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Electrophilic Organoiridium(III) Pincer Complexes on Sulfated Zirconia for Hydrocarbon Activation and Functionalization

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ABSTRACT: Single-site supported organometallic catalysts bring together the favorable aspects of homogeneous and heterogeneous catalysis while offering opportunities to investigate the impact of metal-support interactions on reactivity. We report a $(^{dm}Phebox)Ir(III)$ $(^{dm}Phebox = 2,6-bis(4,4-dimethyloxazolinyl)-3,5-dimethylphenyl)$ complex chemisorbed on sulfated zirconia, the molecular precursor for which was previously applied to hydrocarbon functionalization. Spectroscopic methods such as diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS), dynamic nuclear polarization (DNP)-enhanced solid-state nuclear magnetic resonance (SSNMR) spectroscopy, and X-ray absorption spectroscopy (XAS) were used to characterize the supported species. Tetrabutylammonium acetate was found to remove the organometallic species from the surface, enabling solution-phase analytical techniques in conjunction with traditional surface methods. Cationic character was imparted to the iridium center by its grafting onto sulfated zirconia, imbuing high levels of activity in electrophilic C–H bond functionalization reactions such as the stoichiometric dehydrogenation of olefins was also facilitated by the sulfated zirconia-supported ($^{dm}Phebox$)Ir(III) complex, while the homologous complex on silica was inactive under comparable conditions.

Introduction

The ability to stereoelectronically modulate the local environment of a catalytic metal center is paramount to enhancing chemical reactivity and selectivity for desired mechanistic pathways. Heterogeneous catalysts are employed in an estimated 90% of industrial chemical processes,¹ due to their ease of separation, recyclability, and robustness. However, these catalysts generally lack the activity and selectivity associated with homogeneous catalysts. Recently, the use of single-site supported organometallics has emerged as a promising strategy for combining the positive attributes of heterogeneous and homogeneous catalysts.¹⁻⁵ Studies have focused on transition metal complexes grafted on unmodified metal oxides, such as silica and alumina, for hydrocarbon functionalizations including alkane dehydrogenation,⁶⁻⁹ olefin hydrogenation,¹⁰⁻¹⁴ olefin polymerization,¹⁵⁻²⁴ and olefin metathesis.²⁵⁻³⁰ The relatively high Lewis basicity of these surfaces after chemisorption of an organometallic complex generally leads to strong catalyst-surface interactions, decreasing the propensity for electrophilic bond activation mechanisms. More recently, modified acidic metal oxide supports, in particular sulfated zirconia (SO₄/ZrO₂), have been used to imbue electrophilic character to both transition metal and main

group catalysts, analogous to noncoordinating counterions in homogeneous catalysis, such as triflate or perfluorotetraphenylborate.³¹ Sulfated zirconia has been proposed to contain Brønsted acid sites stronger than 100% H₂SO₄,³² although the nature and strength of the acid sites remain debated in the literature.³²⁻³⁵ This solid acid has also previously been shown to exhibit interesting redox activity that facilitates the isomerization of alkanes.³⁶⁻⁴⁰ The application of this material as a support for organotransition metals (such as Zr and Hf) was pioneered by Marks and coworkers, resulting in the generation of single-site supported catalysts active for selective arene hydrogenation and olefin polymerization (Figure 1A).⁴¹⁻⁴⁷ Conley and coworkers have also reported olefin polymerization catalysts using late transition metal Ni(II) and Pd(II) α dimine species^{48,49} (Figure 1B) as well as SiR₃⁺ supported on SO₄/ZrO₂ for C–F bond activation.⁵⁰

Recently, our group reported the chemisorption of Cp*(PMe₃)IrMe₂ on SO₄/ZrO₂ and SO₄/Al₂O₃ to create a highly

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Figure 1. (A) Examples of Zr and Hf complexes supported on sulfated zirconia studied by Marks and coworkers.^{41,47} (B) Ni(II) and Pd(II) α -diimine complexes supported on sulfated zirconia studied by Conley and coworkers.^{48,49}

electrophilic Ir(III) metal center for catalytic H/D exchange of methane under mild conditions.⁵¹ We envisioned expanding this methodology to pincer-ligated iridium complexes, thereby generating thermally-robust organometallic species that could facilitate hydrocarbon functionalization via enhanced electrophilicity at the metal center.^{52,53} Previously, organometallic iridium complexes such as the (^{tBu4}PCP)Ir(I) system (^{tBu4}PCP = κ^3 -C₆H₃-2,6-(CH₂PtBu₂)₂)^{52,53} have been studied, which can facilitate highly endothermic transformations such as non-oxidative alkane dehydrogenation⁵²⁻⁵⁶ under mild conditions with high levels of selectivity.^{52,53} For this set of catalysts, C-H activation of the alkane occurs via oxidative addition to a reactive Ir(I) fragment, which is inhibited by N₂, H₂O, and the alkene product.^{52,53} Consequently, significant effort has also been devoted to the development of catalysts proceeding through alternative alkane activation pathways such as the concerted-metalation-deprotonation (CMD) mechanism.⁵⁷ In this scenario, C-H activation at the Ir(III) center⁵⁸ is facilitated by an internal base at the metal center, such as a carboxylate, through a sixmembered transition state, as shown in Scheme 1.57,59 CMD-type

Scheme 1. CMD-type Activation of Alkanes with 1



bond activation has been investigated extensively with (^{dm}Phebox)Ir systems (^{dm}Phebox = 2,6-bis(4,4-dimethyloxazolinyl)-3,5-dimethylphenyl) (Scheme 1).⁵⁹⁻⁶¹ Previously, it was reported that the activation of *n*-octane occurred in the presence of a base at 160 °C using (^{dm}Phebox)Ir(OAc)₂(OH₂) (1), generating (^{dm}Phebox)Ir(OAc)(*n*-octyl) in 78% yield after 70 h.^{59,60} Goldberg and coworkers showed that β -H elimination occurs in the absence of a base at 200 °C, generating (^{dm}Phebox)Ir(OAc)(H) (2) and the

corresponding olefin.⁵⁹ It was later shown that Lewis acid additives such as NaBAr^F₄ could be used to enhance the rate of β –H elimination, aiding in the opening of a coordination site on the metal center.⁶² The electrophilicity of the metal center could also be increased through the addition of a Lewis acid. Computational investigation demonstrated that more electrophilic (*dm*Phebox)Ir metal centers, generated via modulation of the pincer ligand backbone could decrease the barrier for C–H activation by several kcal/mol, affording more active alkane activation systems, though variation of the X-type carboxylates ligated to the metal center was studied, the results were in agreement with previous experimental and computational studies, in that variation of the carboxylates affected the barrier for β –H elimination, similar to Lewis acids, whereas that of C–H activation was unaffected.⁶⁴

While Goldman, Celik, and coworkers have investigated the chemisorption of phosphine-ligated iridium systems onto silica and alumina via a linkage on the pincer-ligand backbone and their subsequent proclivity for C-H activation via Ir(I),65,66 the catalytic activity observed was similar to that obtained with the molecular precursor. Mezzetti and coworkers were able to graft similar complexes via the metal center onto SBA-15, resulting in supported catalysts more active for olefin hydrogenation than the analogous homogeneous reaction.¹¹⁻¹³ We envisioned that grafting 1 onto SO₄/ZrO₂ by acetate protonolysis would offer an opportunity not only to heterogenize this system but also to study the effect on elementary steps in alkane dehydrogenation, in particular C-H activation and β -H elimination. We hypothesized that an increase in rate may occur through the increase in electrophilicity at the metal center imparted by the weakly coordinating surface. The propensity for stoichiometric alkane dehydrogenation with the supported (dmPhebox)Ir complexes was investigated in addition to the catalytic activity for olefin hydrogenation, the microscopic reverse of alkane dehydrogenation.

Results and Discussion

Synthesis and Characterization of the Supported Ir(III)-Pincer Complex on Sulfated Zirconia. The chemisorption of 1 onto sulfated zirconia (sieved to 125 µm, 120 mesh, with a surface area of 140 m²/g and sulfur loading of 1.58% w/w⁵¹) was initially investigated in order to establish the viability of this material as a weaklycoordinating support for the Ir center through protonolysis of an Xtype⁶⁷ acetate ligand, forming (^{dm}Phebox)Ir(OAc) on SO₄/ZrO₂ (**3**) (Scheme 2). Following addition of sulfated zirconia to a solution of 1 in benzene- d_6 , resonances corresponding to 1 began to decrease in intensity as referenced to an internal standard by ¹H nuclear magnetic resonance (NMR) spectroscopy (Figure S1). 93% of the final saturation loading of 1 was chemisorbed at approximately 1 h, with the remaining 7% deposited over the next 15 h, after which no further changes were observed and 3 could be isolated by filtration. Evolution of acetic acid, typically associated with protonolysis of an X-type acetate ligand by a Brønsted-acidic surface site was not detected over time by ¹H NMR spectroscopy, likely due to physisorption of acetic acid on the surface. The iridium fragment could, in principle, bind the surface through either an L-type bonding interaction⁶⁷ by displacement of water at the labile sixth coordination site,⁶³ or by an X-type interaction via protonolysis of an acetate group (Scheme 2). To investigate the possibility of L-type binding, 3 was washed with tetrahydrofuran (THF), a donating solvent, to displace any datively-bound complexes from the surface (Scheme 2). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of 3 prior to THF washing showed 2.26% Ir deposited on the surface by weight. Analysis of the THF-washed

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Scheme 2. Grafting experiment of 1 onto SO_4/ZrO_2 resulting in a mixture of X-type and L-type bound species, the latter of which can be washed away with THF to give 4



(^{dm}Phebox)Ir(OAc) on SO₄/ZrO₂ (**4**) by ICP-AES revealed a decrease in deposited surface Ir from 2.26% to 1.32%.⁶⁸ Further washing with THF did not remove any additional iridium, suggesting that the material immediately after chemisorption and benzene washes constituted a mixture of L- and X-type binding modes, while that after washing with THF was constituted by only the X-type species. Suspension of **3** in THF-d₈ also led to desorption of complex (^{dm}Phebox)Ir(OAc)₂(THF) (~79% of expected iridium from ICP analysis), corroborating the X-type binding mode of the species left on the surface post-washing (Figure S2, see the Supporting Information for further discussion).

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to provide structural insight into the nature of the surface-supported iridium fragment. C–H stretching vibrations around 3000 cm⁻¹ were observed in **4**, which were qualitatively similar to those found in the pincer ligand manifold for aromatic and aliphatic C–H stretches. Other C–H stretching vibrations corresponding to the pincer ligand were also observed at lower frequencies between 1000 cm⁻¹ and 1700 cm⁻¹, though these overlapped with stretching vibrations associated with sulfated zirconia (see Figure S3 for full DRIFTS spectrum of **4**).

Dynamic nuclear polarization (DNP)-enhanced cross-polarization magic-angle spinning (CPMAS) NMR spectroscopy was next used to obtain detailed structures of the supported iridium species.⁶⁹⁻⁷³ The DNP-enhanced ¹³C CPMAS NMR spectrum of 3 yielded res-onances with chemical shifts in agreement with those of the molec-ular precursor 1, suggesting that the iridium center had maintained its pincer ligand during the chemisorption process (Figure 2A,B). To further confirm this structure and gain additional details con-cerning the spatial arrangement of the complex's ligands we addi-tionally performed 2D ¹³C{¹H} heteronuclear correlation (HETCOR) spectroscopy. A spectrum acquired using a CP contact time of 100 µs shows predominantly one-bond C-H correlations, as expected, as well as two weaker two-bond correlations to quater-nary carbon 'H' (Figure 2A). With a contact time lasting 1000 µs, a number of new through-space correlations appeared (Figure 2B). Notably, the sole correlation to the rather isolated carbon 'B' is to the methyl protons of the acetate ligand ('J'). This confirms that both ligands are simultaneously coordinated to Ir and further provides conformational information about the complex, namely that the acetate ligand is bent over the pincer ligand, possibly due to steric interactions with the support surface. No correlation between the acetate carboxyl moiety ('A') and an acidic hydrogen could be detected, strongly suggesting that the acetate is non-protonated and thus remains an X-type ligand post-grafting. Once the complex was



Figure 2. DNP-enhanced ¹³C CPMAS (top traces) and HETCOR spectra of **3** acquired with CP contact times of 100 μ s (A) and 1000 μ s (B), and of **4** acquired with a contact time of 1000 μ s (C). On the right-hand side of (A) and (B), the observed through-space correlations for **3** are indicated with dashed red lines. The peak labels are assigned to the structure shown in (C). An asterisk denotes the solvent resonance from TCE-*d*₂. In (C) 'x' symbols are placed in the spectrum to indicate new correlations to THF not seen in (B), while some new intensity, which may originate from THF, is also circled.

This can be more clearly seen in Figure S8 in the Supporting Information, which shows the enlarged views of (B) and (C) for $0 \le \delta({}^{13}C) \le 100$ ppm.

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washed with THF to form species 4 we observed a new ¹³C resonance ('L') as well as an increase in intensity which we attributed to carbon 'M' of THF. Again, 2D ¹³C{¹H} HETCOR NMR spectroscopy was performed to decipher the location of the THF molecule. Cross-peaks between the 'L' protons of the THF and the 'K' and 'C' carbon sites of the pincer ligand were observed (Figure 2C) suggesting that, like the acetate, the THF molecule is adjacent to the pincer ligand in the iridium coordination sphere. The 2D NMR spectroscopy thus provided compelling evidence that the pincer ligand adopts a coordination that is trans to that of the support. Although this differs from what was observed in the homogeneous complex, it is unsurprising from both a steric and electronic point of view, given the repulsion between the bulky pincer ligand and the surface, as well as the favorability of positioning the weakly donating surface coordination trans to the strongly donating pincercarbon. The steric demand of the surface similarly plays a role in enforcing the close proximity of the pincer ligand and the THF and acetate ligands on either side, as evidenced by the observed through-space cross-peaks. This proximity between the acetate and the pincer ligands was not observed in the molecular complex where such sterics are absent.⁶¹ We note that such precise conformational details on catalytic surfaces are difficult to obtain by other surface characterization techniques. Similar studies utilizing DNP have also been able to characterize the three dimensional spatial orientation of ligands around a metal.72-73

25 X-ray absorption spectroscopy (XAS) was also used to further in-26 terrogate the structural integrity of the iridium-pincer after chemi-27 sorption. Complete fitting of the X-ray absorption spectra was not 28 possible due to the difficulty in deconvoluting the scattering pat-29 terns obtained for the supported Ir samples. Nonetheless, similar 30 qualitative features were observed in the extended X-ray absorption fine structure (EXAFS) for 1 and 4, supporting the presence of the 31 intact iridium-pincer on the surface after chemisorption. Addition-32 ally, X-ray absorption near-edge structure (XANES) analysis sug-33 gested that the Ir(III) was the predominant oxidation state (Figure 34 S9). Moreover, no evidence of iridium nanoparticle formation was 35 observed. To further characterize the bonding between the iridium 36 center and the sulfated zirconia surface as a polarized X-type ligand interaction, 4 was suspended in a solution of tetrabutylammonium 37 acetate (NBu₄OAc) in methylene chloride- d_2 (see the Supporting 38 Information for stripping procedure) in an attempt to displace the 39 iridium complex from the surface (Figure 3). Monitoring the reac-40 tion by ¹H NMR spectroscopy revealed that after 10 min, **1** is ob-41 served in solution. Minor asymmetric species were also detected by 42 ¹H NMR as doublet of doublets around δ 4.65 ppm. One of these 43 may be consistent with the κ^1/κ^2 asymmetric analog of **1** being present in solution, in which one acetate can bind in κ^2 fashion, dis-44 placing the L-type ligand (Figure 3B). When the stripping experi-45 ment was performed in the presence of residual THF, only the sym-46 metric κ^1/κ^1 analog was observed. The other minor species was 47 assigned as (dmPhebox)Ir(Ph) on SO4/ZrO2 (5), generated after sur-48 face activation of benzene over the course of the grafting reaction, vide infra. The appearance of 1 following treatment with NBu4OAc 49 was significant as it demonstrated the possibility of removing the 50 organometallic species from the surface for characterization via so-51 lution-phase techniques such as ¹H NMR, the employment of 52 which is complementary to surface analytical techniques.^{74,75} The 53 resultant solid material was analyzed by DRIFTS following isola-54 tion by filtration (Figure 3A). C-H stretching vibrations around 55 3000 cm⁻¹ as well as the C=O and C=N 56



Figure 3. Tetrabutylammonium acetate can be used to strip 1 from the surface, leaving behind tetrabutylammonium bound to the surface acidic sites. (A) This was confirmed by DRIFTS. Bottom spectrum shows 4 as prepared with associated IR stretches of 4 indicated (*). Top spectrum shows the material post-stripping with associated IR stretches of tetrabutylammonium indicated (‡). (B) ¹H NMR spectrum of stripping experiment with 4 over time in methylene chloride-*d*₂ with characteristic peaks highlighted. A mixture of asymmetric and symmetric 1 and (*dm*Phebox)Ir(OAc)(Ph) (6) come off the surface, the latter from room temperature activation of benzene solvent during loading. "L" may represent a labile site with THF or aquo bound to the metal center.

stretches from 1200 to 1700 cm⁻¹ associated with the pincer ligand backbone became attenuated, replaced with 'NBu₄+ C–H stretches (Figure 3A). This was further confirmed by comparison to a DRIFTS spectra of **1** diluted with KBr, NBu₄OAc diluted with KBr, and NBu₄OAc physisorbed onto SO₄/ZrO₂ (Figure S20). ICP-AES analysis of the support material after stripping with NBu₄OAc also provided evidence of removal of the Ir from the surface as only 0.156% iridium by weight was remained after acetate stripping, representing a minority of strongly-bound surface sites where acetate could not facilitate removal.

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Figure 4. (A) Reaction of **4** with neat benzene at 80 °C for 24 h generates Ir-Ph on the surface. (B) Reaction of **4** with neat nonane at 120 °C for 24 h generates Ir-H on the surface.

Stoichiometric Reactivity of Supported Ir(III)-Pincer Complex on Sulfated Zirconia Towards Aryl and Alkyl. By recapitulating the stoichiometric reactivity first described by Nishiyama and coworkers⁶¹ and Goldberg and coworkers,⁵⁹ further insight could be gained regarding the impact of the support on reactivity of the metal center. First, 4 was suspended in benzene at 80 °C for 24 h in order to assess whether the supported material could effect CMD C-H activation of the solvent to form 5 by analogy to the homogeneous precedent (dmPhebox)Ir(OAc)(Ph) (6); see Figure 4A.^{59,61} DRIFTS of the isolated material post-benzene-treatment revealed new aromatic C-H stretching vibrations between 3000 cm⁻¹ and 3100 cm⁻¹ consistent with new C_{sp2}-H bonds expected upon generation of 5 (Figure 5A). Furthermore, stripping of the organometallic species from the surface with NBu4OAc in methylene chloride d_2 resulted in the appearance of resonances associated with 6 by ¹H NMR spectroscopy,^{59,61} along with **1** (Figure 5B). Analysis of **5** by DNP-enhanced ¹³C CPMAS NMR spectroscopy⁷⁶ revealed the appearance of two new aromatic resonances from Carom-H ("P") and Carom-Ir ("N") sites from a phenyl ligand. This assignment was then confirmed by the appearance of a new correlation between carbon "B" and the ¹H aromatic region in the corresponding HETCOR spectrum (Figure 6). An attenuated acetate signal in the solid state ¹³C NMR spectrum further substantiated the loss of acetate associated with CMD-type C-H activation.

When 4 was suspended in neat n-nonane for 72 h at 120 °C (Figure 39 4B), analysis of the recovered supported material by DRIFTS re-40 vealed a new IR stretching vibration at approximately 2220 cm⁻¹ 41 (Figure 5A), similar in wavenumber to the stretching frequency ob-42 served for authentically prepared hydride 2 (2194 cm⁻¹), suggesting 43 formation of iridium-hydride in the supported complex. In contrast, 44 the formation of 2 in 96% yield was observed upon heating 1 in a neat solution of n-octane at 200 °C for 72 h,59 but when the temper-45 ature was lowered to 180 °C, only a small amount of iridium-hy-46 dride was observed after five days and at 150 °C no reaction was 47 observed even after heating for six days.⁵⁹ To confirm the charac-48 terization of the IR stretch at 2220 cm⁻¹ as an iridium-hydride, an 49 authentic sample of (dmPhebox)Ir(H) on SO4/ZrO2 (7) was prepared 50 by grafting 2 onto sulfated zirconia (see the Supporting Information). A similar IR signal at 2220 cm⁻¹ was observed upon direct 51 chemisorption of 2, supporting the formation of an iridium-hydride 52 after treatment with *n*-nonane under relatively mild conditions. 53 Solid-state ¹H NMR spectroscopy also revealed a resonance around 54 -35 ppm consistent with an iridium hydride signal,⁵⁹ with a 55



Figure 5. (A) Infrared absorbance spectra of materials following reaction of **4** (blue, as prepared), with benzene for 24 h (black, IR stretches associated with aromatic C–H stretches indicated with *) and with nonane for 72 h (red, IR stretch associated with Ir–H indicated with \ddagger) (B) ¹H NMR spectra enlarged to show the aryl and hydride regions of post C–H activation materials treated with tetrabutylammonium acetate after 20-24 h in CD₂Cl₂. The aromatic proton resonances for Ir-Ph are indicated with * and the resonance associated with Ir–H is indicated with \ddagger .

similar chemical shift to that observed in the ¹H NMR spectrum of the iridium-hydride complex 2 (Figure S24, S26). The DNPenhanced ¹³C CPMAS NMR spectrum also featured a weakened iridium acetate signal consistent with the dissociation of acetic acid following C-H activation. To further determine organometallic speciation and quantify the amount of iridium-hydride formed, the iridium species present after treatment with n-nonane were stripped from the surface with NBu₄OAc in methylene chloride-d₂ (Figure 5B). After 10 min, resonances associated with 2 were observed by ¹H NMR spectroscopy, which continued to increase in intensity until approximately 40 min.⁷⁷ Of the product mixture subsequently obtained, 70% corresponded to 2 by ¹H NMR spectroscopy based on the CAr-H signal integration.⁷⁸ Formation of the iridium-hydride by the putative C–H activation, β –H elimination mechanism was also observed at shorter reaction times, representing 58% of the product mixture after 24 h at 120 °C,79 and 34% of the product mixture after2 h at 120 °C.80 The diacetate starting material (1) was also present in the product mixtures.⁷⁷ The formation of iridiumhydride in appreciable yield under these conditions is notable in





Figure 6. DNP-enhanced ¹³C CPMAS (top trace) and HETCOR NMR spectrum of **5**. An asterisk denotes the solvent resonance from TCE-*d*₂.

comparison to the activity observed with molecular precursor **1** for stoichiometric *n*-octane dehydrogenation. For **1**, C–H activation proceeded at 160 °C and higher temperatures (200 °C) were required in order to observe appreciable amounts of β –H elimination to form the iridium-hydride.⁵⁹ The effect of the surface on the metal center, in particular its tuning of electrophilicity, is similar in nature to what may occur when a Lewis acid interacts with a chelated acetate or if the carboxylate contains electronegative moieties as in the case of the homogeneous reactions,^{62,64} which may offer support for the observed rate enhancement in β –H elimination.

In order to gain further insight into the experimentally observed rate enhancement in the activation and functionalization of nonane with **4**, a computational investigation was undertaken (see the Supporting Information regarding methods). The catalytic pathways of

ethane dehydrogenation were calculated for three systems: (^{dm}Phebox)Ir(OAc)₂ 1, the supported complex 4 on a cluster model of SO₄/ZrO₂, and (^{dm}Phebox)Ir(OAc)(OTf), which was used as a homogeneous analog for the weakly-donating nature of the sulfated zirconia X-type coordination mode (Figure 7). A SZr cluster model was used for the SZr supported Ir complex. The SZr cluster (See Figure S27 in SI), was cleaved from a periodic model that was developed in a previous study. The cluster consists of 3 Zr and 10 O atoms for the ZrO₂ support and a tripodal SO₄²⁻. The O atoms in the ZrO₂ cluster were terminated by protons and one extra proton was added to charge balance the negative charge of SO42-(the other positive charge comes from the Ir center). During geometry optimization, the three Zr atoms were frozen while the other atoms in the cluster were allowed to relax.46 The calculated reaction pathway of ethane dehydrogenation undergoes a C-H activation, followed by a β-H elimination. β-H elimination was found to be the rate-limiting step of the reaction for all three iridium catalysts. Both the cluster model of **4** and the triflate complex had a lower apparent barrier than the bis-acetate molecular analog 1 ($\Delta\Delta G^{\ddagger} = 5.1$ and 3.7 kcal/mol respectively, Figure 7). The relative acceleration of the isolated β -H elimination step was even more extreme, with 4 and the triflate complex undergoing β -H elimination with an intrinsic barrier of 18.9 and 16.9 kcal/mol as compared to 31.0 kcal/mol for 1, however this effect is partially obscured by the increased relative energy of the iridium-alkyl intermediate for 4 and the triflate complex.

The calculated barriers for the C–H activation step were also found to be decreased in the presence of the more weakly-donating spectator ligands, albeit to a lesser extent than the β -H elimination, however this energetic barrier is kinetically irrelevant to the overall system due the endergonic and reversible nature of this step prior to the rate controlling transition state of β -H elimination.



Figure 7. Calculated reaction pathways of C-H activation and β -H elimination using an ethylene model. The values in the figure are relative free energies in kcal/mol at 120 °C using the PBE0 functional with CEP-121G basis set. Computations where carried out using the Gaussian09 software.

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Catalytic Hydrogenation of Propylene and 1,3-Butadiene with Supported Ir(III)-Pincer Complexes on Sulfated Zirconia. Having investigated the stoichiometric reactivity of 4, studies were undertaken to determine its performance under catalytic conditions. At temperatures required to thermodynamically-enable observable dehydrogenation (>300 °C), extrusion of SO2 and SO3 from sulfated zirconia can occur,⁸¹ thus low temperature acceptorless dehydrogenation of nonane under vigorous reflux (T = 151 °C) and gasphase transfer dehydrogenation of propane with ethylene as a sacrificial olefin (T = 50 °C to 300 °C) were undertaken. In the case of acceptorless dehydrogenation, no olefins were observed after heating nonane with 4, possibly due to deleterious reactions with resid-10 ual Brønsted acid sites on sulfated zirconia.75 Similarly, upon at-11 tempting gas-phase transfer dehydrogenation of propane in a plug 12 flow reactor, turnover was too slow to achieve appreciable conver-13 sion under conditions compatible with the catalyst. Thus, in lieu of 14 dehydrogenation, hydrogenation of propylene was used as the model transformation, representing the microscopic reverse of the 15 dehydrogenation of propane. In addition to 4, 1 was also grafted 16 onto silica dehydroxylated at 700 °C (SiO₂₋₇₀₀) and then washed 17 with THF (see the Supporting Information for details) to form 18 $(^{dm}$ Phebox)Ir(OAc) on SiO₂₋₇₀₀ (8; %Ir w/w by ICP-AES = 0.48%). 19 In contrast to 4, this silica-supported species is stereoelectronically 20 more similar to 1 due to the lack of significantly enhanced electrophilicity created at the metal center by sulfated zirconia. Spectro-21 scopic characterization of 8 (see Supporting Information) was also 22 consistent with deposition of the intact iridium-pincer fragment alt-23 hough with decreased iridium surface density after THF washing, 24 presumably due to a minority of the silanol sites having sufficient 25 reactivity to displace an acetate ligand (see the Supporting Infor-26 mation for details). 27

In an initial series of experiments, 4 (2.5 mg, 0.00017 mmol Ir, 5 mg, 0.00034 mmol Ir, and 10 mg, 0.00069 mmol Ir) and 8 (30 mg, 0.00075 mmol Ir) were evaluated for propylene hydrogenation in a

plug flow reactor with silica as a diluent (propylene/H₂ = 1/4.5, see the Supporting Information for further details). Sulfated zirconia supported catalyst 4 was found to display significantly higher hydrogenation activity than the silica-supported analog (8). At 100 °C and 120 °C, an induction period could be observed for 4 in generation of the active catalyst species, with complete conversion observed for higher catalyst loadings (Figure 8). No deactivation of 4 was observed from 100 °C to 120 °C after approximately 52 hours on stream, while slight deactivation was observed at 150 °C (Figure 8). With 2.5 mg (0.00017 mmol) of 4, over 20,000 turnovers were observed after 52 h at 120 °C. Negligible C-C bond cleavage and/or oligomerization were observed during catalysis. In addition, under these conditions, the sulfated zirconia support is inactive towards the hydrogenation of olefin.

Conversely, for 8, little to no activity was observed at 100 °C and only marginal activation at 120 °C (Figure 8). At 150 °C, the catalyst began to show more significant activity, and propylene conversion was observed (Figure 8). As nanoparticle formation from organometallic iridium precursors is well-explored in the literature,82-⁸⁴ the possibility of in-situ nanoparticle formation was then evaluated by analysis of the post-catalysis materials. 4 and 8 were subjected to catalytic conditions and then isolated for characterization by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) to determine whether iridium nanoparticle formation had occurred. For catalyst 4, no iridium nanoparticles were observed by STEM in post-catalysis samples at 120 °C (Figure 9A) and single ions could be observed (Figure 9A, circled in red), offering further support for the presence of single-site organoiridium species. In contrast, for catalyst 8 exposed to reaction conditions at 120 °C, at which it is minimally active, no iridium nanoparticles were observed by STEM (Figure S44). However, for the higher temperature post-catalysis sample of 8, for which the temperature was raised to 200 °C, STEM revealed formation of iridium nanoparticles on the surface (Figure 9B).



Figure 8. Hydrogenation of propylene with 4 (2.5 mg = green, 5 mg = blue, 10 mg = red) and 8 (30 mg = black). Iridium catalyst 4 is active from 100 °C to 150 °C whereas iridium catalyst 7 is not active until at least 150 °C. Conditions: 100, 120, and 150 °C, propylene/H₂ ratio = 1/4.5, 5% propylene/Ar = 1 mL/min, 5.188% H₂/Ar = 4.34 mL/min per flow reactor (see the Supporting Information for more details on conditions and experimental setup).



Figure 9. STEM images of (A) post-catalysis sample of 4 at 120 °C and (B) post-catalysis sample of 8 with temperature ramped from 150 °C (held for 7 h) to 200 °C (held for 7 h) then back down to 100 °C (held for 10 h).

The presence of nanoparticles may explain the onset of activity of the silica-supported samples at higher temperatures, as iridium nanoparticles are known to be very efficient hydrogenation catalysts.⁸²⁻⁸⁴ This provides some evidence that a supported organometallic species was catalytically active at those temperatures on sulfated zirconia, whereas the onset of catalytic activity of the silica supported material correlated with the appearance of nanoparticles, suggesting that the molecular species on the electronically-neutral support is relatively inactive. As achieving product selectivity in complex or multi-step processes is a benefit of supported organometallic species relative to traditional heterogeneous catalysts, the hydrogenation of 1,3-butadiene was then investigated (Table 1). When 4 was treated with 1,3-butadiene and H₂ in flow (see the Supporting Information for discussion of experimental setup and catalytic data), conversion of 1,3-butadiene to butenes and *n*-butane occurred following activation at 120 °C. Approximately 94% selectivity for butenes was observed at 80 °C (initial conversion = 55%, Table 1) with catalyst 4. In contrast, with catalyst 8, 29% selectivity for butenes was observed at 80 °C, following activation at 200 °C (initial conversion = 3.8%, Table 1). In both cases, catalyst deactivation was observed over time possibly due to coke and/or polymer formation. The higher selectivity with 4, were indicative of a supported organometallic complex as the active species, as lower product selectivity values are expected with Ir nanoparticles generated with 8 under reducing conditions.

Table 1. Hydrogenation of 1,3-Butadiene at 80 °C

Ir Cat.	Ir loading (%w/w) ^a	Initial conv. (%)	Sel. for Butenes (%)
4	1.32	55	94
8	0.481	3.8	29

Conditions: 5 mg of each catalyst, 1.01% 1,3-butadiene/Ar = 5.5 mL/min, 4.008% H₂/Ar = 6.3 mL/min, activation of **4** at 120 °C for 6 h and activation of **9** at 200 °C for 6 h then temperature is dropped to 80 °C. Deactivation of the catalyst is observed over time thus initial conversions are presented. ^aBy ICP-AES. Selectivity = (concentration of butenes / sum of product concentrations) * 100.

Mechanistic Studies into Propylene Hydrogenation Using Supported Ir(III)-Pincer Complexes. Having established the benchmark for hydrogenation reactivity of **4**, our subsequent efforts focused on gaining mechanistic insight into this catalytic process. First, the role of the ancillary ligands on the Ir center in **4** was assessed. To determine the necessity of the acetate moiety on the metal center, (^{dm}Phebox)Ir(OAc)(Cl) was grafted onto SO₄/ZrO₂ and washed with THF (**9**), leading to an iridium-chloride species on the sulfated surface, which would be incapable of CMD-type activation. Notably, the activity of **9** (TOF = $62 \pm 2 h^{-1}$) for propylene hydrogenation was similar to that of **4** (TOF = $75 \pm 2 h^{-1}$) (Table 2), indicating that the acetate is not necessary for hydrogenation and that both may be converging to the same active intermediate over the course of the reaction.⁸⁵

Table 2. Effect of Ancillary Ligand Modification on Turnover Frequency (TOF) for Hydrogenation of Propylene at 50 $^\circ\text{C}.$

Ir/ZrS Catalyst	Ir loading (%w/w)	TOF (hr ⁻¹)
4	1.32	75 ± 2
9	1.82	62 ± 2

Conditions: 5 mg of each catalyst, 5% propylene/Ar = 2 mL/min, 3.573% H₂/Ar = 12.6 mL/min, activation at 120 °C for 6 h then temperature is dropped to 50 °C. TOFs are an average of three independent runs with standard deviations listed.

In order to obtain further information regarding the active iridium species, more detailed kinetic analyses were performed. Following activation of **4** at 120 °C for 24 hours, catalytic hydrogenation was studied over a range of temperatures (50 °C, 60 °C, 70 °C, and 80 °C) to gain insight into the activation energy (see the Supporting Information for catalytic data). From the resulting Arrhenius plot, an activation energy of 29.8 kcal/mol was found for the reaction (Figure 10). When varying the H₂ concentration at 50 °C following activation at 120 °C, a first-order rate dependence on H₂ was observed (Figure 11), confirmed by a double log plot with a slope of 1.02 (Figure S31, S32).⁸⁶ Conversely, when varying the propylene concentration at 50 °C, a fractional kinetic dependence between

zero and first order was observed (Figure 11, S34, S35). This kinetic dependence was consistent with a catalytic resting state where the iridium sites are partially saturated with olefin as an iridium-

alkyl or an iridium olefin π -complex. Alternatively, the olefin could be incorporated after the rate-determining step of the reaction.



Figure 10. Elucidation of activation energy in propylene hydrogenation with **4** (1.5 mg). Activation conditions: 120 °C for 24 hours, propylene/H₂ ratio = 1/4.5, 5.001% propylene/Ar = 1 mL/min, 5.188% H₂/Ar = 4.34 mL/min per flow reactor. Temperatures screened were 50 °C, 60 °C, 70 °C, and 80 °C at 2 mL/min 5.001% propylene/Ar and 8.7 mL/min 5.188% H₂/Ar. See the Supporting Information for individual data points and standard deviations and discussion of error.



Figure 11. Dependence of H₂ and olefin in the hydrogenation of propylene with **4** (5 mg). Activation conditions: 120 °C for 6 hours, propylene/H₂ ratio = 1/4.5, 5% propylene/Ar = 1 mL/min, 5.188% H₂/Ar = 4.34 mL/min per flow reactor. H₂ dependence ratios screened propylene/H₂ = 1/6 (2/11.58 mL/min), 1/5 (2/9.64 mL/min), 1/4 (2/7.72 mL/min), 1/2 (2/3.68 mL/min). Propylene dependence ratios screened propylene/H₂ = 0.5/4 (1/7.72 mL/min), 1/4 (2/7.72 mL/min), 1.5/4 (3/7.72 mL/min), 2/4 (4/7.72 mL/min). See the Supporting Information for individual data points and standard deviations and discussion of error.

To interrogate these possibilities, the reaction of supported iridiumhydride **7** with flowing propylene was monitored by DRIFTS (Figure 12, see the Supporting Information for experimental setup). Upon exposure of 7 to propylene at room temperature, a weakening of the characteristic iridium-hydride IR stretch for 7 was observed concomitant with the appearance of a new signal at 2120 cm⁻¹ (Figure 12A). This new species persists at approximately the same ratio under flowing propylene. The in situ DRIFTS cell was then purged with N₂, which resulted in the gradual disappearance of the new peak at 2120 cm⁻¹ and the restoration of the original absorption intensity of the hydride stretch associated with 7 (Figure 12B). When the gas flow was cycled back to propylene, the iridium-olefin species once again increased in intensity while that of iridium-hydride



Figure 12. Infrared absorbance spectra of iridium-hydride 7 reversibly reacting with propylene to form an iridium-olefin species. (A) propylene flow cycle 1, 3% propylene/Ar = 51.8 mL/min, black = initial no flow, red = 2 min under propylene flow, blue = 5 min under propylene flow. (B) N₂ flush, N₂ = 51.5 mL/min, black = initial 10 min propylene flow, red = 2 min N₂ flush, blue = 5 min N₂ flush, green = 10 min N₂ flush, orange = 83 min N₂ flush. (C) propylene flow cycle 2, 3% propylene/Ar = 51.8 mL/min, black = initial 83 min N₂ flush, red = 2 min under propylene flow, blue = 5 min under propylene flow, orange = 30 min under propylene flow.

7 decreased (Figure 12C). The species formed in the presence of gaseous propylene may correspond to the olefin binding at the labile sixth coordination site on the metal center, forming an Ir-olefin π complex on the surface, potentially explaining the partial kinetic order in propylene. The binding of the olefin is in dynamic equilibrium under these conditions and can reversibly occur as evidenced by peak intensity changes when alternating between flowing propylene and N₂ atmosphere.



Figure 13. DNP-enhanced ¹³C CPMAS NMR spectrum of posthydrogenation Ir on sulfated zirconia at 200 °C and 120 °C. An asterisk denotes the solvent resonance from TCE-*d*₂. § indicates location of the attenuated signal for an acetate resonance.

Further spectroscopic characterization of the post-catalysis samples of **4** was undertaken using DNP-enhanced ¹³C CPMAS NMR to gain structural insight. The resonance corresponding to the acetate carboxyl is absent in the CPMAS spectrum (Figure 13) thus indicating its removal during the catalysis. No resolvable alkyl resonances were observed by ¹³C solid-state NMR spectroscopy. The organometallic species were then removed from the surface of **4** post-catalysis by stripping with NBu4OAc (*vide supra*). Treatment of the post-catalysis material with acetate resulted in the desorption of iridium hydride **2**, indicating that it is likely present in the resting state of the catalyst (Figure S46)⁸⁷ The post-catalysis samples were also examined by XAS, revealing a qualitatively similar EXAFS region and XANES when compared to catalyst **4** as prepared (Figure S47).

Conclusions

The ability to modulate the reactivity of a metal center through tailored metal-support interactions aids in the design of supported organometallic complexes with catalytic activity for industrially-relevant processes. Dehydrogenation of alkanes is one such challenging transformation, hence the development of strategies for alkane conversion to alternative chemical building blocks such as olefins remains ongoing. In this study, (^{dm}Phebox)Ir organometallic complexes grafted onto sulfated zirconia proved competent for hydrocarbon functionalization in stoichiometric and catalytic processes, showing a heightened propensity toward bond activation and elimination reactions in comparison to their molecular precursors. Sulfated zirconia-supported samples showed increased reactivity in the stoichiometric dehydrogenation of *n*-nonane, demonstrating the rate-enhancing impact of the surface for β -H elimination, with DFT calculations also confirming the lower barrier. Organometallic speciation can also be assessed and quantified using solution-phase NMR techniques by removal of generated species from the surface, providing a powerful tool for the characterization of surface organometallic complexes in this system. Moreover, these materials were shown to effect olefin hydrogenation, the microscopic reverse of alkane dehydrogenation, with an organometallic species as the active catalyst on sulfated zirconia whereas iridium nanoparticles were likely the active species in silica-supported samples. Tuning the electrophilicity of metal centers to bolster the activation of alkanes is a concept widely applied in homogeneous catalysis. The application of this concept by grafting onto a highly acidic oxide surface offers advantages through the coalescence of properties inherent to homogeneous and heterogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information. Supplemental data includes general discussion of synthetic and experimental procedures, instrumentation, and characterization of materials. The supporting information is available free of charge at the ACS publications website at DOI:

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Notes

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(87) This experiment could not be conducted quantitatively, as the post-catalysis material was exposed to atmospheric moisture and oxygen upon removal from the reactor, and a number of the potential surface species are expected to decompose under these conditions.

