Organometallic Molecule-Inorganic Surface Coordination and Catalytic Chemistry. In Situ CPMAS NMR Delineation of Organoactinide Adsorbate Structure, Dynamics, and Reactivity

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Abstract: A 75.4-MHz ¹³C CPMAS NMR spectroscopic study of the surface structures and reaction chemistry of a series of organoactinides adsorbed on various inorganic supports is reported. On Lewis acid surfaces such as dehydroxylated Al₂O₃, MgCl₂, and SiO₂-Al₂O₃, it is found that organothorium complexes of the type Cp'_2ThR_2 ($Cp' = \eta^5$ -(CH_3)₅C₅; $R = {}^{13}CH_3$, ${}^{13}CH_2{}^{13}CH_3$), $Cp'ThR_3$ ($R = {}^{13}CH_2C_6H_5$), and Cp_3ThR ($Cp = \eta^5$ -C₅H₅; $R = {}^{13}CH_3$), undergo heterolytic Th-C scission to $^{10}CH_2^{-10}CH_3$), Cp 1nK₃ (R = $^{10}CH_2C_6H_3$), and Cp₃1nK (Cp = $\eta^{-1}C_5H_3$; R = $^{10}CH_3$), undergo neterolytic 1n-C scission to transfer an alkyl anion to the surface forming Cp'₂ThR, Cp'ThR_{3-n}, or Cp₃Th adsorbate species with "cation-like" character. Probe studies with paramagnetic Cp'₂U($^{13}CH_3$)₂ indicate that the majority of the transferred methyl groups of Cp'₂U($^{13}CH_3$)₂/DA and Cp'₂U($^{13}CH_3$)₂/MgCl₂ are located $\gtrsim 5$ Å from the U(IV) ion. On less dehydroxylated or more basic supports such as SiO₂-MgO, SiO₂, and MgO, μ -oxo species of the type Cp'₂Th(CH₃)O- are formed, by Th-C protonolysis or by transfer of an alkyl group to the surface. For Cp'₂U($^{13}CH_3$)₂/SiO₂, the majority of the resulting $^{13}CH_3$ -Si(surface) functionalities are an alkyl group to the surface. For Cp'₂U(¹²CH₃)₂/SiO₂, the majority of the resulting ¹²CH₃-Si(surface) functionalities are $\gtrsim 5 \text{ Å}$ from the actinide center. In agreement with heterogeneous catalytic studies, the NMR data reveal that only a small percentage of Cp'₂Th(¹³CH₃)₂/DA or Cp'Th(¹³CH₂C₆H₃)₃/DA surface sites undergo reaction with ethylene or H₂ at 25 °C. In contrast, 50 ± 10% of Cp'₂Th(¹³CH₃)₂/MgCl₂ sites undergo reaction with ethylene; >90 ± 10% of ethylene insertion/ polymerization occurs at Th-CH₃ with k(propagation)/k(initiation) ≈ 12 in the initial stages. There is no evidence for methane evolution via C-H functionalization nor for significant rates of Th(CH₂CH₂)_n¹³CH₃-Mg(surface) alkyl group permutation. At 25 °C, a large percentage of Cp'₂Th(¹³CH₃)₂/MgCl₂ Th-CH₃ and Mg-CH₃ functionalities undergo hydrogenolysis, with Th-CH₃ being slightly more reactive. In competition experiments Th-CH₃ is far more reactive than Mg-CH₃ in migratory Th-CH₃ being slightly more reactive. In competition experiments, Th-CH₃ is far more reactive than Mg-CH₃ in migratory CO insertion, and products are inferred to be, inter alia, η^2 -acyl complexes. Cp'_2Th(${}^{13}CH_3$)₂/MgCl₂ undergoes reaction with propylene to yield methane (derived from Th-CH₃), a Th(η^3 -allyl) complex, and what appear to be propylene oligomers.

It is well-established that adsorption on high surface area metal oxides can profoundly enhance the reactivity/catalytic activity of metal hydrocarbyls.¹⁻³ While such phenomena are of considerable scientific and technological interest, our understanding of the surface coordination chemistry, much less the nature of the active catalytic sites, is at a very primitive level. Moreover, it is not clear that conventional photon/particle absorption, scattering, or diffraction surface science tools^{4,5} will be particularly incisive in structurally characterizing such adsorbates on irregular surfaces at less than monolayer coverage.

Recent research in this laboratory has employed organoactinides⁶ as model hydrocarbyl adsorbates.⁷ Organoactinides have well-defined/controllable oxidation states, useful spectroscopic markers, a diversity of ligational possibilities, and a developing mechanistic/thermochemical foundation. Furthermore, adsorption of molecules such as Cp'_2AnR_2 ($Cp' = \eta^5$ -(CH_3)₅ C_5 ; An = Th, U; R = alkyl) on dehydroxylated γ -alumina⁸ (DA; σ -OH ≈ 0.1 nm⁻²) affords heterogeneous catalysts with very high activity for olefin hydrogenation and polymerization.⁷ In contrast, adsorption upon partially dehydroxylated alumina⁸ (PDA; σ -OH $\approx 4 \text{ nm}^{-2}$) or silica⁸ (partially dehydroxylated or dehydroxylated; PDS or DS) yields adsorbates with marginal catalytic activity,^{7b} while adsorption on MgCl₂ affords catalysts with intermediate activity.^{7a} Interestingly, quantitative CO or protonolytic poisoning experiments indicate that ~4% of Cp'_2An(CH_3)_2/DA and ~35% of $Cp'_2An(CH_3)_2/MgCl_2$ sites are catalytically important in such transformations.^{7a,9}

The above catalytic phenomenology suggests an intricate relationship between surface/adsorbate microstructure and activity and one that can only be partially addressed with chemical probes

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(e.g., tracing the origin of methane evolved during adsorption).^{7b} In this context, high-resolution solid-state NMR spectroscopy¹⁰ offers considerable promise as a surface structural tool,¹¹ and in our earliest 15 MHz ¹³C CPMAS studies of Cp'₂Th(¹³CH₃)₂/DA, we detected an unprecedented transfer of a methyl group to an Al site on the surface (A).^{12a} The Lewis acid character of the



surface receptor sites, spectral similarities to cationic Cp'2Th- $(CH_3)^+BPh_4^-/Cp'_2Th(CH_3)(THF)_2^+BPh_4^-$ complexes,¹³ and growing evidence that Cp'₂ThR⁺-like species will be highly reactive^{11e,14} suggested that A has electrophilic, "cation-like" character. In contrast, the negligible catalytic activity of Cp'₂Th(CH₃)₂ on PDA, PDS, and DS, along with spectral similarities to unreactive Cp'₂Th(CH₃)OR compounds,¹⁵ suggests different, "µ-oxo-like" adsorbate structures B, C, and D, respectively.¹² Nevertheless, these preliminary oxide support results leave many questions unanswered. From a descriptive, coordination chemistry standpoint, the generality of this picture in regard to support (other oxides, halides) and complex (other precursor structures) is unclear. Whether A might be a μ -alkyl,¹⁶ E, whether Th-R and Al-R groups can interchange,16 and what the reactivity of such surface functionalities is with respect to olefins, H_2 , CO, etc., remain to be answered. Finally, the relevance of the above phenomenology to the observed catalytic properties and the structural models to the actual catalytic sites are unexplored.

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In the present contribution, we present a full discussion of our high field (75.4 MHz), high-resolution solid-state ¹³C NMR investigations of supported organoactinide structural and surface chemistry.^{17,18} This includes a full examination of a range of supports (Al₂O₃, MgCl₂, SiO₂-Al₂O₃, SiO₂-MgO, MgO) and metal complexes (Cp'₂AnR₂, Cp'AnR₃, Cp₃AnR), in situ chemical dosing/adsorbate reactivity studies, and the use of paramagnetic U(IV) adsorbates in a new approach to probing metrical aspects of the surface complexation. It is seen that this integrated chemical/spectroscopic approach affords a far more complete picture of this unusual but, in all likelihood, generalizable¹⁻³ surface organometallic chemistry. Moreover, important connections are demonstrated between the heterogeneous catalytic phenomenology and the spectroscopic structure/reactivity observations.

Experimental Section

Materials and Methods. All procedures were performed in Schlenktype glassware interfaced to a high-vacuum (10⁻⁴-10⁻⁵ Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an efficient recirculating atmosphere purification system (typically 2-3 ppm O₂). Argon (Matheson, prepurified), hydrogen (Linde), and CO (Matheson CP) were purified further by passage through MnO/Vermiculite and Davison 4A molecular sieves. Other gases including pro-pylene (Matheson), ethylene (Matheson), ethylene- $1,2-^{13}C_2$ (99% $^{13}C_1$; Cambridge Isotopes), CO-13C (99% 13C; Cambridge Isotopes), and propylene-2-13C (60% 13C; MSD Isotopes) were purified by passage through MnO/SiO2. The 3,3-dimethylbutene (Aldrich) was dried over Na/K, vacuum transferred into a storage tube equipped with a Teflon valve, and stored under an argon atmosphere. Pentane (Aldrich HPLC grade) was vacuum transferred from either Na/K or CaH2 and stored in vacuo over Na/K in bulbs on the vacuum line.

Na/K in bulbs on the vacuum line. The compounds ${}^{13}CH_3Li\cdot LiI$, ${}^{12a}Cp'_2Th(CH_3)_2$, ${}^{19}Cp'_2Th({}^{13}CH_3)_2$, ${}^{12a}Cp_3Th(CH_3)_2$, ${}^{20}[Cp'_2Th(\mu-H)H]_2$, ${}^{19}Cp'Th(CH_2C_6H_5)_3$, ${}^{21}Cp'_2Th(CH_2CH_3)_2$, ${}^{19}andCp'_2Th(CH_2CH_2CH_3CH_3)_2$, were prepared according to published procedures. $Cp'_2Th({}^{13}CH_3)_2$ was prepared from $[Cp'_2Th(\mu-H)H]_2$ and 90% ethylene-1,2-{}^{13}C_2, ${}^{19}andCp_3Th({}^{13}CH_3)$ was synthesized from Cp_3ThCl and ${}^{13}CH_3Li\cdot LiI$. 20 By using the synthetic procedure for $Cp'Th(CH_2C_6H_3)_3$, ${}^{21}Cp'Th({}^{13}CH_2C_6H_5)_3$ was prepared from $C_6H_5{}^{13}CH_2Li$ and $Cp'Th(CH_2C_6H_5)_3$ was prepared from $C_6H_5{}^{13}CH_2Li$, was in turn prepared from $C_6H_5{}^{13}COOH$ (Cambridge Isotope, 99% ${}^{13}C$). 24 The complex $Cp'_2U({}^{13}CH_3)_2$ was prepared from Cp'_2UCl_2 and ${}^{13}CH_3Li\cdot LiI$ by using the method for $Cp'_2U(CH_3)_2$. and ¹³CH₃Li-LiI by using the method for Cp'₂U(CH₃)₂.¹⁹ The purity of these reagents was checked by ¹H NMR.

The supports DA and DS were prepared as previously described.^{7,12} Magnesium chloride (surface area $\approx 100 \text{ m}^2 \text{ g}^{-1}$) was supplied by Dow Chemical Co. and was pretreated under high vacuum (10⁻⁵ Torr), 300°, 2 (this code indicates heating at 300 °C for 2 h). Alternatively, MgCl₂ was prepared by reaction of dibutylmagnesium (Lithium Corp. of America) with HCl (Matheson VLSI grade) in pentane by using greaseless high vacuum line techniques (surface area $\approx 100 \text{ m}^2 \text{ g}^{-1}$). It was again pretreated under high vacuum, 300°, 2. SiO₂-Al₂O₃ (Davison 970 grade, 13% Al₂O₃, 60-80 mesh material) was purified by the same procedure as for PHF Al₂O₃, 12 followed by treatment in flowing He, 950°, 0.5 (surface area $\approx 56 \text{ m}^2 \text{ g}^{-1}$). Partially dehydroxylated MgO (Calgon Maglite CG-1) was treated in flowing He, 680°, 0.5 (surface area ≈ 46 m² g⁻¹), and SiO₂-MgO (Grace SM-30) was treated in flowing He, 800°, 0.5 (surface area $\approx 275 \text{ m}^2 \text{ g}^{-1}$). All supports were stored in vacuumtight glass storage tubes under an inert nitrogen atmosphere.

Impregnation of Supports with Organoactinide Complexes. In a twosided, fritted reaction vessel interfaced to the high vacuum line, a pentane

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solution containing a measured quantity of the organoactinide complex of interest was filtered onto a carefully weighed quantity of support. The resulting slurry was then stirred for at least 2 h with exclusion of light. The slurry was next filtered, and the impregnated support was collected on the glass frit. This material was then washed with 5×5 mL portions of pentane distilled and condensed from the filtrate and was dried in vacuo. Maximum loadings of organoactinides on MgCl₂ were ~0.25 An/nm², while higher loadings (~0.5 An/nm²) are achievable on DA and DS.

Reactions of Supported Organoactinides with Small Molecules. The following experiment is illustrative of the procedure used. In the recirculating glovebox, Cp'₂Th(¹³CH₃)₂/DA (1.5 g, 160 µmol Th) was spread on the bottom of a 250-mL Erlenmeyer flask. The flask was equipped with a Teflon valve adapter through which it could be interfaced to the high vacuum line. The flask was sealed, removed from the glovebox, connected to the vacuum line, and evacuated. The vessel was then cooled to 77 K, and a measured quantity of ethylene was admitted. The flask was maintained at 77 K for 30 min and was then allowed to warm slowly to room temperature while continuously monitoring the pressure. At ca. -10 °C, uptake of ethylene began. After ensuring that the reaction was complete (4 h at room temperature), the flask was evacuated to remove any volatiles, resealed, and returned to the glovebox so that an NMR sample could be prepared. Reactions of CO, ¹³CO, propylene, 60% propylene- $2^{-13}C$, and 3,3-dimethylbutene were conducted in the same way. For reactions with hydrogen, the procedure was modified such that after the initial evacuation of the flask containing the supported organoactinide, it was filled to ca. 1 atm with hydrogen and sealed off. After the desired reaction time, the excess hydrogen was removed in vacuo.

High-Resolution Solid-State ¹³C NMR Spectroscopy. All ¹³C solidstate NMR spectra were recorded on a Varian VXR300 spectrometer (75.4 MHz) equipped with either a Doty Scientific 7 mm or 5 mm high speed solids probe. High-power ¹H decoupling (\sim 65 kHz decoupling field), cross-polarization (CP), and magic angle spinning (MAS) were employed for routine experiments. Air-sensitive samples were loaded into cylindrical sapphire rotors in the glovebox. The rotors were capped at both ends with either O-ring sealed Macor caps (7- and 5-mm rotors) or Kel-F caps (5-mm rotors only). Both types of caps provide an air-tight seal under nonspinning conditions. MAS was achieved by using boil-off nitrogen as the spinning gas to prevent sample exposure to air. Spinning rates of 3.5-4.2 kHz were routinely achieved with the 7-mm probe. With the 5-mm probe, spinning rates of up to 8.5 (Macor rotor caps) and 10.0 kHz (Kel-F caps) could be achieved. Control experiments using highly sensitive samples that undergo distinct color changes upon oxidation $(NaC_{5}H_{5}; Cp'_{2}U(CH_{3})_{2}/DA)$ or in which the rotor cap was briefly removed in air (to determine oxidation-induced spectral changes) indicated negligible sample deterioration in this spinning configuration over time periods as long as 72 h. For both probes, the magic angle was initially set by using neat KBr. The stability of the angle setting was routinely monitored by observing the aromatic carbon line shape of neat hexamethylbenzene. Spectra were referenced to tetramethylsilane (δ 0) by using the aromatic carbon resonance of hexamethylbenzene (δ 132.1) as a secondary reference by the substitution method. The ¹³C 90° pulse width and the initial Hartmann-Hahn matching condition were determined by using the hexamethylbenzene standard sample.

For routine spectra of neat and supported organoactinides, the optimum cross-polarization contact time was found to be 4.0-4.5 ms (7-mm probe) and 2.5 ms (5-mm probe). The optimum recycle time was found to be 4-5 s. For neat organoactinide complexes, satisfactory spectra could be obtained by coaddition of 100-500 transients, while for supported organoactinides, the coaddition of 5000-15 000 transients was necessary. Before Fourier transformation, all FID's were weighted with a standard apodization function, $\exp(-t^2/a^2)$, where a = 0.04 s for neat organoactinides (~3 Hz line broadening) and a = 0.003 s for supported organoactinides (~120 Hz line broadening).

Because of the paramagnetism, atypical methods were necessarily employed to obtain $Cp'_2U({}^{13}CH_3)_2 {}^{13}C$ NMR spectra. The solution ${}^{13}C|^{1}H|$ spectrum (C_6D_6) of $Cp'_2U({}^{13}CH_3)_2$ was measured on the JEOL FX90 using a 50 kHz window. The U- ${}^{13}CH_3$ resonance was located at δ 1480, and variation of the transmitter offset confirmed that this peak was not a foldover. The $Cp'-CH_3$ resonance was located at δ -30, and the Cp'-C signal was not observed. In the solid-state ${}^{13}C$ CPMAS NMR spectrum of $Cp'_2U({}^{13}CH_3)_2$ obtained by the standard procedure (vide supra), the $Cp'-CH_3$ resonance was very broad (2500 Hz) and appeared at δ -32. No other resonances were observable by using CP techniques, presumably due to the short ${}^{13}C$ T₁'s. However, the U- ${}^{13}CH_3$ resonance could be observed by application of simple 90° ${}^{13}C$ observation pulses combined with dipolar ${}^{1}H$ decoupling and MAS. This resonance evidenced an extensive manifold of spinning sidebands, and the largest possible spectral window was employed (100 kHz). The spectrum was referenced by setting the upfield edge of the window to δ 200 by using the carbonyl resonance of liquid acetone (δ 205.4) as a secondary reference. With this external referencing, the U-¹³CH₃ isotropic chemical shift was located at δ 1430 and confirmed by varying both the transmitter offset and the spinning speed. Unfortunately, the spectral window was not large enough to encompass the entire sideband pattern.

Results and Discussion

We begin with a structurally oriented discussion of the ¹³C CPMAS NMR spectroscopy of $Cp'_2Th(^{13}CH_3)_2$ adsorbed on various dehydroxylated (i.e., having the lowest surface OH coverage readily achievable by thermal or chemical means) supports. We then probe the generality of selected aspects of the surface chemistry by using $Cp'Th(^{13}CH_2C_6H_5)_3$, $Cp_3Th(^{13}CH_3)_1$, and $Cp'_2Th(^{13}CH_2)_1^{13}CH_3)_2$ as labeled adsorbates. Methyl group spatial relationships in surface complexes are next examined by using paramagnetic $Cp'_2U(^{13}CH_3)_2$ as an adsorbate. Finally, the surface chemistry of the $Cp'_2An(^{13}CH_3)_2$ /support complexes is examined, in situ, with respect to ethylene polymerization and H_2 , CO, and propylene reactivity.

NMR Spectroscopy of Cp'₂Th(¹³CH₃)₂ Adsorbed on Various Supports. Dehydration of γ -alumina at 950-1000 °C produces a mixture of γ (cubic) and δ (orthorhombic) alumina (DA) having a coverage of ~0.1 Bronsted acid OH groups, 4 Lewis base oxide groups, and 5.5 Lewis acid Al³⁺ centers nm^{-2,7b,8} Figure 1A shows the 75.4-MHz ¹³C CPMAS spectrum of Cp'₂Th(¹³CH₃)₂ adsorbed on DA at a coverage of ca. 0.25 Th nm⁻². Assignments (Table I) follow straightforwardly from ${}^{13}C/{}^{12}C$ substitution, dipolar dephasing experiments,²⁵ and data for model compounds. The low field (δ 71.0) methyl signal is assigned to a "cation-like" Th⁺-CH₃ functionality (cf., δ 71.8 in Cp'₂Th(CH₃)⁺B(C₆H₅)₄⁻)¹³ and the upfield signal to an ²⁷Al-CH₃ functionality. This latter assignment and the quadrupole-induced broadening²⁶ are supported by model compounds,^{12a} and the expected²⁶ line narrowing is observed at higher magnetic fields. Several experiments were also carried out to probe the motional characteristics of $Cp'_2Th(^{13}CH_3)_2/DA$. Cessation of dipolar decoupling and Bloch decay experiments^{10,27} yielded featureless spectra, while variable CP time experiments²⁷ (0.8–10.0 ms) produced no significant changes in relative spectral intensities. Thus, any motional processes that appreciably average C-H dipolar interactions do not differ greatly in anisotropy. Spectra of Cp'₂Th(¹³CH₃)₂/DA frequently exhibit a second, smaller Th-¹³CH₃ signal at $\delta \approx 60$. This feature is the dominant Th-13CH₃ resonance in Cp'₂Th- $(^{13}CH_3)/PDA$ and is assigned to a $Cp'_2Th(CH_3)O-\mu$ -oxo species (B) on the basis of $Cp'_2Th(CH_3)OR$ model compound data (δ 58.4 for R = CH(t-C₄H₉)₂).^{12b} It likely arises from protonolysis^{7b} by residual surface AlOH groups.

 $MgCl_2$ crystallizes in the layered CdCl₂ structure with octahedrally coordinated Mg^{2+} cations between sheets of Cl⁻ anions.²⁸ High surface area $MgCl_2$ prepared via prolonged grinding or chemical routes has a more complex and poorly understood structural chemistry.^{3,28} This material is the preferred support for "third generation" Ziegler-Natta catalysts³ and exhibits a Lewis acid surface chemistry.³ The spectrum of Cp'₂Th-

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complex

Cp'₂Th(¹³CH₃)₂ Cp'₂Th(¹³CH₃)₂/DA

Cp'2Th(13CH3)2/DS

Cp'2Th(13CH3)2/DSA

Cp'2Th(13CH3)2/MgCl2

 $Cp'_{2}Th(^{13}CH_{3})_{2}/SiO_{2}-MgO Cp'_{2}Th(^{13}CH_{3})_{2}/MgO$

Table I.	Solid-State	¹³ C NMR	Chemical S	Shift Data	and As	ssignment
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Cp'-C

123.1 124.2

124.0

124.2

124.1 121.3

7 1351 Billion					
$An-C(\alpha)^b$ $Cp'-CH_3$		others			
68.5	12.0				
71.0	10.2	-12.0 (Al-CH ₃)			
69.0	10.0	-8.0 (Mg-CH ₃)			
59.0	9.2	-5.4 (Si-CH ₃)			
74.0	10.0	-6.0 (Al-CH ₃ and/or Si-CH ₃)			
60.0					
59.1	8.7	-7.3 (Si-CH ₃ + Mg-CH ₃)			
62.1	9.8				
55.5					
52.3					

 $Cp_{1}^{\prime}Th(^{13}CH_{1})[OSiMe_{2}(t-Bu)]^{c}$ 122.7 59.2 12.6 21.7 (t-Bu-CH₃), 20.3 (t-Bu-C), 1.1, -0.2 (Si-CH₃)

	123.4			
$Cp'_{3}Th(^{13}CH_{3})[OCH(t-Bu)_{2}]^{c}$	123.2	58.4	13.5	94.4 (O-CH), 38.5 (t-Bu-C), 30.6 (t-Bu-CH ₃)
Cp^{\prime} , Th(¹³ CH ₂)Cl ⁴	126.3	67.6	12.5	
$Cp_{Th}^{(13}CH_{2})_{2}/PDA^{d}$	125.0	66.3	10.7	
$Cp'_{3}Th(^{13}CH_{3}^{13}CH_{3})_{3}$	122.2	69.6	12.2	11.4 (Th-CH ₂ CH ₃)
Cp'aTh(¹³ CH ₂ ¹³ CH ₂) ₂ /MgCl ₂	126.3	76.0	10.0	20.0 (br. Mg-CH ₂ CH ₂ , Mg-CH ₂ CH ₃ , Th-CH ₂ CH ₃)
$Cn_{3}Th(^{13}CH_{3})$		36.3	••••	117.6 (Cp-C)
$C_{\rm p}$ Th(¹³ CH ₃)/DA				119.2 (Cn-C)
opjin(onj)/ Dri				-15.4 (Al-CH ₂)
$Cn'Th(^{13}CH_{*}C_{*}H_{*})$	123 3	81.6	13.0	145-120 (C.H.)
op m(ongoing);	12515	78.9	10.0	
		76.0		
C_{n} T_{n} $(^{13}CH_{*}C_{*}H_{*})_{*}/DA$	126.8	95.0	10.1	$20.2 (A) - CH_{1}C_{2}H_{2}$
ep m(engenis); bh	120.0	75.2	10.1	20.2 (/// 0/1206/13)
		66.4		
$[C_{n'},T_{h}(u,H)H]$	123.5	00.4	127	
$[Cp'_{2}Th(\mu H)H]_{2}$	125.5		10.7	
$[C_{p}/T_{h}(\mu - 1)]_{2}/D_{h}$	129.0		11.5	
C_{n} Th(CU CU CU CU CU)	120.0	81.0	11.5	$24.2, 22.1$ (θ and ϕ CH)
$Cp_2 m(Cn_2 Cn_2 Cn_3)_2$	122.2	02.9	11.0	15.2 (CU)
	122.7	75.0 25.4		15.5 (CH ₃)
$Cp Tn(Cn_2C_6n_5)(OC_6n_5)_2$	138.0	33.4		
		32.3	25	
$Cp_2 U(Cn_3)_2$		1430	-25	
$Cp_2 U((CH_3)_2/DA)$				-14.4 (AFCH ₃)
$Cp_2 \cup (CH_3)_2 / Mg Cl_2$				$-10.4 (Mg-CH_3)$
$Cp'_2 U("CH_3)_2/DS$				-/.4 (SI-CH ₃)

Versus external TMS. ^bσ-bonded carbon atom. ^cReference 12b. ^dReference 12a.

 $({}^{13}CH_3)_2/MgCl_2$ (Figure 1B; ca. 0.25Th nm⁻²) is similar to that of $Cp'_{2}Th(^{13}CH_{3})_{2}/DA$ with a "cation-like" Th-CH₃ resonance and a Mg-CH₃ resonance at δ -8.0 (cf., δ -10.8 in solid CH₃MgBr).²⁹ Dipolar dephasing and ¹³C/¹²C substitution support this assignment (Table I). Interestingly, Bloch decay experiments yield a featureless ¹³C spectrum except for a weak signal in the Mg-CH₃ region, suggesting limited isotropic mobility of these surface functionalities. The weak spectral feature at ca. δ 60 can be assigned on the basis of results with PDA (vide infra)^{11a} and other supports (vide infra) to a Cp'₂Th(CH₃)O- species (B).^{30a}

Figure 1C presents the CPMAS spectrum of Cp'₂Th(¹³CH₃)₂ adsorbed on highly dehydroxylated (ca. 0.4 σ -OH nm⁻²)^{30b} silica (DS; ca. 0.25Th nm⁻²). Assignments are given in Table I. On the basis of model compounds, the resonance at δ -5.4 is ascribed to a surface Si–CH₃ functionality (cf., δ –1.0 for ¹³CH₃Li adsorbed on DS).^{12b} The Th–CH₃ resonance at δ 59.0 occurs at considerably higher field than is associated with "cation-like" species (vide supra), but in close proximity to δ Th-CH₃ for Cp'₂Th(CH₃)OR' model complexes (δ 59.2, R' = Si(CH₃)₂(t-C₄H₉)).^{12b} These results are most compatible with a fully Th–O $\sigma\text{-bonded}$ " $\mu\text{-}$ oxo-like" structure (e.g., D). Noteworthy in addition to the ab-sence of a "cation-like" species is the complete lack of olefin hydrogenation activity by $Cp'_{2}Th(^{13}CH_{3})_{2}/DS$.

Highly dehydroxylated SiO_2 -Al₂O₃ (DSA) is a strong Lewis acid.⁸ The CPMAS spectrum of $Cp'_2Th(^{13}CH_3)_2/DSA$ (Figure 1D) bears similarities to those of both $Cp'_2Th(^{13}CH_3)_2/DS$ and



Figure 1. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition, 4.5 ms contact time) of (A) $Cp'_2Th(^{13}CH_3)_2/DA$ (13 200 scans), (B) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ (6050 scans), (C) $Cp'_2Th(^{13}CH_3)_2/DS$ (10125 scans), (D) $Cp'_2Th(^{13}CH_3)_2/DSA$ (16 100 scans), (E) $Cp'_2Th(^{13}CH_3)_2/(SiO_2/MgO)$ (11 450 scans), and (F) $Cp'_2Th(^{13}CH_3)_2/MgO$ (11 563 scans).

 $Cp'_{2}Th(^{13}CH_{3})_{2}/DA$. Peaks assignable (Table I) to Si-CH₃ (δ -6.0) and $Cp'_{2}Th(^{13}CH_{3})O-(\delta 60.0)$ species are clearly discernable as is a Th-CH₃ resonance in the "cation-like" region (δ

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Figure 2. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) Cp'Th(¹³CH₂C₆H₅)₃ as a neat solid (1220 scans), (B) Cp'Th(CH₂C₆H₅)₃ as a neat solid (620 scans), (C) Cp'Th-(13CH₂C₆H₅)₃/DA (3000 scans), and (D) Cp'Th(CH₂C₆H₅)(OC₆H₅)₂ as a neat solid (896 scans); X denotes a spinning sideband.

70.0). Although an accompanying Al-CH₃ functionality cannot be rigorously identified, the spectral line shape in the δ -20-20 region is consistent with the presence of an underlying, quadrupolar-broadened ²⁷Al-CH₃ signal superimposed upon the narrower Si-CH₃ resonance. The spectrum on DSA is thus compatible with both structures A and D. $Cp'_2Th(CH_3)_2/DSA$ catalyzes the hydrogenation of propylene.^{7a}

The surface of dehydroxylated SiO_2 -MgO (DSM) functions as a weak Lewis acid,^{8d,h} while that of MgO (NaCl crystal structure³¹) functions as a weak Lewis base.^{8d,h} The CPMAS spectrum of Cp'₂Th(¹³CH₃)₂/DSM (Figure 1E, Table I) exhibits a high field resonance at δ -7.3 assignable to Si-CH₃ and/or Mg-CH₃ groups (vide supra). The Th-CH₃ signal at δ 59.1 is consistent with a Cp'₂Th(CH₃)O- σ -bonded structure. The CPMAS spectrum of Cp'₂Th(¹³CH₃)₂/partially dehydroxylated MgO (PDM, Figure 1F, Table I) provides no evidence of methyl transfer to surface Mg^{2+} centers. Rather, only relatively high field Th-CH₃ signals at δ 62.1, 55.5, and 52.3 are observed. These can be ascribed to Cp'₂Th(CH₃)O- species with the multiplicity of Th-CH₃ chemical shifts presumably reflecting the heterogeneity of surface microenvironments. The basic spectral pattern is reminiscent of that exhibited by $Cp'_2Th({}^{13}CH_3)_2/PDA.{}^{12a}$ At-tempts to further dehydroxylate MgO by heating in flowing He at 900 °C yields a low surface area material ($<10 \text{ m}^2/\text{g}^{-1}$) which does not adsorb significant quantities of Cp'₂Th(¹³CH₃)₂. In accord with the lack of detectable "cation-like" species for $Cp'_2Th(^{13}CH_3)_2/DSM$ and $Cp'_2Th(^{13}CH_3)_2/PDM$, neither substance exhibits significant olefin hydrogenation activity.7

Spectroscopy of Other Actinide Hydrocarbyls Adsorbed on Alumina and Magnesium Chloride. Figure 2A presents the ¹³C CPMAS spectrum of solid Cp'Th(13 CH₂C₆H₅)₃. The resonances at δ 123.3 and δ 13.0 are ascribed to the Cp'-C and Cp'-CH₃ groups, respectively (Table I). The crystallographically nonequivalent²¹ Th-¹³CH₂ moieties give rise to the three intense signals at δ 81.8, 79.0, and 76.2; assignment is confirmed by the diminution of these features in $Cp'Th(CH_2C_6H_5)_3$ (Figure 2B). The aromatic benzyl carbon atoms give rise to several resonances in the δ 145-120 region. The CPMAS spectrum of Cp'Th-($^{13}CH_2C_6H_5$)₃/DA is shown in Figure 2C. In addition to Cp'-C and Cp'-CH₃ resonances at δ 126.8 and 10.1, respectively, an intense ${}^{27}Al-CH_2$ signal is observed at δ 20.2 (δ 21.0 in Al- $(CH_2C_6H_5)_3)^{32}$ and downfield shifted Th-CH₂ features at $\sim \delta$ 95

(31) As probed by LEED, the (100) surface of single crystal MgO differs imperceptibly from the bulk structure: Urano, T.; Kanaji, T.; Kaburagi, M. Surf. Sci. 1983, 134, 109-121.



Figure 4. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) $Cp'_2Th({}^{13}CH_2{}^{13}CH_3)_2$ as a neat solid (572 scans) and (B) $Cp'_2Th({}^{13}CH_2{}^{13}CH_3)_2/MgCl_2$ (5620 scans).

(other Th-CH₂- resonances at δ 75.2 and 66.4). The ²⁷Al-CH₂ assignment is additionally supported by the observation of an identical feature when $Li^{13}CH_2C_6H_5$ is adsorbed on DA. These results for Cp'Th(${}^{13}CH_2C_6H_5$)₃/DA are in accord with benzyl transfer to Al³⁺ surface sites and the formation again of "cation-like" species (e.g., F). Evidence against a σ -bonded μ -oxo species (e.g., G) is provided by the spectrum of the aryloxide



 $Cp'Th(CH_2C_6H_5)(OC_6H_5)_2^{33}$ (Figure 2D). As in the case of Cp'₂Th(CH₃)₂ versus Cp'₂Th(CH₃)OR (vide supra), alkoxide ligands induce an upfield displacement of hydrocarbyl α -carbon resonances. Thus, the Th-CH₂ signals now occur at δ 35.4 and 32.3. In accord with the "cationic" formulation for Cp'Th- $(CH_2C_6H_5)_3/DA$, this material exhibits very high activity for olefin hydrogenation and polymerization (higher than $Cp'_2Th-(CH_3)_2/DA$).^{7b,34} However, as assayed by CO poisoning experiments, less than $\sim 3\%$ of the Cp'Th(CH₂C₆H₅)₃/DA sites are catalytically significant.7b

The CPMAS spectrum of solid Cp₃Th(¹³CH₃) (Figure 3A)^{35a} consists of readily assigned^{35b} resonances at δ 117.6 (Cp–C) and δ 36.3 (Th–¹³CH₃). When Cp₃Th(¹³CH₃) is adsorbed upon DA, the spectrum (Figure 3B, Table I)^{35a} shows essentially complete transfer of the methyl groups to surface Al³⁺ sites, as evidenced by an ²⁷Al-CH₃ resonance at δ -15.4. The Cp-C resonance is assigned at δ 119.2 with no residual Th-CH₃ signal detected (Table I). The formulation of surface Cp₃Th⁺ cationic species (e.g., H) finds close analogy in known $(RC_5H_4)_3Th^+B(C_6H_5)_4^-$

complexes.^{13a} Consistent with the lack of a Th-C/H σ -bond and a high degree of coordinative saturation, Cp₃ThCH₃/DA is inactive for olefin hydrogenation except at very high temperatures.76

Additional experiments were conducted on MgCl₂, beginning with $Cp'_{2}Th(^{13}CH_{2}^{13}CH_{3})_{2}$, for reasons that will become evident in a following section. In the spectrum of neat Cp'_2Th - $(^{13}CH_2)^{13}CH_3)_2$ (Figure 4A), four resonances are observed and can be readily assigned (Table I): δ 122.2 (Cp'-C), 69.6 (Th-CH₂-), 12.2 (Cp'-CH₃), and 11.4 (Th-CH₂CH₃). Cp'₂Th- $(CH_2CH_3)_2$ exhibits a similar spectrum with less intense resonances where expected. Although the Cp' line widths are unaffected by ¹³C enrichment, both ethyl resonances are noticeably

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(34) Gillespie, R. D.; Burwell, R. L., Jr.; Marks, T. J. Unpublished results.
(35) (a) See section at end regarding Supplementary Material. (b) Fischer, R. D. In Fundamental and Technological Aspects of Organo-f-Element Chemistry; Marks, T. J., Fragalà, I. L., Eds.; Reidel: Dordrecht, 1985; Chapter 8, and references therein.

broader in $Cp'_2Th(^{13}CH_2)^{13}CH_3)_2$ (~150 Hz broader with the same FID weighting). This broadening is doubtless a consequence of residual $^{13}C^{-13}C$ dipolar coupling^{36a} that is not completely removed by the MAS employed as well as $^{13}C^{-13}C$ scalar coupling (anticipated to be ~35 Hz^{36b}). The spectrum of $Cp'_2Th(^{13}CH_2)^{13}CH_3)_2/MgCl_2$ (Figure 4B) is consistent with the "cation-like" model advanced for $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ with Cp'-C at δ 126.3, a Th-CH₂- resonance centered at lower field (δ 76.0), a broad Mg-CH₂- resonance centered at ca. δ 20 (δ -2.9 in CH₃CH₂MgBr), ^{29b} and sharper coincident Th-CH₂CH₃, Mg-CH₂CH₃, and Cp'-CH₃ signals at δ 10.0 (δ 12.2 in CH₃CH₂MgBr). An alternative assignment would attribute the broad envelope at δ 40-0 to overlapping Mg-CH₂- and Mg-CH₂CH₃ resonances, broadened by the heterogeneity of surface environments, residual ¹³C-¹³C dipolar coupling, and scalar coupling.

Attempts were also made to adsorb $Cp_3Th(^{13}CH_3)$ on $MgCl_2$ by using the standard procedures. However, thorough pentane washing removed all traces of the organometallic, and a CPMAS spectrum could not be detected.

A Paramagnetic Probe of Surface Alkyl-Actinide Spatial Relationships. The great bulk of Th(IV) and U(IV) organometallic chemistry is rather similar^{6,19,37} as are the catalytic properties of Cp'2Th(CH₃)₂/DA and Cp'2U(CH₃)₂/DA.^{7b} However, U(IV) is paramagnetic (5f²), and ligand resonances generally experience large paramagnetic shifts combined with relatively narrow (due to short electron spin-lattice relaxation times) line widths.^{6,19,38,39} In general, the observed solution paramagnetic shifts are composed of "dipolar" (from magnetic anisotropy in the absence of cubic symmetry) and "contact" spin density delocalization (from a variety of mechanisms, including polarization of ligand orbitals by metal 6s and 6p orbitals as well as direct covalent spin density transfer from metal 5f orbitals) contributions.³⁸⁻⁴⁰ Assuming a purely f orbital description for U(IV) (unquenched orbital angular momentum) and a point dipole approximation, the dipolar shift for ligand nucleus i in solution can be expressed in terms of structure-dependent geometric factors and the magnetic anisotropy of the complex (eq 1).^{38,39} Here, N is Avogadro's number, the

$$\Delta H_{i}^{dip} = -\frac{1}{3N} [\chi_{zz} - \frac{1}{2} (\chi_{yy} + \chi_{xx})] \frac{3 \cos^{2} \theta_{i} - 1}{\mathbf{r}_{i}^{3}} - \frac{1}{2N} (\chi_{xx} - \chi_{yy}) \frac{\sin \theta_{i}^{2} \cos 2\psi_{i}}{\mathbf{r}_{i}^{3}}$$
(1)

 χ 's are magnetic susceptibility tensors, \mathbf{r}_i is the metal-to-nuclear distance, and the angles θ and ψ fix the \mathbf{r}_i vector within the molecular coordinate system. For axial symmetry, the expression simplifies considerably (eq 2).^{38,39} In cases of axial symmetry

$$\Delta H_{i}^{dip} = -\frac{1}{3N} (\chi_{\parallel} - \chi_{\perp}) \frac{3 \cos^{2} \theta_{i} - 1}{\mathbf{r}_{i}^{3}}$$
(2)

(uranocenes, Cp_3UX), it has been possible to approximately decompose the observed paramagnetic shifts into dipolar and spin



Figure 5. Solid-state ¹³C NMR spectra (75.4 MHz) of neat Cp'_2U -(¹³CH₃)₂. (A) Downfield region acquired with MAS only (5 s repetition, 522 scans). The arrow indicates the centerband of the spectrum. (B) Upfield region acquired with CPMAS (5 s repetition, 4.5 ms contact time, 512 scans).



Figure 6. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) $Cp'_2Th(^{13}CH_3)_2/DA$ (1330 scans) and (B) $Cp'_2U(^{13}CH_3)/DA$ (8938 scans). Adamantane (resonances denoted by S) added as an internal intensity standard.

delocalization contributions.^{39,40} No attempt has been made to perform such a decomposition for $Cp'_2UR_2^{15a,b,19}$ complexes; however, the signs and magnitudes of the observed paramagnetic shifts are roughly similar to those of the corresponding (same R) Cp_3UR complexes.^{39b,c}

In randomly oriented powders or when immobilized on a surface, the ligand NMR spectra of organoactinide complexes will be modified by those anisotropic components of the dipolar^{40,41} and spin delocalization^{38,40} shifts which are normally averaged to zero by rapid tumbling in solution. To a first approximation, these should be similar in form to chemical shift anisotropies⁴² and the anisotropic components of Knight shifts⁴³ and should in principal be removable (or reduced to a tractable sideband pattern)^{10,43a,44} by sufficiently rapid MAS. The solution ¹³C NMR

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spectrum of Cp'₂U(13 CH₃)₂ exhibits a U–CH₃ resonance at δ 1480 ppm, considerably downfield from that of the diamagnetic thorium analogue (δ 68.5). Hence, the effects of the U(IV) center are extremely large for this directly σ -bonded alkyl group. The Cp'-CH₃ resonance occurs at δ -30.0, and the Cp'-C signal could not be located. For solid $Cp'_2U({}^{13}CH_3)_2$, it was found that the U-CH₃ signal could be most effectively observed (presumably because of the very short T_1 and very large shift) without CP techniques. As a consequence of the large solid-state paramagnetic anisotropy, an extensive spinning sideband pattern is observed (Figure 5A). Variation of the spectral window and spinning rate allowed location of the U-CH₃ resonance at δ 1430 ± 20. Considering the slight differences in the FX90 and VXR300 probe temperatures and the experimental difficulties in acquiring the solid-state spectrum, this result is in good agreement with that in solution (δ 1480, vide supra). The Cp'-CH₃ signal could be observed by standard CPMAS as a broad peak at δ -25 (Figure 5B), only slightly displaced from the solution position (δ -30, vide supra). These results indicate that useful ${}^{13}C$ spectra of Cp'_2UR_2 complexes can be recorded in the solid state and that MAS sufficiently removes condensed phase anisotropy effects to reveal isotropic spectral features. The large shifts imparted to proximate nuclei suggest an efficacious means to probe metal-alkyl group distances on the surface.

Figure 6A and B shows CPMAS spectra of Cp'₂Th-(¹³CH₃)₂/DA and Cp'₂U(¹³CH₃)₂/DA, respectivley, at identical loadings. Adamantane has been added as an internal standard for normalizing intensities. The spectrum of $Cp'_2U(^{13}CH_3)_2/DA$ evidences no obvious Cp'U or U-CH₃ specral features either in Figure 6B or in scans over wider sweepwidths. Of course, such features are expected to be broad and rather weak under these conditions (cf., Figure 5). In contrast, the center of the Al-CH₃ signal in $Cp'_2U({}^{13}CH_3)_2/DA$ is only slighly displaced upfield ($\lesssim 5$ ppm) from that in $Cp'_{2}Th(^{13}CH_{3})_{2}/DA$, is only slightly broadened, and represents $90 \pm 10\%$ of the expected spectral intensity. If the $Cp'-CH_3$ resonance were present at the same field position as in neat $Cp'_2U({}^{13}CH_3)_2$, it would be a broad envelope extending from $\sim \delta$ -50-0, having ca. 1/10 the intensity of the Al-CH₃ signal, i.e., it would likely be obscured by the Al-CH₁ resonance. These results indicate that little if any U(IV) unpaired spin density or magnetic anisotropy is transmitted to the majority of the Al-CH₃ moieties. In similar experiments Th, U pairs were also examined for the $Cp'_2An(^{13}CH_3)_2/MgCl_2$ (Figure 7) and Cp'_2An(13CH_3)_2/SiO_2 (Figure 8) systems. In both cases, the surface methyl group signals experience little displacement (≤ 5 ppm) and only minor broadening. In both cases, $90 \pm 10\%$ of the methyl signal intensity is accounted for. Again, little inter-



Figure 8. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) $Cp'_2Th(^{13}CH_3)_2/DS$ (4668 scans) and (B) $Cp'_2U(^{13}CH_3)/DS$ (10000 scans). Adamantane (resonances denoted by S) added as an internal intensity standard.

action is observed between the majority of surface methyl groups and the U(IV) center.

While exact quantitative analysis of U---CH₃(surface) interactions requires detailed, presently unavailable knowledge of surface Cp'₂UCH₃⁺ magnetic anisotropy and spin delocalization, it is still possible to make physically reasonable, qualitative estimations of the range of possible U···CH₃(surface) distances. In doing so, it is pragmatically assumed that spin delocalization and dipolar shifts are roughly similar to those in the well-studied, axially symmetric Cp₃UR series.^{35b,38b,39b,c,45} That observed solution shift patterns for alkyl groups are similar in Cp₃UR and $Cp'_2UR_2/Cp'_2U(Cl)R/Cp'_2U(\bar{O}R')\hat{R}$ complexes^{15a,19,45} argues that the sums of the spin delocalization and dipolar terms are not terribly different. Where data exist for similar ligands, U-(IV)-induced spin delocalization shifts do not differ greatly.^{38a,39,46} In Cp₃UCH₃ at room temperature, $\Delta H^{dip} \approx +130$ ppm (upfield) and $\Delta H^{spin deloc} \approx +50$ ppm (upfield; in accord with a 5f² polar-ization mechanism).^{38,39} If a similar magnetic anisotropy is assumed for $Cp'_2U(CH_3)_2$, then geometric factors (eq 2) and metrical data lead to an estimate for $\Delta H^{dip}(U^{-13}CH_3)$ of ca. +300 ppm upfield. That a large, polarization-derived downfield shift dominates the observed spectral characteristics (vide infra) should not be surprising for a directly bound nucleus.^{38,39} The simplest model for adsorbate structure would involve incremental displacement of the methyl group from the U(IV) center (I). Since

the spin delocalization shift is ultimately dependent on metalligand orbital overlap, 38,39 it is expected to attenuate far more rapidly with increasing r than the through-space dipolar term. Assuming the magnetic anisotropy and angular part of the geometric factor remain approximately constant with changing r in structure I, the question becomes how large r must become to reduce ΔH^{dip} to the magnitudes observed in the spectra of adsorbed $Cp'_2U({}^{13}CH_3)_2$ (Figures 6-8). This dipolar-shift-only analysis is admittedly approximate but allows an assessment of how the surface CPMAS spectra can vary with r. Assuming that U-CH₃ = 2.43 Å in $Cp'_2 U(CH_3)_2$,^{37c} then the diminution $\Delta H^{dip} = 300$ \rightarrow 10 ppm corresponds to an ca. 7.6 Å increase in r. Even a more conservative $100 \rightarrow 10$ ppm decrease would correspond to an ca. 5.3 Å increase in r. This argument would be equally applicable to cases in which ΔH^{dip} was of opposite sign. For dynamic systems, ΔH^{dip} would be the weighted average of the spectral parameters

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Figure 9. ¹³C CPMAS NMR spectra (75.4 MHz, 5 s repetition time, 4.5 ms contact time) of (A) Cp'_2Th(¹³CH₃)₂/DA (13 200 scans) and (B) Cp'_2Th(¹³CH₃)₂/DA exposed to 30 equiv of ethylene (8835 scans). PE denotes a polyethylene ($-CH_2CH_2-$)_x resonance, an X a spinning sideband.

in the instantaneous geometries occupied. Importantly, these results readily rule out μ -alkyl geometries such as structure E and argue that the location of the transferred methyl group on the surface must be some angstroms distant from the actinide center (≥ 5 Å).

Adsorbate Reaction Chemistry. Ethylene. In addition to probing adsorbate structure, CPMAS NMR offers the fascinating opportunity to directly probe adsorbate reactivity. For example, the relative reactivity of An-alkyl versus surface-alkyl groups or of "cation-like" versus " μ -oxo" species can be *directly* examined via in situ competition experiments with a variety of reagents. It will be seen that the study of polymerization processes by using isotopically labeled reagents is particularly informative since the immobilized products encode "memory" effects. Experiments were first carried out in which $Cp'_2Th(^{13}CH_3)_2/support$ systems were incrementally dosed with measured amounts of gaseous reagents and CPMAS spectra recorded. All possible efforts were made to rigorously exclude oxygen and water (see Experimental Section).

Ethylene polymerization was investigated by using high vacuum line experiments in which Cp'₂Th(¹³CH₃)₂/support catalysts were exposed to measured quantities of ethylene. Exposures were carried out at 77 K to allow diffusion of ethylene into the pores of the catalyst prior to polymerization, thus minimizing mass transport effects. The catalyst was then slowly warmed to room temperature, during which time ethylene uptake could be detected manometrically. The $Cp'_{2}Th(^{13}CH_{3})_{2}/DA$ + ethylene system (Figure 9) reveals that incremental doses of olefin result in the growth of polyethylene resonances, with PE-CH₂- expected at δ 33 and PE-CH₃ expected at δ 10-15 (degenerate with the Cp'-CH₃ signal),⁴⁷ but induces no perceptible changes in the $Cp'_{2}Th({}^{13}CH_{3})_{2}/DA$ spectrum. Since insertion of ethylene into a Th- ${}^{13}CH_{3}$ or Al- ${}^{13}CH_{3}$ bond would result in large ${}^{13}CH_{3}$ chemical shift displacements, and since no obvious diminution of relative signal intensities is evident, it is concluded that only a small percentage of the surface sites is responsible for the polymerization ($\leq 10\%$). Importantly these results agree well with the aforementioned carbonylation and protonolysis poisoning assays^{7a,b} of the active site percentages, i.e., ≤4%. As a point of reference, note that at room temperature in toluene solution, neither Cp'₂Th(CH₃)₂ nor typical Cp'₂Th(CH₃)X compounds (X = alkoxide, Cl, O_3SCF_3) undergo significant reaction with ethylene (1 atm) over the course of several hours. However, the cationic complex $Cp'_{2}Th(CH_{3})^{+}B(C_{6}H_{5})_{4}^{-}$ catalyzes ethylene polymerization with $N_t \approx 1 \text{ min}^{-1.12}$

Ethylene dosing experiments were also conducted with CpTh(${}^{13}CH_2C_6H_5$)₃/DA and Cp₃Th(${}^{13}CH_3$)/DA. In the former case, the growth of polyethylene signals was detected, but no change in either Th- ${}^{13}CH_2$ - or Al- ${}^{13}CH_2$ - resonances could be observed. Again, polymerization is deduced to occur at only a small percentage of the surface sites, in agreement with catalytic poisoning assays.^{7b} Exposure of Cp₃Th(${}^{13}CH_3$)/DA samples to





Figure 10. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ (6050 scans), (B) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ exposed to 5.0 equiv of ethylene (5700 scans), (C) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ exposed to 10.0 equiv of ethylene (5700 scans), (D) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ exposed to 16.0 equiv of ethylene (5900 scans), and (E) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ exposed to 350 equiv of ethylene (6000 scans). PE denotes the location of a polyethylene signal.

ethylene doses under identical conditions results neither in the development of polyethylene signals nor in alteration of the existing adsorbate spectrum. This result is also in accord with results of catalytic studies^{7b} and with a polymerization mechanism requiring an initiating, surface Th-alkyl or Th-H functionality.

In principal, it should be possible to estimate the degree of ethylene polymerization from these CPMAS spectra via the relative intensities of the CH_2 and CH_3 signals. However, since longer chains will have considerable mobility, which in turn will degrade CP efficiency,^{27,47} we are reluctant to quantitatively analyze such data without exhaustive calibration studies. Furthermore, as noted above, the $Cp'-CH_3$ and PE-CH₃ signals are nearly coincident.

One characteristic of MgCl₂-supported Ziegler-Natta catalysts vis-à-vis those supported on more conventional materials (e.g., Al₂O₃, SiO₂) is a far higher percentage of active sites.³ This effect is also observed in catalytic studies of MgCl₂-supported organoactinides.^{7a} The results of progressively dosing a Cp'₂Th-(¹³CH₃)₂/MgCl₂ catalyst with ethylene are shown in Figure 10. In contrast to Cp'₂Th(¹³CH₃)₂/DA + ethylene, the development of polyethylene resonances is accompanied by an unambiguous initial decay of the Th-¹³CH₃ signal relative to the Cp'-C resonance. The intensity of this signal continues to fall with ethylene dosing, finally levelling off at ~50% of the initial signal area relative to Cp'-C. During this same period, the polyethylene-CH₂ resonance continues to increase in relative intensity, while that



Relative CPMAS spectral peak areas of a Cp'2Th-Figure 11. $(^{13}CH_3)_2/MgCl_2$ sample exposed to the quantities of ethylene indicated.

of the Mg-13CH₃ signal is essentially unchanged. Spectra of $Cp'_{2}Th(^{13}CH_{3})_{2}/MgCl_{2}$ and $Cp'_{2}Th(^{13}CH_{3})_{2}/MgCl_{2} + 5$ equiv of ethylene recorded as a function of Cp contact time (1, 3.5, 4, and 9 ms) indicate that this quantitation is not adversely affected by changes in CP dynamics. Indeed, a strength of this assay is that it quantitates untransformed starting material of known CP and spin-lattice relaxation characteristics, rather than an emerging product of unknown characteristics.

Relative spectral peak areas for the Cp'₂Th(¹³CH₃)₂/MgCl₂ + ethylene experiment are plotted in Figure 11 as a function of equivalents of added ethylene. It is concluded that $50 \pm 10\%$ of the Th-CH₃ sites undergo olefin insertion under the experimental conditions. This result is in favorable agreement with protonolytic poisoning experiments, which indicate $35 \pm 10\%$ of Cp'₂Th- $(CH_3)_2/MgCl_2$ sites are active for propylene hydrogenation at -63 °C.^{7a} In terms of selectivity, greater than 90 ± 10% of olefin insertion events take place at the surface Th-CH₃ functionality versus less than $10 \pm 10\%$ at the Mg-CH₃ bond. Furthermore, comparison of the Th-CH₃ peak intensity in Figure 11 versus the summed Cp'-CH₃ + PE-CH₃ peak intensities as a function of added ethylene provides an important self-consistency check. If PE-13CH₃ formation only occurs at the expense of Th-13CH₃ moieties, then the consumption of the latter species should be correlated with the formation of the former. The coincidence of the levelling-off portions of the PE-¹³CH₃ and Th-¹³CH₃ plots in Figure 11 substantiates this relationship. That the entirety of the Th-13CH₃ intensity is not recovered in the PE-13CH₃ resonance is evidence of (not surprisingly) rather different methyl group motional characteristic, hence CP efficiencies.^{27,47} It is also possible to estimate $k_{\text{propagation}}/k_{\text{initiation}}$ for the polymerization via analysis of the diminution of the Th-¹³CH₃ signals as a function of ethylene uptake. Assuming that 50% of the Cp'₂ThCH₃⁺ surface sites undergo ethylene insertion at a uniform rate ($\theta_{\text{ThCH}}, k_i P_{\text{olefin}}$), that subsequent ethylene insertions also occur at a uniform rate $(\theta_{\text{Th}(CH_2CH_2), \alpha CH_3}k_p P_{\text{olefin}})$, and that neither chain transfer (β -H elimination) nor chain termination is important, then eq 3 applies.48 M is equivalents monomer consumed, I_0 is the initial equivalents of initiator (Th-CH₃) present, and f is the fraction of the initiator

$$\frac{M}{I_0 f} = -\frac{k_p}{k_i} \left[1 + \frac{\ln(1-f)}{f} \right] + 2$$
(3)

consumed. For the initial region of ethylene uptake in Figure 10 (0-5 equiv), this relationship yields $k_p/k_i \approx 12$ ($M \approx 5$; $f \approx 0.6$). This result can be compared to relative ethylene insertion rates in the analogous, homogeneous Cp'_2Sc-R system of k(R = $CH_2CH_2CH_3)/k(R = CH_3) = 7.5$ (4) at -80 °C.^{51c}

An alternative or at least competing interpretation of the spectral changes observed in Figure 10 would be a vinylic C-H activation process,^{16a,49-52} which would also result in ethylenedependent decay of the $Th^{-13}CH_3$ signal (eq 4). To test such



an alternative, gases evolved in the $Cp'_2Th(CH_3)_2/MgCl_2$ + ethylene reaction were collected by vacuum line techniques (77 K silica gel trap) and released as a pulse to a calibrated gas chromatography system.^{7a,b} Any evolved methane was below the detection limits, hence $\leq 2\%$ of the Th sites react in this manner.

The experiments of Figure 10 reveal other interesting aspects of Cp'₂Th(¹³CH₃)₂/MgCl₂ surface chemistry. First, the Th-¹³CH₃ feature at δ 60 assigned to a Cp'₂Th(CH₃)O- species (B) does not significantly change in intensity with ethylene dosing. This lower reactivity is in accord with other observations on Cp'₂Th-(OR')CH₃ chemistry in solution.^{15a,b,19} Second, these spectra and those recorded several days later evidence no perceptible variations in the residual Th-13CH₃ and Mg-13CH₃ spectral intensities. Thus, transalkylative exchange of Th-R and Mg-R' groups must be slow on the time scale of days.

In principle, it should also be possible to carry out an experiment complementary to Figure 10 in which Cp'₂Th(CH₃)₂/MgCl₂ is incrementally dosed with ¹³CH₂=¹³CH₂. In this case, the relative reactivity (but not the fraction of reactive sites) of the Th-CH₃ and Mg-CH₃ moieties would be monitored by the growth of the corresponding Th-13CH2- or Mg-13CH2- signals. Efforts to conduct such experiments and to observe well-resolved M-13CH2signals as opposed to broad envelopes were frustrated by several factors. First, for significant degrees of ethylene polymerization, the very large (¹³CH₂¹³CH₂)_n resonance creates severe dynamic range problems and spinning sidebands in the spectral region expected for the Th- $^{13}CH_2$ - signal (cf., Figure 4). Secondly, the $M^{-13}CH_2^{13}CH_2^{-}$ resonances are expected to be broadened by $^{13}C^{-13}C$ scalar and unremoved dipolar coupling (vide supra).³⁶ Thirdly, diffraction structural, NMR spectroscopic, and theoretical results indicate that Cp'₂AnR₂ complexes occupy a very shallow potential energy surface for deformations of the Th-C(α)-C(β) valence angles.^{6d,52b,53} Such distortions are frequently accompanied by $\tilde{C}(\alpha)H$ "agostic" interactions, (e.g., \hat{J}). For NMR



spectroscopy, solid-state $\delta^{13}C(\alpha)$ parameters can therefore occur over a surprisingly broad spectral range and $C(\alpha)$ nonequivalences are common in Cp'₂ThR₂ CPMAS spectra.^{52b,54} A relevant example containing an *n* alkyl group is that of $Cp'_{2}Th(n-C_{4}H_{9})_{2}$ (Figure 12,^{35a} Table I). Assignment of the solution spectrum follows straightforwardly from ${}^{13}C{}^{1}H$ and coupled spectra: δ

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122.2 (Cp'-C), 89.2 (Th-CH₃), 31.4, 31.1 (C(β) and C(α)), 14.4 $(C(\delta))$, and 11.2 (Cp'-CH₃). The major difference in the CPMAS spectrum (Figure 12B) is the large magnetic nonequivalence observed for the C(α) resonances, viz., δ 81.0 and 93.8. Similar effects are observe in $Cp'_2Th[CH_2C(CH_3)_3]_2$ ($\Delta \delta \approx 26$) and $Cp'_{2}Th[CH_{2}Si(CH_{3})_{3}]_{2}$ ($\Delta \delta = 27$) and are associated with major solid-state structural distortions (e.g., J).6d,52b This behavior suggests that the Th-C(α) resonances of surface-bound Th-(¹³CH₂¹³CH₂)_nCH₃ species are likely to occur over a broad spectral range, reflecting the modest energies required for Th-C(α)-C(β) deformation, differing n values, and the heterogeneity.

Supported organoactinide hydrides are also active olefin hydrogenation and polymerization catalysts.^{7b} That the surface chemistry is similar to that of the supported hydrocarbyls is verified by CPMAS studies of $[Cp'_2Th(\mu-H)H]_2/MgCl_2$. The spectrum of the supported complex is essentially identical with that of $Cp'_{2}Th(^{13}CH_{3})_{2}/MgCl_{2}$ except for the absence of $Th^{-13}CH_{3}$ and $Mg^{-13}CH_3$ signals (Table I). Dosing with ethylene gives rise to the characteristic signatures of polyethylene (Figure 13)^{35a} minus, of course, the strong PE-13CH₃ resonance previously observed at δ 12 (Figure 10). In work to be reported elsewhere,⁵⁵ we show that ¹H MAS NMR spectroscopy is an effective method to detect surface-bound organoactinide hydrides and to monitor their chemical transformations.

Additional Adsorbate Chemistry. Hydrogenolytic transformations of actinide-alkyl bonds are important in both olefin hydrogenation⁴ and, for molecular weight control, in polymerization catalysis. Exposing Cp'₂Th(¹³CH₃)₂/DA samples to large molar excesses of H₂ at temperatures up to 100 °C for a period of several hours effects no perceptible changes in the CPMAS spectrum. This result agrees excellently with the low percentage of active olefin hydrogenation sites inferred from poisoning studies.^{7a,b} We estimate that $<10 \pm 10\%$ of the Th-CH₃ or Al-CH₃ sites undergo hydrogenolysis under these conditions. In contrast, exposure of $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ to excess H₂ at room temperature for 1 h (Figure 14) results in diminution of both the $Th^{-13}CH_3$ and $Mg^{-13}CH_3$ signals, with the former decaying slightly more rapidly. Interestingly, samples exhibiting a significant Cp'₂Th(¹³CH₃)O- resonance at $\delta \approx 60$ respond differently in that hydrogenolytic diminution of the $\delta \approx 70 \text{ Cp}'_2\text{ThCH}_3^+$ resonance is not accompanied by a significant decay of the μ -oxo Th-13CH, signal. This additional example of lower surface $Cp'_{2}Th(CH_{3})O-$ reactivity is again in accord with the solution chemistry of these less electrophilic species.^{13,21} That the chemistry of Figure 14B indeed generates reactive surface hydrides is confirmed by the observation that exposure of such samples to ethylene results in the formation of polyethylene (Figure 14C).

The potency of CO as a poison of Cp'₂Th(CH₃)₂/support catalytic activity promoted studies with this reagent. The reaction of $Cp'_2Th(CH_3)_2/MgCl_2$ with 1 equiv of ¹³CO (CO/Th = 1) is quantitative by manometry; however, no new ¹³CO-derived features are evident in the δ -50-489 region of the CPMAS spectrum. In contast, exposure of Cp'₂Th(¹³CH₃)₂/MgCl₂ to 1 equiv of either CO or ¹³CO results in a nearly identical spectrum with disappearance of the Th-13CH3 signal, no change in the Cp'-C, Cp'-CH₃, or Mg-¹³CH₃ resonances, and two new features of approximately equal intensity at δ 31 and δ 17 (Figure 15).^{35a} No other resonances are observed in the δ -50-489 spectral region. Although the interpretation of these changes is not unambiguous, note that typical organothorium dihaptoacyl (K) chemical shifts are $\sim \delta 350$ (-13C(O)CH₃) and $\sim \delta 30$ (-C(O)¹³CH₃).^{6b,37,45,56,57}



Figure 14. ¹³C CPMAS NMR spectra (75.4 MHz, 4 s repetition time, 4.5 ms contact time) of (A) $Cp'_2Th(^{13}CH_3)_2/MgCl_2$ (8082 scans), (B) Cp'₂Th(¹³CH₃)₂/MgCl₂ exposed to a large excess of H₂ (9492 scans), and (C) $Cp'_2Th(^{13}CH_3)_2/MgCl_2 + H_2$ followed by treatment with excess (20 equiv) ethylene (6220 scans).

The CSA of an acyl carbon is likely to be large, and combined with the heterogeneity of surface environments as well as possible coordination to acidic sites (e.g., L),58 it is not surprising that this signal is not readily detected.



The reactivity of Cp'₂Th(¹³CH₃)₂/MgCl₂ with respect to propylene was also investigated. CPMAS NMR (Figure 16A)^{35a} of a sample exposed to 15 equiv of propylene (6 h at 25 °C) reveals almost complete disappearance of of Th⁻¹³CH₃ and partial disappearance of Mg-13CH₃. Gas-trapping/GC-based experiments reveal that under these conditions propylene exposure releases 1.1 \pm 0.3 CH₄/Th. This observation suggests an allylic C-H activation process, previously observed for analogous (Cp'2Ln-R, R = alkyl) organolanthanide complexes⁵⁹ (eq 5). Subsequent ex-

$$Cp'_{2}Th^{+}-CH_{3} + \sim cp'_{2}Th^{+}-)$$
 + CH_{4} (5)

posure of this sample to H_2 (1 h at 25 °C) released 0.2 CH₄/Th, large quantities of propane and propylene, but no detectable C_4 products (isobutane, isobutylene, n-butane, etc.). Higher propylene oligomers would not be detected in this assay. Treatment with water also failed to evolve C_4 products. These results are in accord with the aforementioned NMR spectroscopic evidence (Figure 16A)^{35a} for some residual surface methyl groups. Since the support was likely to have adsorbed propylene during the initial propylene dosing and since Cp'₂Th(CH₃)₂/MgCl₂ is a propylene hydrogenation catalyst,^{7a} nothing about an η^3 -allyl (eq 5) can be inferred from the C_3 products. However, the absence of isobutane argues

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⁽⁵⁷⁾ For example, in Cp'₂Th[η^2 -C(O)CH₃]⁺B(C₆H₃)₄⁻, δ (CO) = 348.2 and δ (CH₃) = 33 (toluene-d₈ solution; Lin, Z.; Marks, T. J. Unpublished results)

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against significant Th-CH₃ single step insertion chemistry (e.g., eq 6). However, the NMR feature at $\sim \delta$ 25 is conceivably a

$$Cp'_{2}Th^{+}-CH_{3} + \bigcirc - Cp'_{2}Th^{+} \bigcirc (6)$$

¹³CH₃ end group of a propylene oligomer which would not have been detected in the trapping/GC assays (cf., δ 22.5 in solid isotactic and δ 21.0 in solid syndiotactic polypropylene^{60,61}). Cp'₂Ln(η ³-allyl) and Cp'₂Ln(isobutyl) compounds are known to undergo propylene insertion (in competition with allylic C-H activation) to yield propylene oligomers.^{50,59} Further support for the importance of allylic C-H functionalities here is provided by the observation that prolonged exposure of Cp'₂Th(¹³CH₃)₂/MgCl₂ to 3,3'-dimethylbutene has no effect on the CPMAS spectrum (eq 7).

$$Cp'_2Th^+-1^3CH_3$$
 + $N.R.$ (7)

Additional information on the $Cp'_2Th({}^{13}CH_3)_2/MgCl_2 +$ propylene reaction is provided by studies with propylene 60% ${}^{13}C$ labeled in the C-2 position. The CPMAS spectrum (Figure 16B) 35a reveals a multiplicity of resonances in the δ 20–70 and δ 120–150 regions. The most straightforward interpretation is in terms of repetitive propylene insertion by a surface η^3 -allyl (M) to yield a mixture of oligomers (eq 8) of varying chain length (note



that an η^3 -allyl can be regenerated via a competing process⁵⁹ analogous to eq 5), end group, and stereo- and possibly regioregularity. Thus, spectral features in the δ 140–155 region can be assigned to C2 resonances of an η^3 -allyl (δ 147.3 and δ 153.3 in solid Cp'Th(η^3 -C₃H₅)₃^{33,62}) or to the C2 carbon of an olefinic end group (cf., eq 8; δ 140–145 in analogous olefins⁶³). The resonance at $\sim \delta$ 60 is assigned to an unreactive Cp'₂Th(¹³CH₃)Ospecies, while the signals in the δ 20–45 region must be due, predominantly, to labeled positons of propylene oligomers. Note that methine resonances in regioirregular polypropylenes fall in the range $\sim \delta$ 28.3–38.5 in solution.⁶¹ It is conceivable that lower molecular weights, different chain folding on the surface, olefin isomerization, and possible chemisorptive interactions with the surface⁸ would increase the chemical shift dispersion further.

Conclusions

The results of this chemical/spectroscopic investigation considerably amplify what is known about organoactinide hydrocarbyl adsorbate structure and reactivity. Connections have been drawn between catalysis and spectroscopy which also convey implications for other adsorbed hydrocarbyl systems.³

Basically, three CPMAS spectroscopic patterns are observed for supported actinide hydrocarbyls. On strong Lewis acids (DA, MgCl₂, DSA), transfer of alkyl groups to acceptor sites on the surface is observed and is accompanied by residual low field Th- $^{13}C(\alpha)H_2R$ adsorbate resonances. The nature of the surface receptor site and NMR spectral similarities to species such as

Cp'₂Th(CH₃)⁺BPh₄⁻ and Cp'₂Th(CH₃)(THF)₂⁺BPH₄⁻¹³ suggest "cation-like" character. The present work shows this pattern is generalizable to other supports (MgCl₂, DSA), complexes (Cp'ThR₃, Cp₃ThR), and hydrocarbyl groups (ethyl, benzyl). From NMR experiments using paramagnetic U(IV) probes, it can be surmised that the great majority of Cp'₂Th(CH₃)₂-derived adsorbate molecules on both DA and MgCl₂ are not μ -alkyls (E) but rather the transferred surface alkyl moiety is $\gtrsim 5$ Å displaced from the actinide center. The second type of CPMAS pattern is observed on hydroxylated supports (PDA, PDS, MgO) where it is known⁷ that extensive An-R protonolysis occurs. Here, the Th- ${}^{13}C(\alpha)H_2R$ resonance is at considerably higher field (in the region of Cp'₂Th(CH₃)O-type complexes), and no transferred surface alkyl group is evident. A " μ -oxo-like" structure (B, C) is suggested for these adsorbates. Traces of these structures are occasionally observed on Lewis acid supports and provide an interesting reactivity comparison. The third type of spectroscopic pattern is observed on dehydroxylated supports without strong Lewis acid character and having relatively weak surface metaloxygen bonds (DS, portions of the DSA surface). Here both a " μ -oxo-like" Th-¹³C(α)H₂R resonance and a transferred surface alkyl resonance are observed, suggesting a structure such as D. Paramagnetic probes indicate that the majority of the surface alkyl groups are $\gtrsim 5$ Å from the actinide center.

In regard to heterogeneous olefin hydrogenation and polymerization catalysis, the present NMR results add considerably to the structure-catalytic activity picture that is emerging. Importantly, significant catalytic activity is only observed in systems exhibiting "cation-like" spectral signatures^{11e,13} (and metal alkyl or hydride bonds to effect the catalysis), while negligible activity is observed in systems exhibiting only "µ-oxo-like" (Cp'2Th-(CH₃)O-) spectral features.^{12b,19} Moreover, "µ-oxo-like" species do not display significant reactivity in direct competition with "cation-like" species on the same surface. These reactivity trends accord well with solution chemical expectations.^{6,13,14,15,19} Furthermore, the fractions of surface organoactinide complexes reactive in stoichiometric dosing experiments monitored by NMR are in good agreement with percentages of active sites assayed by catalytic CO and/or H_2O poisoning experiments.^{7a,b} Thus, only ~4% of Cp'₂Th(CH₃)₂/DA sites are important in propylene hydrogenation and ethylene polymerization as deduced by catalytic poisoning,^{7a,b} while the present NMR studies evidence ethylene polymerization by a fraction of sites below the detection limit (Figure 9; $\leq 10\%$ of the total) and response to hydrogenolysis at the same level. In contrast, $35 \pm 10\%$ of $Cp'_2Th(CH_3)_2/MgCl_2$ sites are found to be significant for propylene hydrogenation by catalytic poisoning,^{7a} while the present NMR studies show 50 \pm 10% of the observed sites active for ethylene insertion (Figures 10 and 11) and a comparable or larger percentage reactive with respect to hydrogenolysis (Figure 14).

The gross structural formulation for alkyl-transferred surface sites as "cation-like" (A) follows from chemical, structural, and spectroscopic analogies to solution chemistry.^{13,14} Not surprisingly, the chemical properties of a particular "cation-like" adsorbate are expected to be highly dependent upon the characteristics of the local counterion—in this case, the local support microstructure. This surface is not expected to be topologically uniform⁸ and it is likely, depending upon the bulk support structure and local heterogeneities, that different adsorbate sites will experience different counterion/surface interactions. The present results for spectroscopically "cation-like" Cp'_2Th(CH_3)_2/DA and Cp'_2Th-(CH_3)_2/MgCl_2 adsorbates underscore this point, and solution^{12,13,64,65} results tell us that a completely noncoordinating anion

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is difficult to achieve.

Further surface-solution chemistry connections are seen in Cp'₂Th(CH₃)₂/MgCl₂ CO dosing experiments, which evidence irreversible migratory insertion processes, most likely of the type previously observed in solution. Cp'2Th(CH3)2/MgCl2 propylene chemistry is dominated by initial allylic C-H activation/methane elimination. Subsequent chemistry involves olefin insertion and oligomerization as well as η^3 -allyl formation. All of these have been previously noted in f-element solution chemistry.

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Supplementary Material Available: Figures 3, 12, 13, 15, and 16 showing NMR spectra (6 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of Metallacycle-Carbene and -Bis(carbene) Complexes. A New Intramolecular Carbene-Carbene Coupling Process

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Abstract: Halide ion abstraction from the neutral iridiacyclopentadiene complexes, Ir(CR=CRCR=CR)(PPh₃)₂Cl (1, R = CO_2CH_3), and $Ir(CR=CRCR=CR)(PPh_3)_2(CO)(Cl)$ (2, R = CO_2CH_3), leads to high yields of the cationic complexes, $lr(CR=CRCR=CR)(PPh_3)_2(L)(L')^+BF_4^-$ (3, L = CO, L' = H₂O; 4, L = CO, L' = NCCH₃; 5, L = L' = NCCH₃; and 6, L = CO, L' = PMe_3). Reaction of complex 1 and 3-butyn-1-ol generates the first example of a metallacycle-carbene complex Ir(CR=CRCR=CR)(PPh₃)₂(Cl)[=C(CH₂)₃O] (7; 81%). Similarly, reaction of 3 or 4 and 3-butyn-1-ol leads to formation of the carbene complex Ir(CR=CRCR=CR)(PPh₃)₂(CO)[=C(CH₂)₃O]⁺BF₄⁻ (8; 96%). Reaction of 4 and 4-pentyn-2-ol gives a 95% yield of the substituted carbene complex Ir(CR=CRCR=CR)(PPh₃)₂(CO)[=C(CH₂)₂CHCH₃O]⁺BF₄⁻ (9). The acetonitrile analogues, Ir(CR=CRCR=CR)(PPh₃)₂(NCCH₃)[=C(CH₂)₃O]⁺BF₄⁻ (10) and Ir(CR=CRCR=CR)-(PPh₃)₂(NCCH₃)[=C(CH₂)₂CHCH₃O]⁺BF₄⁻ (11), are also prepared in excellent yield. The bis(carbene) complex Ir- $(CR=CRCR=CR)(PPh_3)_2[=C(CH_2)_3O]_2^+BF_4^-$ (12) is available in one step from 5 (87%). The mixed bis(carbene) complex $Ir(CR=CRCR=CR)(PPh_3)_2[=C(CH_2)_2CHCH_3O][=C(CH_2)_3O]^+BF_4^-$ (13) is prepared from 7 by sequential reaction with AgBF₄ and 4-pentyn-2-ol. Complex 8 crystallizes in space group Cc, with a = 12.723 (2) Å, b = 21.195 (4) Å, c = 18.432(3) $\mathring{A}, \beta = 90.37$ (1)°, V = 4970 (1) $\mathring{A}^3, Z = 4, R(F) = 3.11\%$, and $R_w(F) = 3.76\%$. Complex 12 crystallizes in space group $P\overline{1}$, with a = 12.951 (2) $\mathring{A}, b = 13.371$ (2) $\mathring{A}, c = 18.071$ (4) $\mathring{A}, \alpha = 78.42$ (2)°, $\beta = 79.27$ (2)°, $\gamma = 78.14$ (1)°, V = 2966(1) Å³, Z = 2, R(F) = 4.35%, $R_w(F) = 4.87\%$. Reaction of compounds 8 and 9 with pyridine gives the pyridinium-substituted acyl complexes $Ir(CR=CRCR=CR)(PPh_3)_2(CO)[C(=O)CH_2CH_2CH_2NC_5H_5]^+BF_4^-$ (14) and Ir(CR=CRCR=CR)-CRCR=CR $(PPh_3)_2(CO)[C(=O)CH_2CH_2CH(CH_3)NC_5H_5]^+BF_4^-(17)$. Methylamine and bis(oxacyclopentylidene) complex 12 give a nearly quantitative yield of the iridium hydride complex Ir(CR=CRCR=CR)(PPh₃)₂(NH₂CH₃)(H) (19), CH₃NH₄+BF₄-, and 2-(2(5H)-furanylidene)tetarhydrofuran (20; 92%). The mixed bis(carbene) complex 13 undergoes reaction with methylamine to give iridium hydride 19 and the carbene coupling products 2-(2(5H)-furanylidene)-5-methyltetrahydrofuran (24; 45%) and 2-(2(5-methyl)furanylidene)tetrahydrofuran (25; 55%). Iridium hydride 19 reacts with HCl to regenerate 1 and with HBF4 in acetonitrile to regenerate the bis(carbene) precursor 5. The mechanism of this novel carbene ligand coupling chemistry

Introduction

is discussed.

Interest in the properties and reactivity of metal-carbene complexes has continued unabated since E. O. Fischer reported the first examples of this compound class over 20 years ago.² Current interest in this area stems from the role of metal carbenes in alkene metathesis,³ alkene and alkyne polymerization,⁴ and cyclopropanation chemistry,⁵ and as intermediates in an impressive array of synthetic methodology.^{6.7} In an effort to develop new

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