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**SUPPORTED ORGANOMETALLIC COMPLEXES:
SURFACE CHEMISTRY, SPECTROSCOPY, AND CATALYSIS**

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ABSTRACT

The long-range goal of this project is to elucidate and understand the surface chemistry and catalytic properties of well-defined, highly-reactive organometallic molecules (principally based upon abundant actinide, lanthanide, and early transition elements) adsorbed on metal oxides and halides. The nature of the adsorbed species is probed by a battery of chemical and physicochemical techniques, to understand the nature of the molecule-surface coordination chemistry and how this can give rise to extremely high catalytic activity. A complementary objective is to delineate the scope and mechanisms of the heterogeneous catalytic reactions, as well as to relate them both conceptually and functionally to model systems generated in solution.

I. INTRODUCTION

Many important transformations in heterogeneous catalysis involve the creation or modification of surface-bound metal-hydrocarbyl (alkyl, aryl, etc.) functionalities. An attractive approach to understanding the properties of such highly reactive species is to create them by the adsorption of well-defined molecular precursors onto carefully prepared surfaces.^{1,2} For several classes of early transition metal hydrocarbyls, it has been known since the 1960's that adsorption on high surface area metal oxides is accompanied by dramatic but poorly understood enhancements in activity for olefin transformations such as polymerization and metathesis.^{1,3,4} The study of such materials is of both fundamental scientific significance (What unique surface coordination chemistries give rise to such enhancements in chemical reactivity?) as well as technological interest (What clues are offered regarding the nature of highly efficient current generation heterogeneous and homogeneous olefin polymerization catalysts? Is it possible to "tailor" catalysts with improved chemo-, regio-, and stereoselectivity?). Despite these motivations and considerable empirical data, it is fair to say that our understanding of the overall surface coordination chemistry as well as the precise nature of the catalytically active sites has been at a very primitive level. There is clearly a need for more chemical/structural information, acquired under carefully controlled conditions and connected to current day molecular organometallic phenomenology via functional solution phase models.

Efforts at Northwestern to characterize such molecule-surface interactions have focused on characterizing the species found when selected actinide and group 4 alkyls are adsorbed on surfaces such as dehydroxylated or partially dehydroxylated Al_2O_3 , MgCl_2 , MgO , SiO_2 , etc.⁵ Characterization tools have ranged from product analysis (What gaseous products are evolved upon adsorption? How are isotopic labels distributed?), to catalytic analysis (kinetics and rate law, regiochemistry, isotopic labelling, poisoning to determine % of active sites), to stoichiometric probes (reagents selective for surface hydride or hydrocarbyl functionalities), to spectroscopic methods (CPMAS and MAS NMR, XPS, UV-VIS, FT-IR, EPR). Since many of these adsorbate centers have high catalytic activities for

certain olefin transformations (*vide infra*), the nature of the adsorbate centers becomes particularly intriguing. Closely connected to the surface studies have been efforts to model the proposed active sites in homogeneous solution. These latter investigations have been fruitful, and the products additionally offer an attractive means of understanding several important yet elusive classes of homogeneous catalysts. Thus, we see the combined heterogeneous /homogeneous research activities as being highly symbiotic, with the former teaching us new things about homogeneous catalysis, and vice versa.

The reader is referred to the relevant literature for background discussion of solution organo-f-element chemistry,⁶ the properties of the inorganic supports,^{7,8} experimental surface chemical/physicochemical techniques⁹, and solid state NMR spectroscopy.¹⁰

II. RESEARCH ACCOMPLISHED TO DATE UNDER DOE SUPPORT

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

A. Organoactinide/Organo-Groups 4,5 Surface Chemistry and Heterogeneous Catalysis.

Using several different classes of ancillary ligation, studies of hydrocarbyl adsorption chemistry and catalysis have been carried out under rigorously anhydrous/anaerobic conditions at coverages of ~ 0.25 - 0.50 molecules/nm².¹¹ Among the reaction pathways identified, alkyl abstraction by dehydroxylated Lewis acidic supports (e.g. Al₂O₃, MgCl₂, e.g. eq. (1)) represents a heretofore unrecognized surface reaction pathway and a plausible route to unsaturated, electrophilic surface sites.¹² Paramagnetic probe studies (An = U) indicate the abstracted CH₃ group is ≥ 5 Å from the

A

actinide center. This reaction mode is generalizable to other actinide coordination geometries (B, $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$; C)¹² and to group 4 (D).¹³ In contrast, hydroxylated surfaces and dehydroxylated SiO_2 give rise to M- μ -oxo species such as E (via protonolysis) and F (via Si-O cleavage), respectively.¹⁴

A detailed kinetic/mechanistic poisoning study of heterogeneous propylene and isobutylene hydrogenation by $\text{Cp}'_2\text{An}(\text{CH}_3)_2$ / support complexes yields results in accord with Scheme I (support = dehydroxylated Al_2O_3).¹¹ Poisoning studies show that ~4% of the adsorbate sites sustain the bulk of the catalytic activity (a common situation for heterogeneous catalysts); these sites have turnover frequencies for propylene hydrogenation greater than the active sites of Pt/SiO_2 under the same conditions ($N_t \sim 2 \text{ s}^{-1}$ vs. 0.05 s^{-1} at -63°C). Activation energies, $N_t(\text{H}_2)/N_t(\text{D}_2)$, and substrate substituent effects are reminiscent of homogeneous catalysis by structurally analogous lanthanide complexes (G).¹⁵ Complexes of type B are even more active for olefin hydrogenation, with active site N_t values ($\sim 20 \text{ s}^{-1}$ at -63°) equalling or exceeding those for Rh/SiO_2 , the most active heterogeneous olefin hydrogenation catalyst known. Species C, which possesses no metal-ligand σ bonds, is catalytically inactive. In contrast to $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{Al}_2\text{O}_3$, the poisoning-derived percentage of active sites for propylene hydrogenation by

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$\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{MgCl}_2$ is rather large ($40 \pm 10\%$), and it is possible to directly monitor heterogeneous ethylene polymerization (these are rather active catalysts) by *in situ* CPMAS NMR (Scheme II).¹² The NMR-derived active site percentage ($50 \pm 10\%$) is in good agreement with the catalytic poisoning

Catalytic Olefin Hydrogenation by Supported Organosactinide Complexes

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Scheme I

Tracing the Pathway(s) for Surface Ethylene Polymerization

Scheme II

results (vide supra). We also find $k_1(\text{Th}) \gg k_1(\text{Mg})$ and that $k_1(\text{Th})/k_p(\text{Th}) \approx 0.08$, similar to homogeneous organoscandium results.¹⁶ In all of these catalysts, the exact nature of the cation-support/counterion interaction, which presumably plays a major role in determining the percent active sites and active site reactivity, remains imprecisely defined.

Recent efforts to further decrease adsorbate coordinative unsaturation led to studies of $\text{Th}(\eta^3\text{-allyl})_4/\text{Al}_2\text{O}_3$.¹⁷ After activation with H_2 , these complexes are highly active catalysts for ethylene and propylene polymerization. Moreover, these supported complexes are highly efficient catalysts for arene hydrogenation ($N_t \approx 20,000 \text{ h}^{-1}$ at 90°C , 12 atm H_2), rivalling the most active platinum metal catalysts in activity. For benzene, the preliminary reaction kinetics are zero-order in substrate. Interestingly, $\text{C}_6\text{H}_6 + \text{D}_2 \rightarrow \text{C}_6\text{H}_5\text{D}$ and $\text{C}_6\text{D}_6 + \text{H}_2 \rightarrow \text{C}_6\text{D}_5\text{H}$ only, however once substrate is expended, rapid H/D scrambling is observed in the cyclohexane products. Preliminary EPR and XPS measurements give no evidence for Th(III) (Th(IV) is exceedingly difficult to reduce¹⁸).

Preliminary ^{13}C CPMAS NMR studies have also been carried out on current-generation Mo- and W-based heterogeneous olefin metathesis catalysts. In principle, M-alkyl, -alkylidene, and -alkylidyne functionalities and the transformations they undergo should be readily discernible. Spectroscopy of the $\text{MoO}_3/\text{TiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ catalyst¹⁹ 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 (H, I). These features

completely dominate the spectrum, and those due to surface organomolybdenum species are not easily detected. More promising results have been obtained on the $\text{WCl}_6/\text{SiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ catalyst²⁰ where loadings as high as 0.40 mmol W/g catalyst can be used. We find by CPMAS NMR that stannylation of the support is a minor pathway and that the major product is clearly a surface W-CH₃ group. Efforts to observe a surface alkylidene at this point or after gentle heating (eq. (2)) afford a number

of weak, poorly defined spectral features at the expected²¹ low field positions. The spectroscopic model complex $\text{W}[^{13}\text{CH}_2\text{C}(\text{CH}_3)_3][^{13}\text{CHC}(\text{CH}_3)_3][^{13}\text{CC}(\text{CH}_3)_3]\text{P}(\text{CH}_3)_3)_2$ has now been synthesized, and CPMAS NMR used to assign all relevant ^{13}C chemical shift tensors. These neat sample results reveal extremely large chemical shift anisotropies and accompanying elaborate sideband patterns²² for W=CHR and W=C functionalities, indicating that surface alkylidene and alkylidyne spectra will only be straightforwardly observed using our recently acquired, high-speed spinning accessory. Studies at high spinning speeds are beginning with $\text{WCl}_6/\text{SiO}_2/\text{Sn}(^{13}\text{CH}_3)_4$ and $\text{WCl}_6/\text{SiO}_2/\text{Sn}[^{13}\text{CH}_2(\text{CH}_3)_3]_4$ catalysts. The latter system is likely to give α -elimination (cf., eq. (2)) products in higher yields. The direction of further investigations will depend upon these results.

B. Equipment Upgrades

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 CVC cold cathode gauge for monitoring system integrity and an H-P electronic 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 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,²³ quadrupole moments (e.g., ^{27}Al),²³ and dipolar interactions (e.g., in ^1H MAS).²⁴ These benefits greatly outweigh the slightly smaller sample size (5 mm. vs. 7 mm rotors).

C. Homogeneous Model Studies

At the outset of this work (1985), little or no precedent existed for cationic species (especially base-free), such as **A** in either organoactinide or group 4 organometallic chemistry. Indeed, it was not clear whether such species could be prepared and if so, whether they would exhibit the spectroscopic characteristics and extraordinary reactivity seen on the surfaces. Crucial design questions concern the selection of charge-compensating anion (X^- in **J**) and the preparative route. Regarding the former, experience indicates that oxoanions (e.g., CF_3SO_3^- , ClO_4^-) usually afford inert, covalent complexes,²⁵ while conventional fluoro anions (e.g. BF_4^- , PF_6^-) yield covalent complexes or undergo fluoride abstraction.²⁶ The ideal, minimally coordinating anion for a $\text{Cp}'_2 \text{AnR}^+$ acid must have sterically screening (to impede close cation-anion approach), charge-delocalized structure with non-polar/non-coordinating peripheral substituents.²⁷ The preparative route must avoid coordinating solvents and oxidizing agents.

Protonolytic reagents²⁸ in the form of sterically encumbered ammonium salts provide an

efficacious route to $\text{Cp}'_2\text{ThCH}_3^+\text{X}^-$ complexes (eq. (3)).²⁹ Complexes **1b** and **1c** exhibit

R = *n*-butyl

1a $\text{X}^- = 1/2 \text{M}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$, M = Fe, Co

1b $\text{X}^- = \text{B}(\text{C}_6\text{H}_5)_4^-$

1c $\text{X}^- = \text{B}(\text{C}_6\text{F}_5)_4^-$

characteristic "cation-like" low-field $\text{Th-}^{13}\text{CH}_3$ signals ($1\text{c} < 1\text{b} < 1\text{a}$) agreeing well with the surface spectroscopic data. However, **1a-c** differ enormously in solution reactivity for ethylene polymerization and 1-hexene hydrogenation ($1\text{c} > 1\text{b} \gg 1\text{a}$) with $\text{Cp}'_2\text{ThCH}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ approaching the reactivity of the supported $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{Al}_2\text{O}_3$ catalyst. The reasons for these marked reactivity differences appear to derive from the structural nature of the cation-anion interaction, with **1c** structurally exhibiting the greatest degree of the "naked" cation character (Figure 1). The substantial modulation of cation chemical reactivity by subtle variations in the cation-anion interaction conveys intriguing implications for support effects in the heterogeneous analogues as do the observed support effects for the homogeneous systems.

Figure 1. Molecular structure of $\text{Cp}'_2\text{ThCH}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**1c**). Important bond distances (Å) and angles (deg) are as follows: $\text{Th-C}(21)=2.399$ (8), $\text{Th-C}_{\text{ring}} = 2.754$ (3) (av), $\text{Th-F}(18) = 2.757$ (4), $\text{Th-F}(19) = 2.675$ (6), $\text{C}(43)\text{-F}(18) = 1.325$ (6), $\text{C}(44)\text{-F}(19) = 1.344$ (7), and ring centroid-Th-ring centroid = 140.1 (3).

In addition to affording a better understanding of cationic adsorbate species (D), the synthesis of stable, base-free, highly electrophilic $\text{Cp}_2\text{ZrR}^+\text{X}^-$ complexes would offer models for several classes of important yet poorly understood, soluble olefin polymerization catalysts. Indirect evidence has argued that catalysts prepared from metallocene dialkyls and large excesses of Lewis acid cocatalysts such as methylalumoxane (" $\text{Al}(\text{CH}_3)\text{O}$ ")_n)^{3,30} are in fact Cp_2ZrR^+ complexes.³¹⁻³⁷ If true, such chemistry would represent a direct parallel to the aforementioned organo-group 4 surface chemistry. Solution phase models of eq. (1) must conform to many of the guidelines set forth for $\text{Cp}'_2\text{ThR}^+\text{X}^-$ complexes (*vide supra*). We sought a hydrocarbon-soluble, charge-delocalized organo-Lewis acid devoid of nucleophilic/coordinating substituents. Using tris(pentafluorophenyl)borane, intermediate in Lewis acidity between BF_3 and BCl_3 , the first stoichiometrically precise, isolable/crystallographically characterizable, highly active "cation-like" zirconocene polymerization catalysts were prepared (eq. (4)).³⁸ NMR spectroscopic properties of 2a ($\delta \text{Zr}-\text{C}_5\text{H}_5$ and $\delta \text{Zr}-\text{CH}_3$) are remarkably similar to those

of $\text{Cp}_2\text{Zr}(\text{}^{13}\text{CH}_3)_2/\text{DA}$ as well as those of the zirconocene complex prepared in the reaction of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ with methylalumoxane (eq (5)). Ethylene dosing studies of **K** monitored by CPMAS NMR

K

reveal insertion reactivity patterns similar to those found for $\text{Cp}'_2\text{Th}(\text{}^{13}\text{CH}_3)_2/\text{MgCl}_2$ (cf, Scheme II) except that 100% of the cation sites are reactive.³⁹

The crystal structures of 2b (Figure 2) and 2c (Figure 3) reveal metrically "loose" and ancillary ligand-dependent pairing. The $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ geometries are pseudo-tetrahedral. Because the η^5 -ring nuclei of 2b are diastereotopic, NMR can be used to probe the energetics of ion pair reorganization in

Zr - C15	2.252(4) Å		
Zr - C34	2.549(3)	Zr - H34A	2.71(3)
B - C34	1.663(5)	Zr - H34B	2.25(3)
Zr - C34 - B	161.8(2)°	Zr - H34C	2.30(3)

Figure 2. Crystal structure of compound 2b.

Zr - C21	2.223(6) Å		
Zr - C40	2.640(7)	Zr - H40A	2.507
B - C40	1.66(1)	Zr - H40B	2.432
Zr - C40 - B	176.6(4)°	Zr - H40C	2.526

Figure 3. Crystal structure of compound 2c.

solution (Scheme III). Clearly the activation energies for ion pair reorganization are substantial, and this conveys implications for stereochemical/tacticity effects in catalytic processes. Complexes 2a-c are active catalysts for homogeneous olefin polymerization. Ethylene polymerization proceeds at 25°C, 1 atm pressure with $N_t(2a) = 45 \text{ s}^{-1}$ ($\sim 4.5 \times 10^6 \text{ g PE/mol Zr h atm}$), comparable in activity to typical zirconocene/alumoxane catalysts.³⁰ With propylene at 25°C, 2a yields atactic polypropylene with $N_t(2a) = 42 \text{ s}^{-1}$ ($\bar{M}_w = 15,600$, $\bar{M}_n = 3,000$). NMR experiments in which a toluene- d_8 solution of 2a is exposed to 5 equiv. propylene at -25°C indicate that > 70% of 2a undergoes olefin insertion under these conditions, arguing that the observed activity is not due to a minor component.

MOLECULAR/ION PAIR DYNAMICS OF $B(C_6F_5)_3$ COMPLEXES

Scheme III

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