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SUPPORTED ORGANOMETALLIC COMPLEXES:
SURFACE CHEMISTRY, SPECTROSCOPY, AND CATALYSIS

Progress Report
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The goal of our program is to define those modes of interaction that take place between organometallic molecules and inorganic surfaces and, ultimately, to correlate various molecule-surface structures with catalytic properties.

A. Organoactinides Adsorbed on Alumina

Detailed studies of the adsorption and catalytic chemistry of $\text{Cp}_2\text{M}(\text{CH}_3)_2$ and $\text{Cp}_2\text{M}(\text{CD}_3)_2$ (I, M=Th and U) complexes on partially dehydroxylated (PDA),

I

deuterated partially dehydroxylated (PDA-d), dehydroxylated (DA), and deuterated dehydroxylated (DA-d) alumina have been carried out.^{7a,9} Correlated but less extensive studies have also been conducted on compounds II-VI.^{7a,10} The

II

III

IV

V

VI

R = CH₃ R = neopentyl R = benzyl R = CH₃ n-C₄H₉

general picture emerging from evolved product analysis and ¹³C CPMAS nmr¹¹ is that alkyl group transfer from actinide to Lewis acid surface Al⁺³ sites occurs

on DA, giving rise to organoactinide cations (e.g., eq.(1), VII). Such

species have not previously been identified for an adsorbed organometallic compound and offer the catalytically attractive potential for both enhanced unsaturation and electrophilicity. Using several techniques, no evidence is found for isotropic mobility which is rapid on the nmr timescale.¹¹ Dosing $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$ with H_2 , ethylene, or H_2 then ethylene, produces no detectable changes in the adsorbate CPMAS spectrum, although the latter two protocols give rise to intense polyethylene spectral features.^{11b} Clearly, only a small percentage of the surface sites is highly reactive, in accord with catalytic poisoning results (*vide infra*), but not results on all supports (*vide infra*).

It is also possible to probe the actinide...CH₃-Al surface distances in species such as VII using the paramagnetic uranium analogue (VIII).¹² Large

dipolar and hyperfine shifts are expected for $\text{Cp}'_2\text{U}^{\text{IV}}\text{-CH}_3$ functionalities ($\delta(^{13}\text{CH}_3) \approx 1400$ ppm in $\text{Cp}'_2\text{U}(^{13}\text{CH}_3)_2$ ¹²) which should attenuate with U-CH₃ distance.¹³ Although quantitative analysis of these data are still in progress, it is already evident that the Al-CH₃ group is not proximate to the U(IV) ion

in such surface complexes and that $\mu\text{-CH}_3$ structures (e.g., IX) can be ruled out.

CPMAS studies of complexes III, V, and VI (M = Th) on DA provide evidence for cationic surface species X, XI, and XII, respectively.^{11b} The heterolytic

scission of the Th-C sigma bonds in X and XII correlates well with the low catalytic activity (*vide infra*).

Organoactinide adsorption chemistry on PDA is dominated by protonolytic reactions (e.g., eq.(2)). Such systems exhibit low catalytic activity because

requisite M-C sigma bonds are destroyed, but also because alkoxide ancillary ligands greatly depress the reactivity of proximate M-C sigma bonds. The latter phenomenon has been quantitatively characterized for actinides in solution mechanistic studies and appears to reflect increased electron density at the actinide center (decreased electrophilicity) as well as enhanced actinide-alkyl bond enthalpies.¹⁴

As already noted, $\text{Cp}_2\text{M}(\text{CH}_3)_2/\text{DA}$ catalysts exhibit very high activity for the hydrogenation of simple olefins (N_t at -63°C for propylene is comparable to that of $\text{Pt}/\text{SiO}_2^{15}$). Efforts during the past grant period have focused on detailed kinetic and mechanistic characterization of the catalytic cycle (isotopic labelling, determination of rate law, determination of isotope effects, quantitative poisoning studies, assessment of heat and mass transport effects, variation of temperature, variation of olefin, examination of factors governing catalyst lifetimes, etc).¹⁶ The mechanistic scenario emerging is illustrated in Scheme I for propylene. The hydrogenolysis process described by

k_2 necessarily involves a four-center heterolytic transition state (XV)¹⁴

XV

since Th(IV) cannot undergo oxidative addition. The rate law differs slightly from that found for isoelectronic Cp_2LnR complexes in solution ($k_1 \gg k_2$)¹⁷ in that regimes arise on the surface where $k_1 \approx k_2$, and eq.(3) is obeyed (olefin

$$\text{rate} = \frac{k_1 k_2 \theta_0 P_{\text{H}_2}}{k_{-1} + k_1 \theta_0 + k_2 P_{\text{H}_2}} \quad (3)$$

coverage $\theta_0 = 1$). Activation parameters and kinetic isotope effects (H_2/D_2) for propylene and isobutene hydrogenation are remarkably similar to those observed for analogous solution phase, f-element centered processes.^{14,17}

Quantitative poisoning experiments with CO indicate that less than 5% of the $\text{Cp}_2\text{M}(\text{CH}_3)_2/\text{DA}$ sites account for the bulk of catalytic hydrogenation activity.^{7a,15} Although this characteristic is rather common for heterogeneous catalysts,¹⁸ the reason is seldom understood at the atomic level. For the present studies, this result has motivated work with other metal complexes and supports as well as additional physical measurements (vide infra). For the $\text{Cp}_2\text{M}(\text{CH}_3)_2/\text{DA}$ catalysts, the relative ordering of olefin reactivity in *cis*-2-butene > *trans*-2-butene > propylene >> isobutylene.¹⁶ The higher reactivity of the more substituted olefins generally parallels the trend found in the Cp_2LnR series.¹⁶

The catalytic olefin chemistries of complexes II, III, V, and VI on DA have also been surveyed.^{7a,10} Thorium complexes III/DA and VI/DA are essentially inactive with respect to olefin hydrogenation. This behavior is explicable on the basis of the aforementioned nmr evidence^{11b} for Th-C heterolysis (X,XII). Complex II/DA is approximately as active as $\text{Cp}_2\text{Th}(\text{CH}_3)_2/\text{DA}$ for propylene hydrogenation, and the percentage of sites which are catalytically active appears to be only slightly greater than in the latter

system ($\leq 9\%$ vs $\leq 5\%$). Preliminary high speed ^1H MAS nmr studies¹⁹ indicate that the Th-H functionality of II/DA can be readily observed at high spinning rates, indicating that nmr monitoring of hydride reactivity patterns should be possible (vide infra). Complex V/DA is the most active catalyst so far examined. For propylene hydrogenation, turnover frequencies at -63°C are comparable to those for Rh/SiO_2 , the most active heterogeneous olefin hydrogenation catalyst known.^{7a,21} Poisoning experiments indicate $\leq 10\%$ of the sites are catalytically important. Preliminary experiments also indicate rapid hydrogenation of 1-butene, cis- and trans-2-butene, and isobutene by V/DA.^{10,16} As already noted, CPMAS studies of $\text{Cp}^*\text{Th}(\text{}^{13}\text{CH}_2\text{Ph})_3/\text{DA}$ reveal the formation of one or more cationic centers (e.g., XI).^{11b}

B. Organoactinides Adsorbed on Other Supports

Silica offers an intriguing contrast to alumina in that the surface OH groups are stronger Brønsted acids, yet surface Lewis acid sites are not present. Furthermore, silicas with a wide range of surface OH coverages are now readily accessible.²⁰ In preliminary studies, we found that supporting $\text{Cp}_2^*\text{M}(\text{CH}_3)_2$ on partially dehydroxylated silica (PDS) results in substantial protonolysis (cf., eq.(2)) and negligible catalytic activity.¹⁰ More intriguing is the observation that $\text{Cp}_2^*\text{M}(\text{CH}_3)_2$ complexes liberate only small amounts of CH_4 on dehydroxylated silica (DS) and yet are also catalytically inactive.^{10a} CPMAS nmr studies combined with data from model systems reveal that eq.(4) is the predominant reaction pathway.²² These results provide some

of the best evidence to date that Si-O alkylation/cleavage processes can be an important reaction mode for silica surfaces (where Si-O-Si bonding is believed to be highly strained²³) and also explain the low olefin hydrogenation activity. Presently in progress are parallel studies with $\text{Cp}'_2\text{U}(\text{}^{13}\text{CH}_3)_2/\text{DS}$ (cf., VIII) to probe the $\text{U} \cdots \text{CH}_3\text{Si}$ distance.

High surface area MgCl_2 is the preferred support for "third generation" Ziegler-Natta catalysts.³ Among other reasons, the coordinative unsaturation of the Mg^{+2} surface sites is thought to be crucial. In contrast to alumina-supported systems, MgCl_2 -supported Ziegler-Natta catalysts appear to have a far greater percentage of sites which are catalytically active. CPMA studies of $\text{Cp}'_2\text{Th}(\text{}^{13}\text{CH}_3)_2/\text{MgCl}_2$ reveal the formation of cationic adsorbate species (eq.(5), XVII) which exhibit little isotropic mobility on the nmr time-scale.^{11b,24} In marked contrast to the $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$ system, a high

percentage (~50%) of the adsorbate species is reactive in dosing experiments, and it has proven possible to spectroscopically investigate surface reaction pathways in considerable detail (eqs.(6)-(8)).^{11b,24} Thus $k(\text{initiation})/$

$k(\text{propagation})$ has been estimated for eq.(6) as well as the rate (very slow) of Th-alkyl/Mg-CH₃ interchange. A large number of other informative "in situ" experiments should also be possible (vide infra). Presently in progress are studies of U...CH₃Mg distances using Cp₂U(¹³CH₃)₂/MgCl₂¹² and kinetic/mechanistic measurements of Cp₂Th(CH₃)₂/MgCl₂ catalytic activity.²⁵

Preliminary studies of Cp₂Th(CH₃)₂/MgO reveal only weak catalytic activity for propylene hydrogenation on this rather basic support.²⁶ CPMA studies of adsorbate structure will commence shortly and should be highly informative.

C. New Metals and Catalytic Reactions

Supported organozirconium catalysts are reported to be active catalysts for olefin polymerization,^{2c,h,3h} however very little is known about adsorbate structure and in some cases, reported catalyst activation conditions are rather drastic. Far less is known about the olefin hydrogenation activity of such catalysts.²⁶ We find that supported cyclopentadienyl organozirconium

complexes are highly active catalysts for olefin hydrogenation and polymerization.²⁷ Relative activities on DA follow the approximate order $\text{Cp}^*\text{Zr}(\text{CH}_3)_3 \gg \text{Cp}_2\text{Zr}(\text{CH}_3)_2 > \text{Cp}^*\text{Zr}(\text{CH}_3)_2$, with the $\text{Cp}^*\text{Zr}(\text{CH}_3)_3$ complex ca. 1/4 as active as the most active supported organoactinides. Preliminary poisoning experiments with CO indicate that $\leq 4\%$ of the surface zirconium sites are responsible for the bulk of the catalysis. CPMAS nmr studies of $\text{Cp}_2\text{Zr}(\text{}^{13}\text{CH}_3)_2/\text{DA}$ reveal the formation of organozirconium cations (eq.(9), XVIII) with ^{13}C spectral

parameters in close correspondence with those of the highly reactive $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{L}^+$ complexes prepared by Jordan.^{28,29} Interestingly and in contrast to the organoactinide surface chemistry, these organozirconium complexes display some catalytic activity for olefin hydrogenation even when adsorbed on PDA (N_t is ca. 1/3 of that on DA).²⁷ The explanation is evident from CPMAS spectra²⁷ which indicate the presence inter alia, of organozirconium cations on PDA. This result is consistent with the lower protonolytic reactivity of Zr-C bonds versus actinide-C bonds and further reinforces, in conjunction with solution data,^{28,29} the hypothesis that surface organometallic cations are the catalytically active centers. Quantitative epr spin-counting experiments on $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{DA}$ place the detectable Zr(III) sites at $\sim 1 \times 10^{-4} \%$ of the Zr present before passing H_2 over the catalyst, and at $\sim 3 \times 10^{-2} \%$ after H_2 activation.²⁷ Presently in progress are more detailed kinetic and spectroscopic studies as well as experiments with other supports.

surface W-CH₃ group. Efforts to observe a surface alkylidene at this point or after gentle heating (eq.(10)) afford a number of weak, poorly defined spectral

features at the expected³¹ low field position. Not surprisingly, model CPMAS studies with neat solid W[CH₂C(CH₃)₃][CHC(CH₃)₃][CC(CH₃)₃][P(CH₃)₃]₂³⁴ reveal extremely large chemical shift anisotropies (and accompanying elaborate side-band patterns)^{35,36} for W=CHR and W=CR functionalities, indicating that surface alkylidene and alkylidyne spectra will only be straightforwardly analyzed using our recently acquired, high-speed spinning accessory. Studies at higher spinning speeds are just beginning with WCl₆/SiO₂/Sn(¹³CH₃)₄ and WCl₆/SiO₂/Sn[¹³CH₂C(CH₃)₃]₄ catalysts.³² The latter system is likely to give α-elimination (cf., eq.(10)) products in higher yields.³¹ The direction of further investigations will depend upon these results.

D. Parallel Solution Studies

A central feature of this project is to draw meaningful connections between surface chemistry and chemistry observed in homogeneous solution. The formation of heretofore unknown types of organoactinide cations on inorganic surfaces raises the question of whether such highly electrophilic species can be prepared, isolated, and studied in the absence of the support. We have therefore devised a high-yield protonolytic route to such compounds (eq.(11))

L_n = ancillary ligands

R' = bulky alkyl group

The poorly understood structural nature of the current generation of high-activity heterogeneous olefin metathesis catalysts^{2,30} also presents a fascinating problem and a great contrast to the generally well-characterized state of affairs in groups 5,6-catalyzed homogeneous metathesis chemistry.³¹ The heterogeneous catalysts typically consist of high-valent Mo, W, or Re halides or oxides supported upon hydrous oxides such as silica, alumina, or titania and often include, for reasons that are not entirely well-understood, tin alkyls as co-catalysts. Our initial efforts have focused upon CPMAS nmr studies of these catalysts with the goal being to identify and to monitor the transformations of species such as surface alkyls, alkylidenes, and metalla-cycles. The large quadrupole moments of ^{185}Re and ^{187}Re ($I = 5/2$) turned the initial focus to Mo- and W-based systems. NMR studies of the $\text{MoO}_3/\text{TiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ catalyst³⁰ and $\text{TiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ controls reveal that the great bulk of the tin alkyl is expended in functionalization of the support (XIX, XX).³²

These features completely dominate the nmr spectrum, and those due to surface organomolybdenum species are not easily detected. More promising results have been obtained on the $\text{WCl}_3/\text{SiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ catalyst³³ where loadings as high as 0.4 mmol W/g catalyst can be used. We find by CPMAS nmr that stannylation of the support is a minor pathway here and that the major product is clearly a

which avoids deleterious Lewis base solvents.³⁷ A series of $\text{Cp}'_2\text{ThR}^+$, $\text{Cp}'_2\text{Th}^{+2}$, and $\text{Cp}'\text{ThR}_2^+$ complexes has been prepared and is being characterized by spectroscopic and diffractometric techniques.^{37b-d} Some representative chemistry is shown in Scheme II. While $\text{Cp}'_2\text{Th}^+(\text{CH}_3)\text{BPh}_4^-$ exhibits considerable

Scheme II

enhancement in reactivity over $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$,³⁷ it appears from solution and solid state nmr results that BPh_4^- coordination (XXI) may be reducing the

coordinative unsaturation, hence reactivity.^{28,37} In regard to less coordinating anions, we find that $\text{KB}(\text{n-Bu})_4$ reacts instantly with $\text{Cp}'_2\text{Th}(\text{CH}_3)^+$ to afford $\text{Cp}'_2\text{Th}(\text{CH}_3)(\text{n-Bu})$ and anticipate that fluorinated anions such as BF_4^- , PF_6^- , and SbF_6^- will be unsuitable for highly electrophilic, fluorophilic actinide centers.³⁸ Synthetic efforts are now in progress to prepare sterically more encumbered tetraarylborate salts (XXII, XXIII) and other less

XXII R = t-Bu XXIII R = CH₃, CF₃, t-Bu

coordinating counterions.^{37c,d} This is of course a problem of some generality and importance in contemporary coordination chemistry.³⁹

E. Enhancement of Equipment

During the past grant period, the renovation of two reactor systems for surface chemistry and heterogeneous catalysis has been completed. The newer design allows easier and more rapid handling of catalysts and includes a cold cathode vacuum gauge for monitoring system integrity and an electronic gc integrator for the product detection/analysis system. Improvements have also been made in the purification of solvents for catalyst impregnation solutions and in support activation.

In the area of nmr, the present Doty/Varian 'VXR-300 solid state instrument has been considerably enhanced by the recent acquisition of a high-speed (10-17 MHz) spinning accessory. This addition should be of great benefit in reducing undesirable spectral features accompanying large chemical shift anisotropies,⁴⁰ quadrupole moments (e.g., ²⁷Al)⁴⁰, and dipolar interactions (e.g., in ¹H MAS).⁴¹ These benefits greatly outweigh the slightly smaller sample size.

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