (d, $^3J = 9.2$ Hz), 2.371 (d, $^3J = 15.2$ Hz).

Impregnation of Supports with Organoactinide Complexes. In a two-sided fritted reaction vessel interfaced to the high-vacuum line, a cooled pentane solution containing a carefully measured quantity of the organoactinide complex of interest was filtered onto a carefully weighted quantity of support. The resulting slurry was next stirred for 30 min and filtered and the impregnated support was collected on the glass frit. The catalyst was then washed by transferring pentane from the filtrate to the chilled catalyst zone by distillation in vacuo, followed by suction filtration. This washing operation was repeated three times, and the sample was then dried in vacuo.

Catalytic Heterogeneous Hydrogenation Studies. In a typical experiment, a 60-mL Griffin-Worden quartz medium pressure reactor (Kontes Corp., Vineland, NJ) 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 80 mg of $Th(\eta^3\text{-}C_3H_5)_4/DA$ (3.2×10^{-6} mol of Th). A magnetic stir bar was next introduced, and the apparatus was removed from the glovebox and attached to the high-vacuum line. After thorough evacuation (10^{-6} Torr), 1.0 mL (1.1×10^{-2} mmol) of freshly distilled C_6H_6 was transferred under vacuum at −78 °C onto the supported organoactinide. The reactor was warmed to room temperature and pressurized to 190 psi of H_2. The reactor was then immersed in a thermostated oil bath maintained at 90 ± 0.1 °C and stirred rapidly (800 rpm). Control experiments showed that kinetic measurements (vide infra) were not influenced by H_2 mass transfer effects at stirring velocities greater than ~400 rpm. The decrease in H_2 pressure was measured with an Omega Engineering PX425-300GV digital pressure transducer.

Kinetic Measurements. The constant volume, pseudo-constant pressure hydrogenation apparatus described above was used for all kinetic measurements. Determination of the kinetic order in H_2 pressure involved the use of large quantities of the arene and a ballast at varying high H_2 pressures for refilling the Griffin-Worden vessel after each kinetic measurement. The change in H_2 pressure over the course of any kinetic run was usually less than 5%. In variable P_{H_2} sequences, kinetic data were taken on the same catalyst sample, and the hydrogen pressure was deliberately made the same in the first and last set of measurements to check for possible catalyst deactivation (none was observed). The quantity of the arene consumed in a series of variable P_{H_2} runs was not greater than 10%. The kinetic order in the arene substrate was deter-

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mined by varying the arene concentration in the reactor (dilution with octane) while keeping the initial hydrogen pressure constant. The deuterium kinetic isotope effect was measured in the same manner with use of D_2 instead of H_2.

Instrumentation. ^1H and ^{13}C NMR spectroscopic experiments were performed with a Varian XL-400 or a Varian Gemini 300 instrument. Spectral simulations were carried out with the Varian program SPINS, Version 5.1. $^1H\{D\}$ NMR measurements were performed with a General Electric GN 500-MHz instrument at the University of Illinois, Urbana-Champaign. Mass spectrometry was carried out with a VG702505E high-resolution mass spectrometer which was interfaced to a Hewlett-Packard 5980 gas chromatograph unit using a 15-m standard narrow bore dB-1 fused silica capillary column. ESR analyses were performed at 77 K with a Varian E-4 spectrometer, and "spin counting" experiments employed standard procedures.[20] ICP measurements were performed with a Thermo Jarrell Ash Atom Scan 25 spectrometer. The loading of the organometallic complexes on DA (Th:Al ratio) was measured by digestion at 100 °C for 12 h of a known amount of the supported catalyst in a closed 60-mL Teflon vessel filled with 10:1 HF:HCl solution. Typical loadings were 4×10^{-8} mol of Th/mg of DA (0.08–0.15 molecules/100 Å^2). The same determination found negligible quantities of Mg in the catalyst samples prepared from $Th(\eta^3\text{-}C_3H_5)_4$.

XPS Experiments. In the glovebox, a sample of $Th(\eta^3\text{-allyl})_4$/DA was pulverized and pressed into a piece of In foil (Aldrich, 99.999%, 0.1-mm thickness) and wrapped around a stainless steel sample stub. The sample was then loaded into a portable sample transfer chamber equipped with a load lock system for high-vacuum specimen transfer into the sample chamber of the VG XPS/SIMS instrument. Spectra were calibrated versus the C 1s signal.

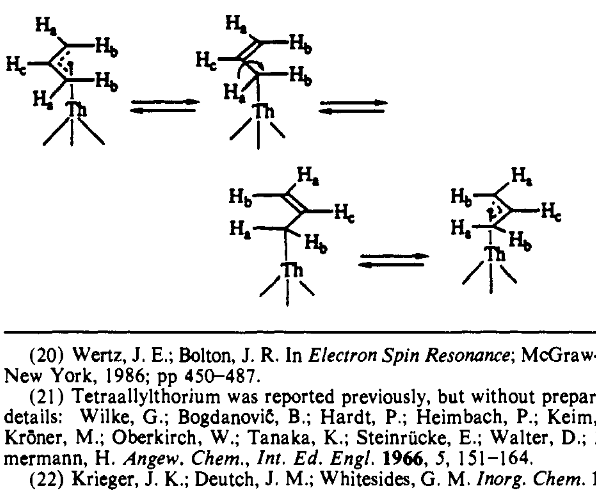
Results

Catalyst Synthesis. All organothorium complexes employed in this study were prepared as described elsewhere,[19] except for the tetraallythorium,[21] which was prepared by the low-temperature reaction of the $ThCl_4{\cdot}3THF$ with an excess of allylmagnesium bromide in diethyl ether (eqs 2 and 3).

$$ThCl_4{\cdot}3THF + 4(C_3H_5)MgBr \xrightarrow[-78\ °C]{Et_2O} Th(\eta^3\text{-}C_3H_5)_4{\cdot}2Et_2O + 4MgClBr \quad (2)$$

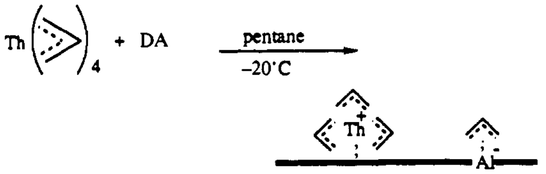
$$Th(\eta^3\text{-}C_3H_5)_4{\cdot}2Et_2O \xrightarrow[-20\ °C]{\text{toluene, pentane}} \underset{\mathbf{3}}{Th(\eta^3\text{-}C_3H_5)_4} + 2Et_2O \quad (3)$$

As noted previously,[21] $Th(\eta^3\text{-}C_3H_5)_4$ is stereochemically nonrigid in solution, with the exchange of syn and anti η^3-allyl protons observable by variable-temperature dynamic ^1H NMR spectroscopy. The exchange mechanism (eq 4) presumably involves an $\eta^3 \rightleftharpoons \eta^1$ intramolecular interconversion analogous to that observed for $Zr(\eta^3\text{-}C_3H_5)_4$ (the slow exchange limit ^1H spectra and temperature-dependent spectral changes for Zr and Th are virtually identical).[22] At the coalescence temperature (40 °C), we estimate via the coalescence point formalism[23] that $k \approx 2170\ s^{-1}$ and $\Delta G^{\ddagger} \approx 14$ kcal/mol.



(4)

The surface of dehydroxylated alumina (DA; γ-Al_2O_3 dehydroxylated at 925 °C under flowing He; 160 m^2/g) is principally composed of ca. 5.5 O^{2-} (strong Lewis base), ca. 5.5 exposed Al^{3+} (strong Lewis acid), and ca. 0.12 residual OH (weak Brønsted acid) functionalities per 100 Å^2.[4,8,24] Supported organothorium catalysts were prepared by impregnating DA with a stirring pentane solution of the complex of interest at −20 °C. The catalyst was collected by filtration and washed by soxhlet extraction with pentane at room temperature to remove any physisorbed material. The quantity of Th incorporated on the support in the absorption process was determined (± 1%) by digesting impregnated DA samples and measuring the Th and Al content by ICP spectroscopy. Organothorium loadings were in the range of $2\text{–}4 \times 10^{-8}$ mol of Th/mg of DA (~0.08–0.15 molecules/100 Å^2). Because of the low coverages, adsorbate resonances could not be observed in ^{13}C CP-MAS NMR experiments. As already noted, the absorption of Cp'_2ThR_2 complexes on DA involves hydrocarbide moiety transfer from the organometallic complex to Lewis acid sites on the surface (eq 1). We presume $Th(\eta^3\text{-}C_3H_5)_4$ adsorption proceeds via a similar pathway (e.g., eq 5). In a similar manner, $Cp'Th(CH_2C_6H_5)_3$ (**1**) is known to transfer one or more benzyl anions upon adsorption,[7a] and $Th[1,3,5\text{-}CH_2C_6H_3Me_2]_4$ (**2**) presumably transfers one or more mesityl anions.



(5)

Catalytic Activity of Supported Organothorium Complexes. Initial Observations. As reported previously,[4] **1**/DA is highly active for ethylene polymerization and propylene hydrogenation. The latter reaction rate at −63 °C is near the limit which is accurately measurable in the plug-flow reactor utilized. Catalyst **1**/DA is not active for propylene polymerization. While survey experiments indicated that the catalytic properties of **2**/DA are similar to those of **1**/DA, **3**/DA behaves rather differently. Thus, **3**/DA catalyzes the rapid hydrogenation of propene in a plug-flow reactor ($N_t \approx 25\ s^{-1}$ at 25 °C), mediates the rapid polymerization of propene at room temperature to yield atactic (by ^{13}C NMR) polypropylene, and catalyzes the rapid hydrogenation of sterically more encumbered olefins (e.g., cyclohexene, 1,3-cyclohexadiene) in slurry reactions at room temperature. Under the present catalytic conditions (90 °C, 190 psi of H_2—vide infra), we find N_t for cyclohexene hydrogenation by **3**/DA to be >540 000 h^{-1}. From what is known from related homogeneous early transition metal[10,25] and organo-f-element catalysis[9,26,27] the cyclohexene and cyclohexadiene transformations can be considered to be sterically rather demanding.

Arene hydrogenation using the supported organothorium catalysts was studied in vigorously stirred non-mass transfer limited[26c,28] slurry reactions. The ballasted constant volume, pseudo-constant pressure reactor[26c] allowed accurate monitoring of reaction rates (turnover frequencies, N_t) via the change in H_2 (or D_2) pressure. Survey experiments with benzene revealed rapid

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(26) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118.

(27) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828–1838.

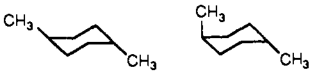
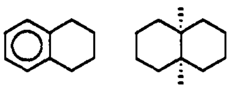
(28) (a) Gonzo, E. E.; Boudart, M. *J. Catal.* **1978**, *52*, 462–471. (b) Madon, R. J.; O'Connell, J. P.; Boudart, M. *A.I.Ch.E. J.* **1978**, *24*, 904–911. (c) Under the present conditions, pore diffusion mass transfer effects should not be significant for this particle size of alumina: Kung, H. H., Ph.D. Thesis, Northwestern University, 1974.

Table I. Kinetic Data for the Catalytic Hydrogenation of Benzene by Various Heterogeneous and Homogeneous Catalysts

complex	temp, °C	pressure, psi	N_t,[a] h^{-1}	ref
$(\eta^5\text{-}Me_5C_5)Th(CH_2C_6H_5)_3$ (**1**/DA)	90	190	765	this work
$Th(1,3,5\text{-}CH_2C_6H_3Me_2)_4$ (**2**/DA)	90	190	825	this work
$Th(\eta^3\text{-}C_3H_5)_4$ (**3**/DA)	90	190	1970 (24 620[b])	this work
$(\eta^3\text{-}C_3H_5)Co[P(OMe_3)]_3$	25	14	0.5	11
$[(\eta^5\text{-}Me_5C_6)RhCl_2]_2$	50	70	6.25	15d
$(\eta^6\text{-}Me_6C_6)Ru(Cl)(PPh_3)(H)$	50	700	48	15c
$[(\eta^6\text{-}Me_6C_6)Ru]_2(\mu\text{-}H)_2(\mu\text{-}Cl)Cl$	50	700	250	15b[c]
$PtCl_2(CH_3CN)_2 + BF_3{\cdot}H_2O$/zeolite	75	800	1330	17a
1% Rh/H-Erionite	80	100	1728	16b
Zr(hydride)/SiO_2	90	20	83	17c
0.5% Rh/$SrTiO_3$	30	14	458	17b

[a] Turnover frequency under conditions quoted. [b] Corrected to turnover frequency per active site. [c] Bennett reports he was unable to reproduce this result (ref 14 in: Fish, R. H. *Aspects of Homogeneous Catalystis*; Ugo, R., Ed.; Kluwer: Dordrecht, 1990).

Table II. Product and Kinetic Data for the $Th(\eta^3\text{-}C_3H_5)_4$/DA-Catalyzed Hydrogenation of Various Arenes[a]

substrate	product	N_t, s^{-1} ± 1.5%
C_6H_6	C_6H_{12}	6.85[b]
C_6D_6	$C_6H_6D_6$	6.78[b]
$CH_3C_6H_5$	$CH_3C_6H_{11}$	4.10[b]
$CD_3C_6D_5$	$CD_{3-x}H_xC_6H_{11}$	4.00[b]
$1,4\text{-}CH_3C_6H_4$	 3 : 1	1.45[b]
naphthalene	 5 : 1	0.001[c]
$C_6H_6 + 1,4\text{-}(CH_3)_2C_6H_4$ 1 : 1	C_6H_{12} + 1,4-Dimethylcyclohexane[d] 97 3 (3:1 trans:cis)	6.80,[e] 1.42[f]

[a] P_{H_2} = 190 psi; [arene] = 11 M (neat), temp = 90 °C. [b] Turnover frequency independent of conversion. [c] Turnover frequency at 5% substrate conversion; solvent = pentane. [d] Product mixture at complete benzene consumption. [e] Initial turnover frequency. [f] Turnover frequency at complete benzene consumption.

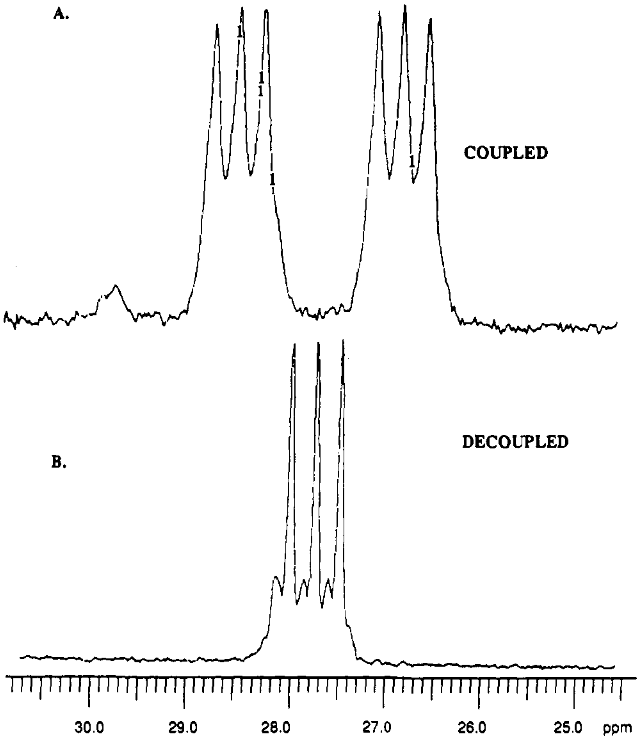


Figure 1. (A) Proton-coupled ^{13}C NMR spectrum (100 MHz) of the cyclohexane product of the $Th(\eta^3\text{-allyl})_4$/DA-catalyzed reduction of benzene by D_2. (B) $^{13}C\{^1H\}$ spectrum of the product in part A.

gas uptake at 90 °C/190 psi, with the relative activities **3**/DA ≫ **2**/DA ≥ **1**/DA. Analysis of reaction mixtures at various stages of conversion by GC-MS indicated that any partially hydrogenated products (cyclohexadiene, cyclohexene) were present at concentrations below the detection limit (≤ 0.0001% of benzene or cyclohexane). This behavior can be contrasted with that of many conventional heterogeneous benzene hydrogenation catalysts where cyclohexene can be detected at partial conversions.[16] In Table I, the rates of the present transformations are compared to those known transition metal homogeneous[11-15] and heterogeneous[16,17] benzene hydrogenation catalysts. Heterogeneous turnover frequency data are normalized per active metal site where such information is available. It can be seen that the benzene hydrogenation activity of **3**/DA is far greater than that of the known homogeneous catalysts and appears to rival or exceed those of the most active heterogeneous systems. In contrast to these observations, catalytic hydrogenation experiments with *solutions* of **3** yielded only propene, with negligible activity for either homogeneous olefin or arene reduction.

Heterogeneous Arene Hydrogenation by $Th(\eta^3\text{-}Allyl)_4$/DA. (a) Scope, Rates, and Regiochemistry. As can be seen in Table II, **3**/DA mediates the hydrogenation of a variety of substituted arenes, with the rate ordering benzene > toluene ≫ *p*-xylene ≫ naphthalene. This ordering parallels that of most conventional heterogeneous arene hydrogenation catalysts (vide infra).[14,15] As in the case of benzene and in contrast to many conventional heterogeneous catalysts,[16] neither partially hydrogenated toluene nor *p*-xylene products are detected in partially converted reaction mixtures. The mixture of 1,4-dimethylcyclohexane regioisomers formed (Table II) indicates that all hydrogen atoms are *not* delivered to the same face of *p*-xylene. In conventional heterogeneous systems, deviations from *all-cis* H_2 delivery can usually be correlated with the presence of unbound, partially reduced intermediates, i.e., with dissociation and recoordination of partially reduced species.[16] The present **3**/DA-derived naphthalene product mix is also not exceptional for a conventional heterogeneous catalyst.[16] When a 1:1 benzene–*p*-xylene mixture is hydrogenated with **3**/DA, there is essentially complete (97:3) selectivity to cyclohexane, before *p*-xylene conversion becomes significant (Table II). The regiochemistry of *p*-xylene reduction in this experiment is indentical to that for neat *p*-xylene. In regard to kinetics, the initial turnover frequency is comparable to that for neat benzene, while N_t after benzene consumption is comparable to that for neat *p*-xylene (Table II). Further mechanistic details will be taken up in the kinetic analysis (vide infra).

Experiments with benzene and D_2 indicate by GC-MS and NMR that $C_6H_6D_6$ is the exclusive reduction product. Analysis of partially converted reaction mixtures gives no evidence of partially reduced species nor of C–H/C–D exchange in the unconverted benzene. Interestingly, C–H/C–D exchange is observed over longer time periods in the cyclohexane products—vide infra. In regard to the regiochemistry of D_2 addition to C_6H_6, room temperature ^{13}C and $^{13}C\{^1H\}$ NMR spectra (where the cyclohexane ring is rapidly inverting) of product $C_6H_6D_6$ samples indicate that each (>95%) carbon is attached to a single H and a single D

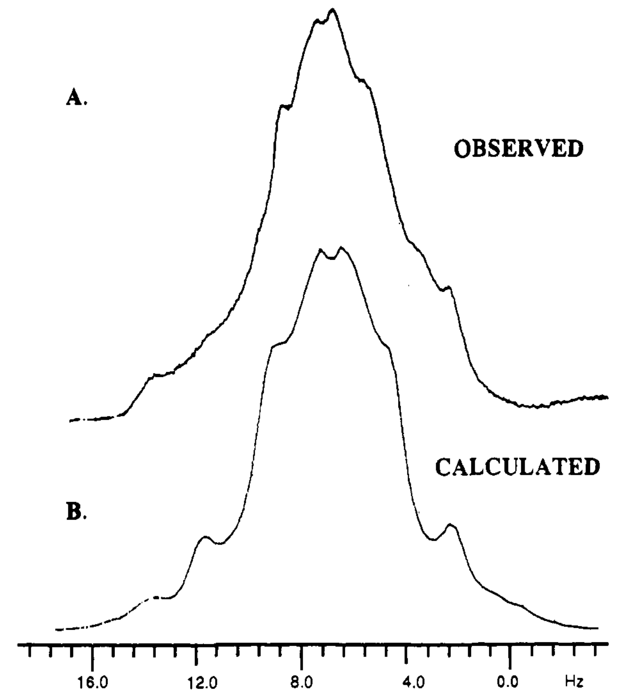
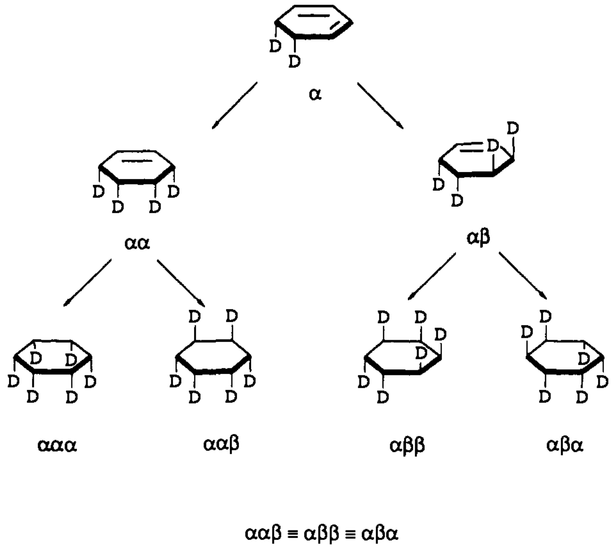


Figure 2. (A) $^1H\{D\}$ NMR spectrum (500 MHz, -100 °C) of the cyclohexane product of the $Th(\eta^3\text{-allyl})_4$/DA-catalyzed reduction of benzene by D_2. (B) Theoretical $^1H\{D\}$ spectrum generated for a 1:3 mixture of $C_6H_6D_6$ isomers $\alpha\alpha\alpha$ and $\alpha\alpha\beta$ of Scheme I.

Scheme I. Distribution of Products in the Reduction of C_6H_6 with D_2



functionality (Figure 1A), and that greater than one regioisomer is present (Figure 1B). The latter data are most simply interpreted in terms of two regioisomers in the ratio of 1.0:2.9. ^{13}C spectroscopy at low temperatures provides no further information.

Low-temperature $^1H\{D\}$ experiments, supplemented by simulation of theoretical spectra, can, in principle, provide additional regiochemical information for partially deuterated cyclohexane derivatives. The 500-MHz $^1H\{D\}$ spectrum (-100 °C) of $C_6H_6D_6$ from the 3/DA-catalyzed reduction is shown in Figure 2A. To interpret the results, we make the initial simplifying assumption, observed in all f-element-catalyzed monoene reductions studied to date,[4b,26,29,30] that D_2 addition is *cis*-1,2. As shown in Scheme I, sequential suprafacial 1,2-D_2 additions to benzene yield two

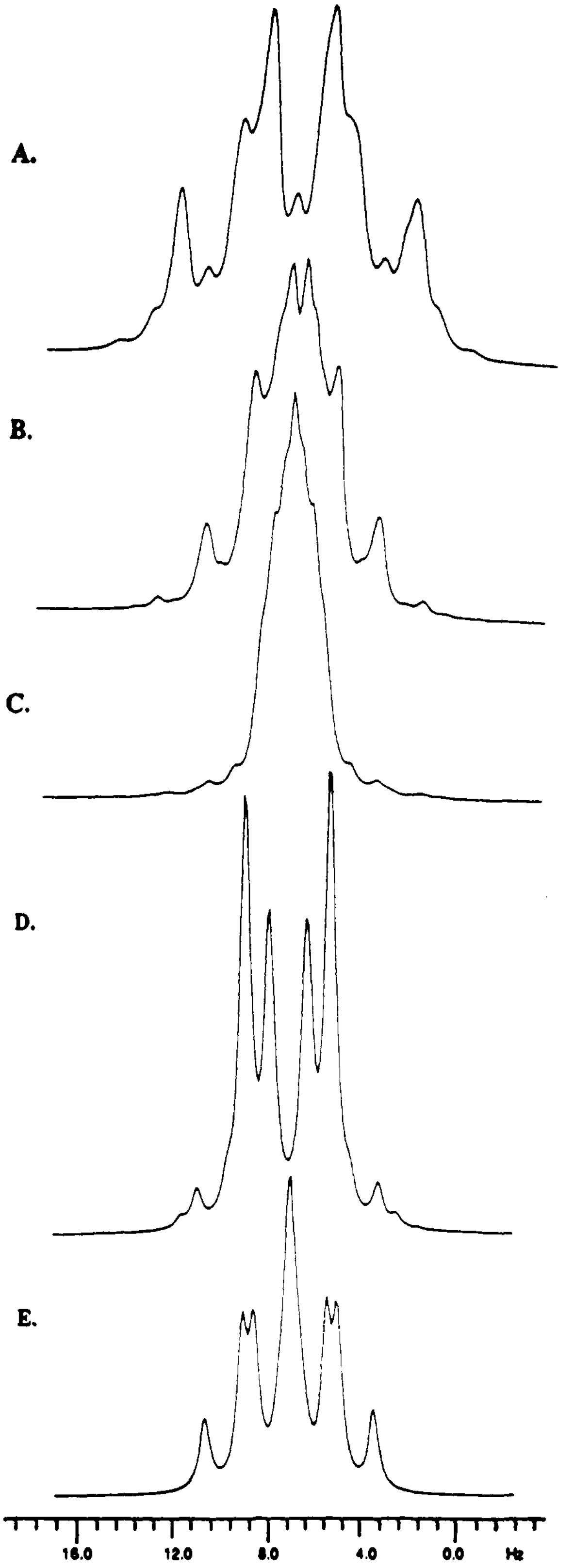


Figure 3. Theoretical $^1H\{D\}$ NMR spectra generated for $C_6H_6D_6$ isomers: (A) $\alpha\alpha\alpha$ (Scheme I), (B) $\alpha\alpha\beta$ (Scheme I), (C) structure **B**, (D) structure C, and (E) structure **D**.

possible $C_6H_6D_6$ regiosomers (in a 1:3 ratio if addition is random). Theoretical $^1H\{D\}$ spectra were next generated for static cyclohexane structures using literature chemical shift and ^1H–^1H coupling constant parameters.[31,32] Comparison of Figure 2A to

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(29) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515–5525.

(30) An exception may be the $Cp'_2Th(CH_3)_2$/DA-catalyzed hydrogenation of butadiene,[4b] where both 1,2 and 1,4 addition (or isomerization subsequent to H_2 delivery) is observed.

(31) A line broadening of 0.8 Hz was introduced to take into account the finite rate of ring inversion at -100 °C and decoupling inefficiency.

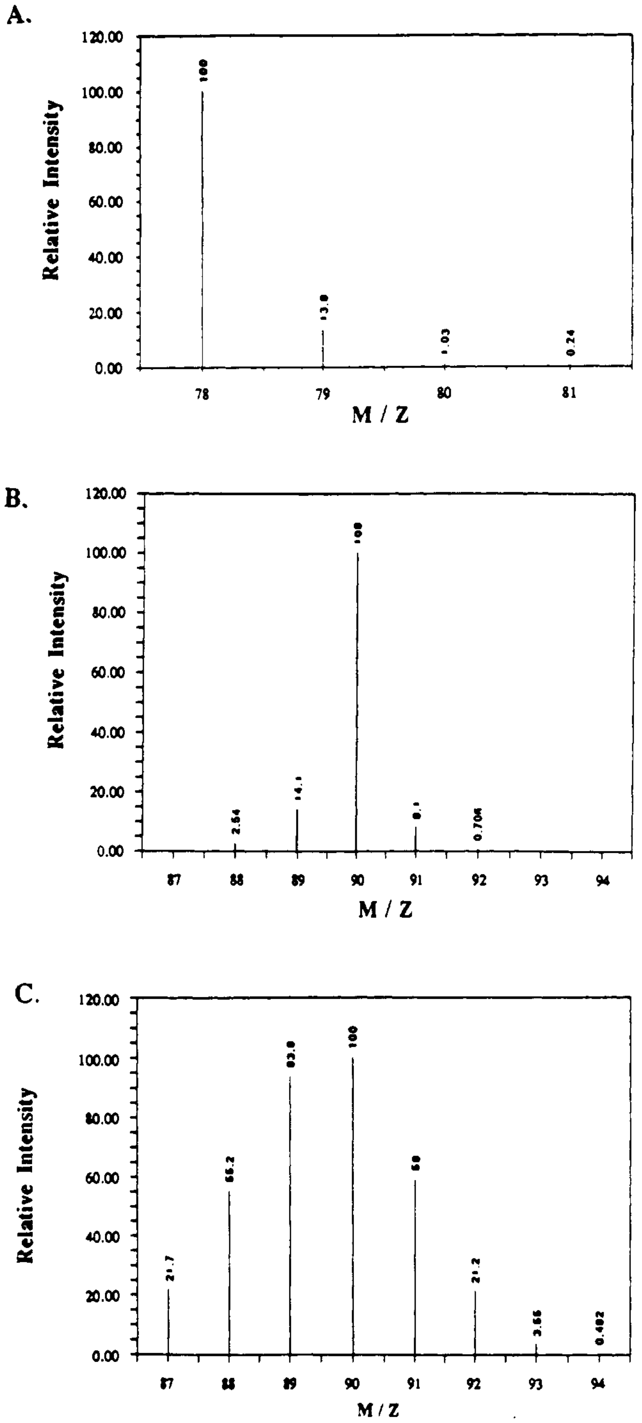


Figure 4. Electron impact mass spectra of (A) C_6H_6, (B) product $C_6H_6D_6$ at the completion of the $Th(\eta^3\text{-allyl})_4$/DA-catalyzed addition of D_2 to C_6H_6, and (C) the product in Figure 4B after an additional 12 h of reaction.

the theoretical spectrum generated for *all-cis* D_2 addition (isomer *ααα* in Scheme I) indicates poor congruence (Figure 3A), hence that D_2 delivery is not regiospecifically *all-cis*. Likewise, the theoretical spectrum for the *cis,cis,trans,cis,trans* product of one D_2 addition to one face and two D_2 additions to the other (isomers *ααβ*, *αββ*, *αβα* of Scheme I) is in poor agreement with experiment (Figure 3B; the theoretical spectrum is clearly too narrow). The

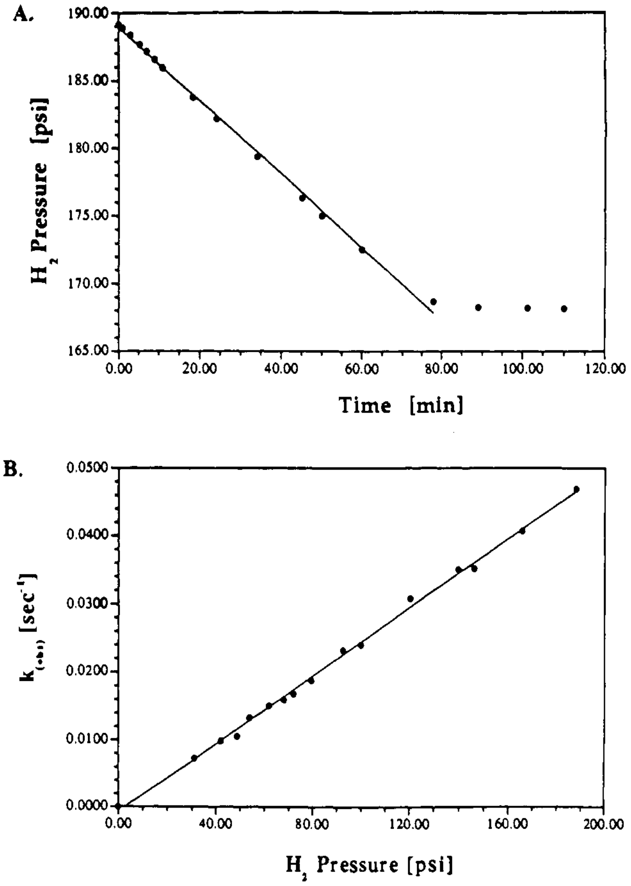
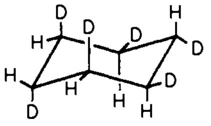
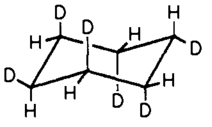


Figure 5. (A) Time dependence of the reactor H_2 pressure in the $Th(\eta^3\text{-allyl})_4$/DA-catalyzed hydrogenation of benzene. (B) Dependence of the observed rate constant for the $Th(\eta^3\text{-allyl})_4$/DA-catalyzed hydrogenation of benzene on the H_2 pressure.

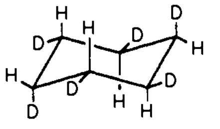
best agreement with the experimental ^{13}C and ^1H data is obtained by assuming a totally random sequence of 1,2-*cis* additions (Scheme I) which would yield a 1:3 (as suggested by Figure 1B) mixture of *all-cis* and *cis,cis,trans,cis,trans* regioisomers (Figure 2B). As an additional check, theoretical spectra were also generated for a *trans,cis,trans,trans,cis* regioisomer (**B**) and two



B



C



D

inequivalent (at −100 °C) *cis,trans,cis,cis,trans* (**C**, **D**) regioisomers (Figures 3, spectra C, D, and E, respectively). Although the chemistry that would lead to such D_2 addition sequences is not immediately obvious, it can be seen that such regiosomers cannot be major components of the present $C_6H_6D_6$ product mix.

Although $C_6H_6D_6$ is the exclusive product of the **3**/DA-catalyzed $C_6H_6 + D_2$ addition reaction at the point where D_2 uptake is complete, reaction for an additional 12 h at 90 °C with 45 psi of D_2 residual pressure after complete substrate reduction yields cyclohexane isotopomers evidencing additional D incorporation (Figure 4). Since the equivalents of available C–H in the sample shown were ca. 3× the available equivalents of gaseous D, any C–H/C–D scrambling should also afford $C_6H_{6+x}D_{6-x}$ ($x \geq 1$) products, as is in fact observed (Figure 4C). In the case of catalytic toluene + D_2 reduction, ^{13}C NMR and GC-MS show that extensive C–H/C–D scrambling occurs at the benzylic positions of the *unconverted* substrate unlike the benzene reduction. DA alone is found not to catalyze these reactions under the conditions employed.

(b) Kinetics. The kinetics of **3**/DA-catalyzed arene hydrogenation were studied in a thermostated constant volume, pseu-

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(32) (a) Muetterties, E. L.; Rakowski, M. C.; Hirsekorn, F. J.; Larson, W. D.; Basus, V. J.; Anet, F. A. L. *J. Am. Chem. Soc.* **1975**, *97*, 1266–1267. (b) Haddon, V. R.; Jackman, L. M. *Org. Magn. Reson.* **1973**, *5*, 333–338. (c) Remijnse, J. D.; Vandeginste, B. G. M.; Webster, B. M. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 804–808. (d) Barfield, M. *J. Am. Chem. Soc.* **1971**, *93*, 1066–1071. (e) Barfield, M.; Chakrabarti, B. *Chem. Rev.* **1969**, *69*, 757–778. (f) Anet, F. A. L.; Bourn, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760–768.

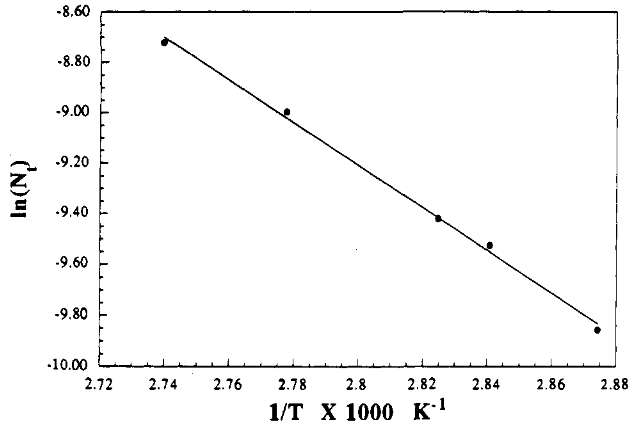


Figure 6. Arrhenius plot for the hydrogenation of benzene catalyzed by $Th(\eta^3\text{-allyl})_4/DA$.

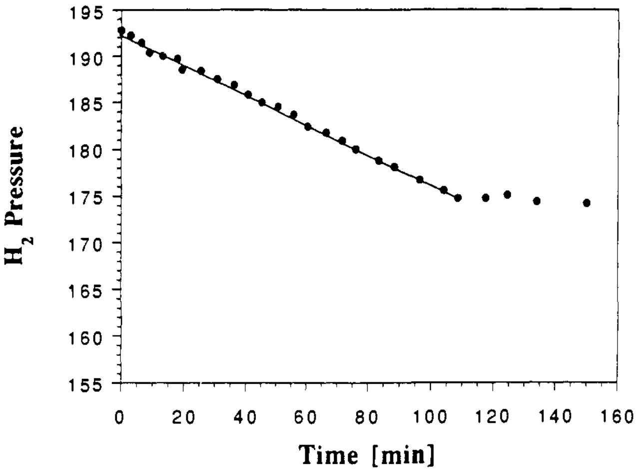


Figure 7. Time dependence of the reactor H_2 pressure in the $Th(\eta^3\text{-allyl})_4/DA$-catalyzed hydrogenation of *p*-xylene.

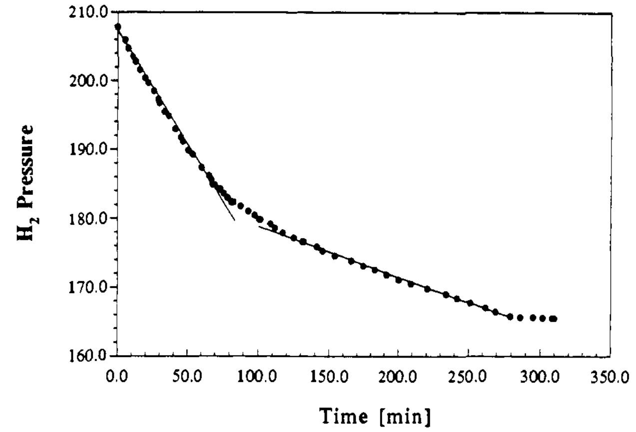
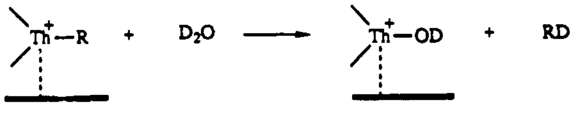


Figure 8. Time dependence of the reactor H_2 pressure in the $Th(\eta^3\text{-allyl})_4/DA$-catalyzed hydrogenation of a 1:1 (molar) mixture of benzene and *p*-xylene. The straight lines show least-squares fits to the data points in the two reaction regimes.

do-constant pressure slurry reactor. Control experiments established that the stirring of the reaction mixture was sufficiently rapid to eliminate H_2 mass transfer effects in the kinetic data. Studies of benzene hydrogenation showed that the rate is zero-order in substrate (time-independent N_t) over a wide benzene concentration range (Figure 5A) and first-order in H_2 pressure over a wide P_{H_2} range (Figure 5B). Parallel kinetic isotope (KIE) effect studies using D_2 yield $N_t(H_2)/N_t(D_2) = 3.5 \pm 0.3$. The kinetics of benzene hydrogenation were also studied as a function of temperature, and an Arrhenius plot is shown in Figure 6. Least-squares analysis of these data yields $E_a = 16.0 \pm 0.3$ kcal/mol. A similar kinetic study of *p*-xylene hydrogenation was also carried out. As can be seen in Figure 7, the reaction is again zero order in substrate over a wide concentration range. In the case of 1:1 benzene–*p*-xylene mixtures, the benzene is a strong inhibitor of the xylene hydrogenation, and even though the turnover frequency ratios of the neat substrates is 4.7:1 (Table I), the product mix is 97:3 cyclohexane–dimethylcyclohexane at the point of complete benzene conversion. As can be seen in Figure 8, the kinetics of the mixture reduction are approximately zero-order in substrate in each regime where the turnover involves predominant reduction of a single substrate.

Active Site Characterization. In the case of $Cp'_2Th(CH_3)_2/DA$, CO poisoning studies in a plug-flow reactor previously indicated that ≤4% of the surface Th sites are of catalytic significance in propene hydrogenation.[4b,d] This is not an unusual state of affairs for either conventional[32] or molecular precursor-based heterogeneous catalysts.[3a,5] In the present study, several quantitative chemical[3a,5] probes were employed to determine the maximum percentage of the $Th(\eta^3\text{-allyl})_4/DA$ sites which are catalytically significant in arene hydrogenation and to assess the chemical nature of these sites. A poisoning experiment was first carried out in which the **3**/DA catalyst was operated through part of a standard slurry benzene hydrogenation cycle. N_t was determined, and then a measured aliquot of degassed D_2O in C_6H_6[34] ($D_2O/Th = 0.040$) was injected using a gas-tight high-pressure syringe through a high-pressure port in the reactor head. Catalytic activity was then measured for 60 min (kinetics remained zero-order in substrate), and N_t was found to have dropped by 50%. This procedure was then repeated with $D_2O/Th = 0.020$, and N_t was found to have dropped an additional 25% (the kinetics remained zero order in benzene). An additional injection ($D_2O/Th = 0.010$) further reduced N_t to 12.5% of the original valve. From these results, it can be estimated that a maximum of 8 ± 1% of the **3**/DA sites are of catalytic importance in benzene hydrogenation and that kinetically these respond identically to D_2O poisoning. This result and other assays which detect Th–H/Th–hydrocarbyl functionalities (vide infra) suggest that the D_2O poisoning process involves protonolytic interception of Th–H or Th–hydrocarbyl bonds[34] (e.g., eq 6 or variants in which greater than one hydride ligand undergoes protonolysis). GC-MS analysis of the reaction mixture subsequent to D_2O quenching indicated that the quantity of labeled RD products was below the detection limit.



(6)

R = H or Organic Fragment

Hydrogenolysis[35] would be another probe of adsorbate reactivity/hydride formation. When initially adsorbed $Th(\eta^3\text{-allyl})_4$ on DA was flushed with flowing H_2 in a plug-flow reactor at 120 °C, followed by flushing with flowing He, GC analysis of evolved organic components revealed exclusive propane formation (<1% propene). The propane/Th ratio was determined to be 10 ± 2%. This result is in good agreement with the catalytic poisoning assay and is in accord with hydrogenolytic/hydrogenative formation of

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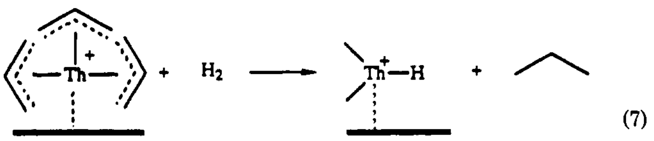
(33) (a) Rooney, J. J. *J. Mol. Catal.* **1985**, *31*, 137–159 and references therein. (b) Boudart, M. *J. Mol. Catal.* **1985**, *30*, 27–37 and references therein.

(34) The solubility of water in C_6H_6 at 25 °C is 0.050 g of H_2O/100 g of C_6H_6: Seidell, A. *Solubilities of Organic Compounds*; D. Van Notrand: New York, 1941; p 368.

(35) (a) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280. (b) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (c) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

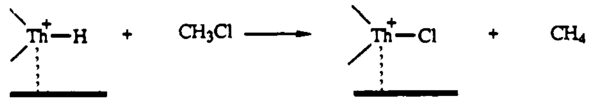
(36) (a) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985 and references therein. (b) Gillespie, R. D.; Burwell, R. L., Jr.; Marks, T. J. *Catal. Lett.* **1991**, *9*, 363–368.

propane and Th–H (e.g., eq 7 or variants in which greater than



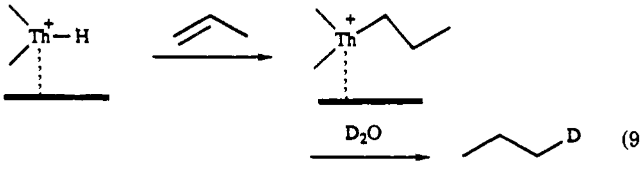
(7)

one allyl ligand is lost). Previous work[7a,c] showed that transferred surface Al–CH_3 functionalities were inert to hydrogenolysis under these conditions.[7a] Control experiments indicate that **3**/DA is a very active catalyst for propene hydrogenation ($N_t \sim 25$ s^{-1} at 25 °C), so that any evolved propene should be largely hydrogenated before exiting the catalyst bed. A third experiment to assay surface Th–H was to flush a **3**/DA catalyst in a plug-flow reactor with H_2 (25 °C) and then He (25 °C) and finally to dose the catalyst bed with measured amounts of CH_3Cl (which is rapidly reduced by Th–H groups[35c]). The evolved CH_4/Th was found to be 8 ± 2%. Assuming quantitative halocarbon reduction by available Th–H functionalities[35c] (e.g., eq 8 or variants involving



(8)

more than one hydride ligand), this assay of active hydride groups is in good accord with the coverage deduced from the D_2O poisoning and hydrogenolysis experiments (vide supra). In the case of $Cp'_2Th(CH_2)_2$/DA, the percent active sites assayed by CO poisoning of propylene hydrogenation was in good agreement with Th–H titrations by CH_3Cl and with propane-d_1 quantitations derived by sequentially flushing the catalyst with flowing H_2, He, propene, and then with D_2O vapor (eq 9).[4b,d]



(9)

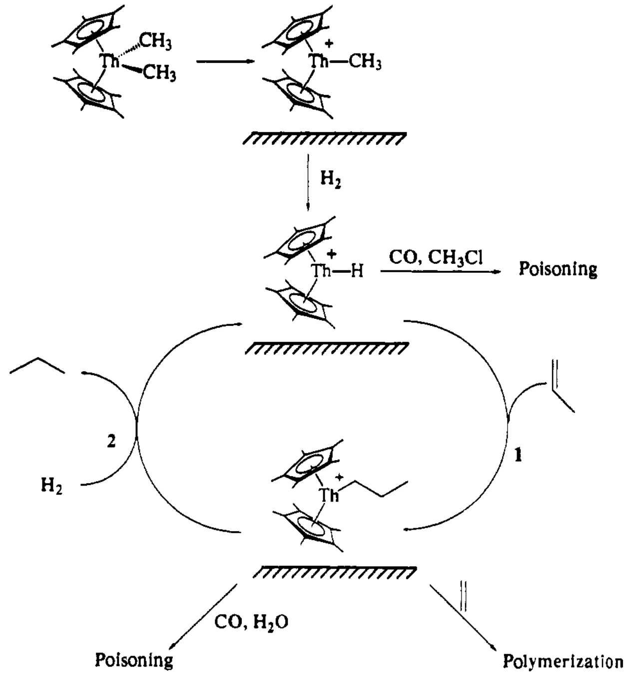
Two types of spectroscopic experiments were also carried out to characterize the nature of the **3**/DA adsorbate species. Th(III) sites are likely to be EPR active,[37,38] and studies of active catalysts (recovered after a complete benzene hydrogenation cycle) were carried out in conjunction with quantitative spin counting procedures. It can be concluded that the quantity of detectable Th(III) is less than 10^{-5}% of the **3**/DA sites. Neither exposure of the solid catalyst to flowing H_2 nor prolonged pumping under high vacuum significantly alters this result. XPS studies of several **3**/DA samples prepared as above were also carried out in instrumentation equipped with an inert atmosphere entry port. Th $4f_{7/2}$ and $4f_{5/2}$ signals are only observed at 338 and 349 eV, respectively, in the expected region for Th(IV), and clearly ruling out significant quantities of Th^0.[39]

Discussion

Mechanism of Arene Hydrogenation. In the case of supported $Cp'_2Th(CH_3)_2$ and its congeners, surface and olefin catalytic chemistry can be described by Scheme II, all transformations of which have firm precedent in homogeneous organothorium chemistry.[4,9,35] Kinetic studies indicate that propene and isobutene hydrogenations are zero-order in olefin and follow the rate law of eq 10, i.e., saturation kinetics are observed at higher H_2 pressures.[4b] Neither olefin insertion (step 1) nor hydrogenolysis (step 2) is operationally reversible or strictly turnover-limiting, D_2 delivery to propene is rigorously 1,2, and $N_t(H_2)/N_t(D_2)$ = 1.5 (±0.1) for propene (–63 °C) and 2.0 (±0.2) for isobutene (0 °C). Arrhenius activation energies (kcal/mol) are 3.6 (±0.2) (propene) and 5.3 (±0.2) (isobutene).

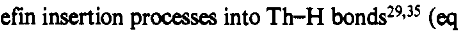
$$N_t = \frac{v_1 v_2 P_{H_2}}{v_1 + v_2 P_{H_2}} \tag{10}$$

Scheme II. Surface Chemistry and Catalytic Olefin Hydrogenation by Supported $Cp'_2An(CH_3)_2$ Complexes



In contrast to the relatively straightforward sequence of well-precedented steps involved in Th(IV)-centered olefin hydrogenation catalysis, those which would effect the hydrogenation of arenes have less precedent. In advancing a mechanistic scenario, we make the following two chemically reasonable assumptions: (i) Th remains in the +4 oxidation state at all times, (ii) the catalysis occurs at single Th surface sites. The first assumption is reasonable in view of the great difficulty in reducing Th(IV)[38] (only a few Th(III) compounds are known and none in lower oxidation states), the present surface spectroscopic observations, and the impossibility of higher Th oxidation states. The second assumption is reasonable in view of the large dispersion of Th sites on the surface and the small percentage of active sites. Neither oxidative addition/reduction elimination reactivity sequences nor multimetallic substrate activation/reduction have precedent in organothorium chemistry.

The mechanistic sequence shown in Scheme III offers many attractive features in portraying a pathway for arene hydrogenation. Steps 1 and 2 are in essence a more elaborate variant of well-known olefin insertion processes into Th–H bonds[29,35] (eq 11).



(11)

Such additions are usually exothermic for f-element complexes (in contrast to many middle and late transition metal complexes).[35] Moreover, in the present case, the coordinatively unsaturated insertion product should be stabilized by polyhapto pentadienyl ligation—an amply precedented coordination mode for f-element and early transition elements.[40,41] Hydrogenation (step 3) would

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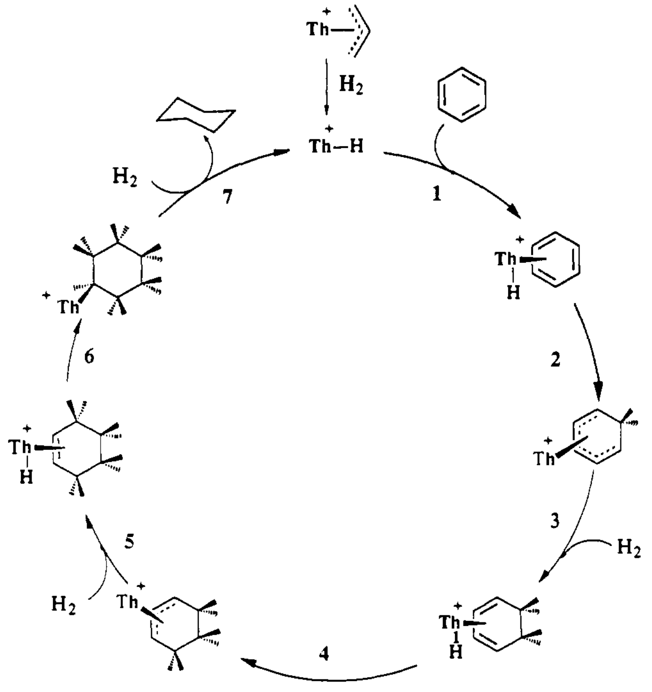
[37] Kot, W. K.; Shalimoff, G. V.; Edelstein, N. M.; Edelman, M. A.; Lappert, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 986–987 and references therein.

[38] (a) Th(IV) is reduced with great difficulty.[37,38b,c] (b) Vallat, A.; Laviron, E.; Dormond, A. *J. Chem. Soc., Dalton Trans.* **1990**, 921–924. (c) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 1860–1869.

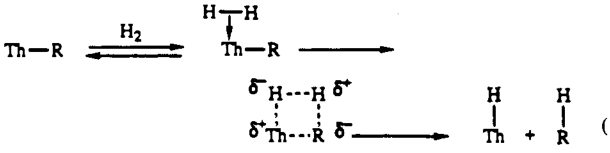
[39] (a) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. In *Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin Elmer: Minneapolis, 1978; pp 164–165. (b) Siegbahn, K.; Nordling, C.; Fahlman, A.; Nordberg, R.; Hamrin, K.; Hedman, J.; Johansson, G.; Bergmark, T.; Karlsson, S.-E.; Lindgren, I.; Lindgerg, B. *ESCA, Atomic Molecular and Solid State Structure Studied by means of Electron Spectroscopy*; Almquist: Upssala, 1967; pp 224–229. (c) Nordling, C.; Hagström, S. *Z. Phys.* **1964**, *178*, 418–432.

[40] (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56–62. (b) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1–53.

Scheme III. Possible Scenario for Th(η^3-allyl)$_4$/DA-Catalyzed Arene Hydrogenation



yield a butadiene complex, for which there is some precedent in organothorium chemistry.[42] Since this is a Th(IV) butadiene complex, rapid insertion (step 4) to yield a precedented η^3-allyl does not seem unlikely. In regard to regiochemistry, the metal-centered character of f-element hydrocarbyl hydrogenolysis processes[35c,36] (eq 12) argues that hydrogen delivery processes would be to the same side of the carbocyclic ring as the coordinated Th ion. The steps from the η^3-allyl to hydride and cycloalkane


(12)

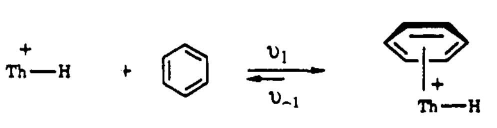
$$\mathrm{Th{-}R} \xrightleftharpoons{\mathrm{H_2}} \overset{\mathrm{H{-}H}}{\mathrm{Th{-}R}} \longrightarrow \begin{matrix} ^{\delta-}\mathrm{H}\cdots\mathrm{H}^{\delta+} \\ ^{\delta+}\mathrm{Th}\cdots\mathrm{R}^{\delta-} \end{matrix} \longrightarrow \begin{matrix}\mathrm{H}\\ |\\ \mathrm{Th}\end{matrix} + \begin{matrix}\mathrm{H}\\ |\\ \mathrm{R}\end{matrix} \qquad (12)$$

have precedent in that $Cp'_2Ln(\eta^3$-allyl) complexes undergo rapid hydrogenolysis to yield alkanes and the corresponding $(Cp'_2LnH)_2$ derivatives.[26] Furthermore, steps 6 and 7 are well-known reaction patterns in organothorium chemistry.[27,35c,36] In support of the overall step 4–7 sequence, Cp'_2Th(butadiene) has been shown to undergo rapid hydrogenation to yield $(Cp'_2ThH_2)_2$ and butane.[42b] Thus, many of the structures and transformations in Scheme III have firm precedent or close analogues.

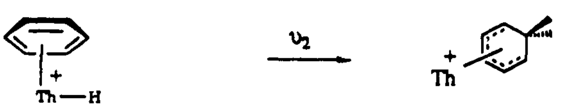
In regard to the kinetics of Th(η^3-allyl)$_4$/DA-catalyzed arene hydrogenation, the present study shows benzene turnover to be zero-order in arene over a wide arene concentration range and first-order in P_{H_2} (eq 13) over a wide H_2 pressure range, with a

$$N_t = vP_{H_2} \qquad (13)$$

KIE of $N_t(H_2)/N_t(D_2) = 3.5 \pm 0.3$. These results introduce significant constraints regarding the probable sequence of events in Scheme III. Thus, initial arene binding must be rapid and essentially irreversible. Whether arene activation proceeds via initial formation of a discrete intermediate π complex (actinide η^6-arene complexes are known[43]) followed by subsequent insertion (eqs 14 and 15) or whether direct, irreversible insertion occurs

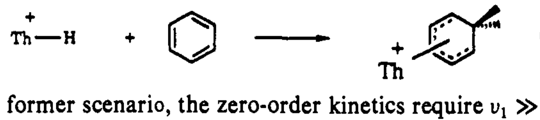


(14)



(15)

(eq 16) cannot be rigorously determined with the data at hand.



(16)

In the former scenario, the zero-order kinetics require $v_1 \gg v_{-1}$ (K_1 is large). The first-order kinetic behavior in P_{H_2} and the significant KIE argue in the simplest scenario for either (i) a slow, possibly turnover-limiting step where a single H_2 molecule is added or (ii) a reversible H_2 addition step followed by some other slow step. The observed kinetic order in P_{H_2} argues that the slow step in (ii) cannot be a second H_2 addition (a P_{H_2} dependence greater than first-order would be observed) nor that a sequence of two or three coupled, rapidly reversible H_2 additions is involved, for the same reason. Furthermore, it is not obvious why rapid, reversible H_2 addition should give rise to a kinetic H_2/D_2 effect of the observed magnitude. In the simplest scenario, the KIE can be most reasonably identified in (i) with steps 2 and 3 in Scheme III. Note that typical KIE values for $Cp'_2Th(OR)R$ hydrogenolysis (R = alkyl) are ~2.5,[36a] those for $Cp'_2Th(CH_3)_2$/DA-catalyzed olefin reduction 1.5–2.0,[4b] and those for $Cp'_2Th(OR)H$ olefin insertion ~1.4.[29] Typical KIE values for H_2 oxidative addition to d^8 complexes are 1.06–1.22.[44] The preceding discussion has of course ignored the possibility that one or more rapid, irreversible H_2 addition steps to form η^2-H_2 complexes[45] could come early in Scheme III (e.g., preceding step 1). These would then exhibit zero-order kinetics in P_{H_2}, and the bound H_2 could then be transferred to the carbocyclic substrate in a series of intramolecular steps, with some later addition of exogenous H_2 being turnover-limiting. This scenario requires the formation of d^0, f^n η^2-H_2 complexes, for which there is little precedent. Such species could not be detected in Cp'_2ThX_2/Cp'_2UX_2[36a] systems, and the only identification ($Cp'_2Eu \leftarrow H_2$)[46] indicates the binding to be weak and labile. Moreover, it is not clear why such binding would be favored over that of the more basic arene, which is present in far higher concentration. In the absence of compelling evidence for Th(η^2-H_2) complexes, this alternative possibility seems best held in abeyance.

The studies of benzene + D_2 and *p*-xylene + H_2 regiochemistry indicate that H_2/D_2 delivery is not to a single arene face. The most reasonable accommodation of these facts would be dissociation/reassociation of the partially reduced arenes, possibly at the diene (after step 3) or olefin (after step 5) stage. Since neither free dienes not olefins are detected in partially converted reactions, the binding of these species must be relatively strong. In control experiments (vide supra) it was found that cyclohexene hydrogenation is far more rapid (>20×) than that of benzene under

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(41) (a) Baudry, D.; Bulot, E.; Ephritikhine, M. *J. Organomet. Chem.* **1990**, *397*, 169–175. (b) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 163–174. (c) DiMauro, P. F.; Wolczanski, P. F. *Organometallics* **1987**, *6*, 1947–1954.

(42) Known examples are best described as 2-butene-1,4-diyl complexes: (a) Erker, G.; Mühlenbernd, Th.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 402–404. (b) Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–561.

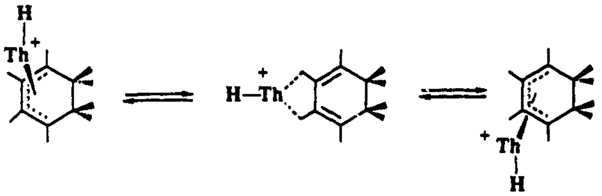
(43) (a) Baudry, D.; Bulot, E.; Charpin, P.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1989**, *371*, 155–162. (b) Cotton, F. A.; Schwotzer, W.; Simpson, C. Q., II *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 637–639. (c) Cotton, F. A.; Schwotzer, W. *Organometallics* **1985**, *4*, 942–943. (d) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1970**, *5*, 439–444.

(44) (a) Zhou, P.; Vitale, A. A.; San Filippo, J., Jr.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 8049–8054. (b) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511–3514.

(45) (a) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299–337. (b) Kubas, G. J. *Acc. Chem. Res.* **1986**, *21*, 126–128. (c) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17–40.

(46) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538–8540.

the same conditions. Hence, the steady-state concentrations of partially hydrogenation intermediate species would reasonably be expected to be very small. Alternatively, it is conceivable that the substrate fragment remains in the Th coordination sphere during the change in bound face, possibly coordinated via "agostic" interactions (e.g., eq 17).



(17)

The experiments relating to the hydrogenation of the benzene–*p*-xylene mixture are also informative about processes at the active site. The initial catalytic turnover frequency is indistinguishable from that for neat benzene, and the kinetics are essentially zero order (Figure 8). At the point of complete benzene conversion, the cyclohexane–dimethylcyclohexane ratio is 97:3. The kinetics for subsequent *p*-xylene hydrogenation are also essentially zero-order in substrate, and the turnover frequency is also identical within experimental error to that of neat *p*-xylene (Table II). Furthermore, the stereochemistry of *p*-xylene reduction is identical to that in neat substrate hydrogenation. Assuming that arene adsorption is not competitive with H_2 adsorption (indeed, H_2 activation is likely to be Rideal-Eley-like and not involve dissociative adsorption[36b]) and that arene adsorption conforms to a simple Langmuir isotherm with rapid, strong arene binding,[16a] the rate of benzene hydrogenation via steps 1–3 in Scheme III can be expressed as in eq 18 (a variant of eq 13), where υ_b is the

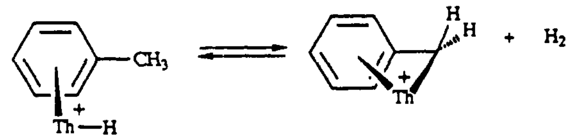
$$\text{rate}_b = \upsilon_b K_b [H_2] \tag{18}$$

rate constant and K_b is the equilibrium constant for benzene binding. Assuming benzene and *p*-xylene compete for the same adsorption/hydrogenation sites, that site equilibration between the two substrates is more rapid than hydrogenation, and that the basic tenets of Scheme III also obtain for *p*-xylene reduction, the relative rates of benzene and *p*-xylene hydrogenation can be expressed as in eq 19, where the subscript x refers to *p*-xylene. Using

$$\frac{\text{rate}_b}{\text{rate}_x} = \frac{\upsilon_b K_b}{\upsilon_x K_x} \tag{19}$$

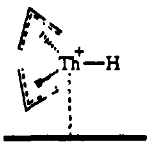
the 97:3 product ratio cited above for $\text{rate}_b/\text{rate}_x$ and υ values derived from the hydrogenation kinetics for the neat substrates yields an active site arene binding constant ratio $K_b/K_x \approx 6.7$.

After the completion of **3**/DA-catalyzed benzene hydrogenation, evidence of facile C–H/C–D scrambling processes was also noted in the cyclohexane product. The most likely mechanism is operation of the reverse of step 7 in Scheme III (and of eq 12).[47] That this reaction is suppressed in the presence of benzene is in accord with the embodiment of Scheme III in which step 1 is fast and essentially irreversible, step 3 is turnover-limiting, and steps 4–7 or 5–7 are rapid and operationally irreversible. The rapidity and broad scope of these saturated hydrocarbon functionalizations vis-à-vis the homogeneous analogues is of intrinsic interest and will be discussed more fully elsewhere.[48] The present study also revealed that C–H/C–D activation at the toluene benzylic positions is more rapid than hydrogenation. A reasonable mechanism could involve toluene π coordination (step 1 and Scheme III), followed by reversible H_2 elimination and the formation of a precedented[49] polyhaptobenzyl actinide complex (eq 20).

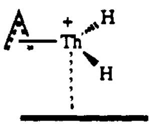


(20)

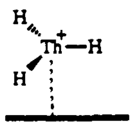
Nature of the Catalytically Active Site(s). The present results indicate that a maximum of 8 ± 1% of the surface organothorium sites are of catalytic significance. From previous surface spectroscopic and solution phase model compound studies, it seems reasonable to assume that the Th(η^3-allyl)$_4$ adsorption/activation process involves allyl anion transfer to coordinatively unsaturated surface Al^{3+} sites resulting in cation-like organothorium centers (e.g., eqs 1 and 5). Poisoning experiments indicate a kinetically homogeneous response of the surface sites with respect to protonolysis, with the number of ligand sites titrated in agreement with those assayed by allyl hydrogenolysis and CH_3Cl dosing (eqs 6–8). Since the latter two probes assay Th–H sites created, the simplest model of the active site could be a structure such as **E**.[50] In principle, hydrogenolysis could remove a second or third allyl



E

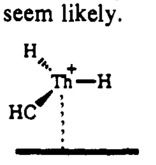


F

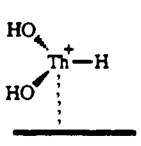


G

ligand per Th site, resulting in the less coordinatively saturated structures **F** and **G**, which would presumably be detected in the CH_3Cl Th–H assay. However, to be stoichiometrically compatible with the D_2O poisoning results, this scenario requires that Th–H deuterolysis be random and the species such as **G**, **H**, and **I** have indistinguishable catalytic activities/N_t values. From what is known about ancillary ligand effects on Th–H reactivity[29,35,36] this does not seem likely.

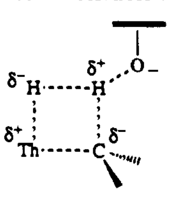


H

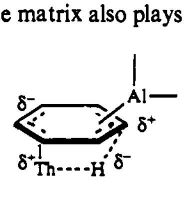


I

The preceding discussion has ignored the role of the alumina support other than abstractive in creating an organothorium cation. It is also conceivable that the metal oxide matrix also plays a role



J



K

in either heterolytic H_2 delivery (**J**)[51] or in arene activation (**K**).

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[47] For examples of homogeneous alkane activation at early transition element/f-element centers, see: (a) Rothwell, J. P. In *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Greenberg, A., Liebman, J. F., Eds.; VCH: New York, 1990; Chapter 3. (b) Watson, P. L., ref 47a, Chapter 4. (c) Rothwell, I. P. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; Chapter V. (d) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. (e) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4327–4336. (f) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56. (g) Smith, G. M.; Carpenter, J. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6807.

[48] Eisen, M. S.; Marks, T. J. *Organometallics*, in press.

[49] Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692–4695.

[50] Since step 5 in Scheme III portrays the hydrogenolysis of an η^3-allyl to a hydride, the stability of the allyl groups in **E** would necessarily reflect a minimum coordination number which was energetically accessible and/or unique steric environments. In an operating catalyst, these might eventually be replaced by η^3-hexenyl ligands.

[51] Many metal oxide surfaces effect the dissociative heterolytic chemisorption of H_2: (a) Ghiotti, G.; Boucuzzi, F.; Scala, R. *J. Catal.* **1985**, *92*, 79–97. (b) Lavalley, J. C.; Saussey, J.; Rais, T. *J. Mol. Catal.* **1982**, *17*, 289–298. (c) D'Amico, K. L.; McClellan, M. R.; Sayers, M. J.; Gay, R. R.; McFeely, F. R.; Solomon, E. I. *J. Vac. Sci. Technol.* **1980**, *17*, 1080–1084. (d) Mehta, S.; Simmons, G. W.; Klier, K.; Herman, R. G. *J. Catal.* **1979**, *57*, 339–346. (e) Dent, A. L.; Kokes, R. J. *J. Phys. Chem.* **1969**, *73*, 3781–3790.

While there is some evidence that $Cp'_2Th(OR)-R$ hydrogenolysis is accelerated by polar solvents,[29] such effects are at present speculative for metal oxide-supported catalysts.

Comparison to Known Homogeneous and Heterogeneous Catalysts. Typical homogeneous transition metal arene hydrogenation catalysts are characterized by relatively low activities (see Table I) and, in some cases, by short catalyst lifetimes. In all instances, the catalytic cycles are believed to involve either two[11,12,14,15] or one-electron[13] oxidation state shuttling at a single metal center. In the one case[12a] where a detailed kinetic study was conducted, the catalysis is first-order in arene and zero-order in H_2. Where investigated, the homogeneous catalysts are generally more active for olefin than for arene hydrogenation, and arene hydrogenation activities decrease with increasing arene substitution.[11] Several of these systems are capable of reducing ketones and nitriles, while in several cases, only polycyclic but not monocyclic arenes can be hydrogenated.[12] Several of the homogeneous catalysts exhibit remarkably high regiospecificity, with H_2 being delivered to only a single arene face.[11,14,15] Most of these catalysts exhibit some degree of functional group tolerance, which in some cases includes ethers, esters, and ketones. None appear to exhibit activity for olefin polymerization. Needless to say, separation of products and catalysts may be inefficient.

Typical supported metal hetergeneous arene hydrogenation catalysts exhibit high turnover frequencies and long lifetimes.[16] Turnover frequencies generally fall with increasing arene substitution, and rate laws are usually zero-order in arene and first-order in H_2.[16] To our knowledge, hydrogenation selectivities of the magnitude exhibited by 3/DA with respect to benzene versus *p*-xylene are not observed. In the heterogeneous systems, delivery of H_2 is seldom exclusively to a single substrate face, and partially hydrogenated products are usually detectable in incompletely converted reaction mixtures.[16] Functional group tolerance depends on the nature of the catalyst, and selective poisoning by various functional groups or impurities can alter the chemo- or regioselectivity of a catalyst. Separation of products and catalysts is usually straightforward.

The organothorium molecule-based supported catalysts as exemplified by $Th(\eta^3\text{-allyl})_4$/DA present an interesting contrast to both conventional homogeneous and heterogeneous arene hydrogenation catalysts. While the molecular nature of the observed chemical transformations and substrate selectivities are similar to those of the transition metal homogeneous catalysts, the very high turnover frequencies and lack of obvious oxidative addition/reductive elimination pathways stand in sharp contrast. Likewise, the differences in regioselectivity, olefin polymerization activity, and likely tolerance of polar functional groups differ greatly between homogeneous transition metal and supported organothorium catalysts. While the supported organothorium systems are similar to conventional heterogeneous arene reduction catalysts in rate law, regiospecificity, and substrate selectivity, the molecular-level nature of the transformations (single site verus multimetal ensembles) must surely be different, as is functional group tolerance and olefin polymerization activity. Future research will continue to explore the scope and mechanisms of catalytic transformations possible at unsaturated, supported organo-f-element centers, as well as the investigation of homogeneous analogues.

Acknowledgment. We are grateful to the Division of Chemical Sciences, Office of Basic Energy Science, Office of Energy Research, U.S. Department of Energy, for support of this research under Grant DE-FG02-86ER13511. We thank Professor Robert J. Burwell, Jr., for helpful discussions. M.S.E. acknowledges the Weizmann Institute of Sciences for a Postdoctoral Fellowship. We thank Dr. Vera Mainz of the University of Illinois, Urbana-Champaign for technical assistance with the 500-MHz $^1H\{D\}$ NMR experiments and the Northwestern Materials Research Center (NSF DMR8821571) for access to EPR and surface analysis facilities.