Communication

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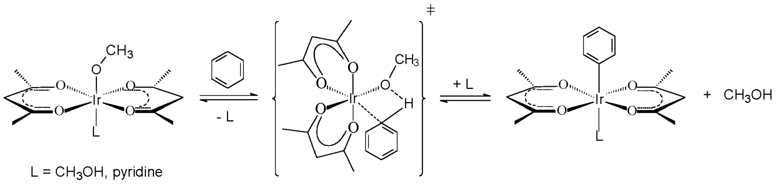

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CH Activation with an O-Donor Iridium−Methoxo Complex

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The CH activation of hydrocarbons to generate M−R intermediates has been the focus of significant effort, given the potential for developing new generations of "single-site" oxidation catalysts that operate at low temperatures with high yields and selectivities.[1] However, while there are now many well-established CH activation systems, relatively few have been successfully incorporated into catalytic cycles to generate oxy-functionalized products such as alcohols.[2] The majority of homogeneous catalysts that have been shown to generate oxy-functionalized products via CH activation are based on electronegative, "soft", redox-active cations such as Pt(II), Hg(II), Pd(II), and Au(III) in poorly coordinating, oxy-acid solvents.[1b] Significantly, as a result of the high electronegativity and oxidation potential of these cations, "oxy-functionalization" of the M−R intermediates by reductive heterolysis or elimination reactions is quite facile, Figure 1A.

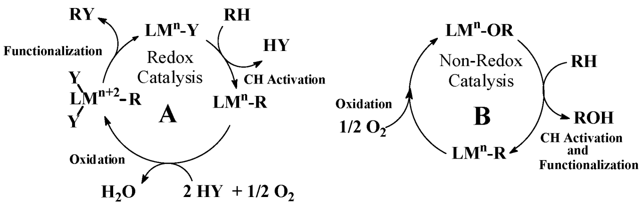
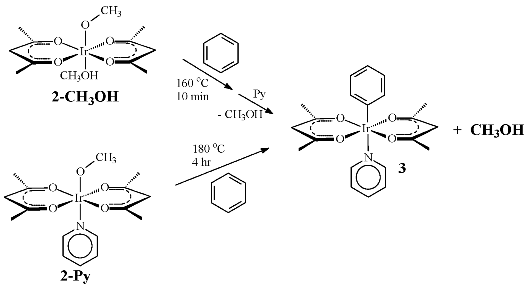


Figure 1. Redox (A) and non-redox (B) catalytic sequences for functionalization of hydrocarbons via CH bond activation.

Facile CH activation is also well known with more electron-rich, less oxidizing systems based on the middle or early transition metals such as Ir, Ru, Zr, etc.[1a] However, to our knowledge, these systems have not been incorporated into catalytic cycles that generate oxy-functionalized products. This is likely because reductive heterolysis or elimination reactions of the M−R intermediates are not facile and/or the systems are not stable to the conditions required for oxy-functionalization. Thus, to develop single-site oxidation catalysts based on these systems, it is likely that new systems that are stable and exhibit both new CH activation and oxy-functionalization reactions will be needed.

To begin to develop such systems with the middle transition metals, we have been investigating the development of catalytic cycles based on the reaction of O-donor metal−alkoxo complexes with CH bonds as shown in Figure 1B. This is of interest because, as shown, the reaction leads to *the simultaneous* CH activation of the hydrocarbon *as well as the formation of a desired oxy-functionalized product*, ROH, in one step. The observation of such a CH activation/oxy-functionalization reaction would be significant since, to our knowledge, there is no precedent for this type of CH activation reaction[3] and because it may be anticipated that there could be complications arising from (a) decomposition of the alkoxo complexes by facile β-hydride elimination reactions or formation of inert dinculear complexes and (b) destruction of the alcohol product during the CH activation reaction of RH. Developing reactions for the conversion of the M−R intermediate to M−OR, for which there is precedent via both free-radical and non-free radical reactions,[4] would complete the catalytic cycle. In this Communication we report evidence for the first part of this conceptual catalytic cycle: facile, selective CH activation with a metal−alkoxo complex.

Scheme 1. CH Activation of Benzene by **2-CH$_3$OH** and **2-Py**



Complex **2-CH$_3$OH** was synthesized from $[Ir(\mu\text{-acac-O,O,C}^3)\text{-}(acac\text{-O,O})(acac\text{-C}^3)]_2$, **1**, in moderate yields (22%) by treatment with an excess of sodium methoxide in methanol at 130 °C for 30 min. The compound is an air and thermally stable orange solid that has been fully characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, high-resolution mass spectrometry, and X-ray crystallography. The exchange of the MeO−Ir groups with CD_3OD solvent is slow on the NMR time scale, and only ~20% exchange (and generation of CH_3OD) is observed after 24 h at room temperature. Addition of pyridine leads to generation of the more stable pyridine complex, **2-Py**, which has also been fully characterized.

The arene CH activation with **2-L**, L = CH_3OH and pyridine, was carried out under an inert atmosphere in neat C_6H_6, Scheme 1. In the case of **2-CH$_3$OH**, the reaction with benzene was carried out at 160 °C for 10 min followed by addition of pyridine.[5] Subsequent removal of all volatiles in vacuo and complete dissolution with $CDCl_3$ containing 1,3,5-trimethoxybenzene as an internal standard showed that **3** was produced in 75% yield based on added **2-CH$_3$OH**. Reaction of benzene with **2-Py** provided **3** in similar yields but required longer reaction times, 4 h, and higher reaction temperatures, 180 °C. In both cases, **3** could be separated from the reaction mixtures by preparative TLC and identified by comparison of the ^1H and ^{13}C NMR spectra and mass peaks to those of independently prepared and fully characterized **3**.[6] When the reaction was carried out in benzene-d_6, labeled methanol, CH_3OD, was produced in >95% yield (based on added **2-L**) and identified by gas chromatography−mass spectrometry analyses. No formaldehyde or other C_1 products were detected. Consistent with

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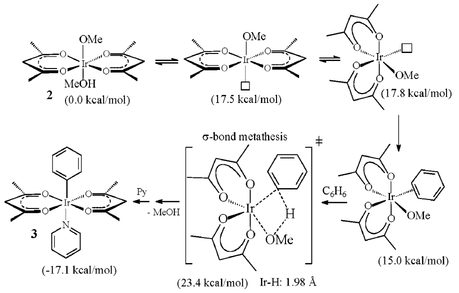
Scheme 2. Proposed Mechanism for the Reaction of **2**^{a}



^{a} Values in parentheses are calculated ΔH.

a non-free radical reaction, the reaction is insensitive to added oxygen and only CH activation of the *m*- and *p*-CH bonds of toluene is observed.

It is significant that this CH activation reaction proceeds cleanly and in high yield, given the possibility for side reactions. This suggests that the CH activation reaction of this d^6, O-donor Ir(III)−methoxo complex is substantially different from that of d^6, Ru(II)−NH_2 complexes, where stoichiometric CH activation is calculated to be unfavorable and has not been observed.[3a] Possible π-type destabilizing interactions between the O-donor ligands, the d^6 Ir(III) center, and the −OMe group along with the increased electronegativity of the Ir in an O-donor ligand field could account for the favorable thermodynamics for this CH activation reaction. It is also likely that these properties of the Ir center in an O-donor ligand field could serve to minimize the expected irreversible side reactions of metal alkoxides, such as (a) β-hydride elimination reactions due to the reduced electron density at the metal center or (b) the formation of bridging alkoxo complexes by the cis-labilization effect of π-donor spectator O-ligands.[7]

Theoretical calculations (B3LYP/LACVP** with ZPE and solvent corrections) are consistent with the reaction proceeding via the coordination pathway shown in Scheme 2. The observation that **2-L**, L = Py reacts more slowly than **2-L**, L = MeOH is consistent with the requirement for reversible loss of L since pyridine is a less labile ligand than methanol. The calculated barrier (23.4 kcal/mol) and favorable thermodynamics (−17.1 kcal/mol) of the reaction with **2-CH$_3$OH** are consistent with the reaction proceeding at 160 °C in ~10 min and in good yield. Interestingly, the transition state for C−H cleavage appears to be best described as a formal σ-bond metathesis. This can be observed in the Ir−H distance of 1.98 Å, Scheme 2, which corresponds to classical σ-bond metathesis geometry. Pathways involving oxidative addition, oxidative hydrogen migration,[8] or ionization of the methoxide group were all found to be higher in energy. It is not yet clear why this system favors a σ-bond metathesis mechanism over one involving oxidative addition. Possible reasons could be that the lone pair on the methoxo oxygen facilitates the hydrogen transfer and the decreased electron density of an Ir with five electronegative O-donor ligands disfavors a transition state with oxidative addition character.

Transition metal alkoxides are well known to decompose to metal hydrides via β-hydride elimination reactions,[9] and Ir−H's are well documented to be highly active for CH activation reactions.[10] For the CH activation reaction to proceed via a mechanism involving Ir−H, the formation of an Ir−H must necessarily be reversible to account for the stoichiometric formation of MeOH. To examine this possibility, we investigated the reaction of (acac-O,O)$_2$Ir-(O^{13}CH$_3$)(Py), **2-^{13}C**, with C_6D_6, as the Ir−H pathway would be expected to lead to generation of the D^{13}CH$_2$OD isotopomer whereas the proposed σ-bond metathesis would lead to ^{13}CH$_3$OH(D). ^{13}C NMR spectroscopy of the crude reaction mixture, showing that only ^{13}CH$_3$OH(D) was formed,[11] supports the mechanism shown in Scheme 2.

We have found that **2-L** catalyzes H/D exchange between D_2O and C_6H_6 at 160 °C. Significantly, the reaction system is stable over the time period studied (6 h), and turnover frequencies of 2.7×10^{-3} s^{-1} were observed based on added **2-CH$_3$OH**. We anticipate that the Ir−OCH$_3$ is converted to the related Ir−OH complex that reversibly activates the CH bonds of benzene, generating Ir−Ph and water. In this issue, Gunnoe reports evidence for related catalytic benzene H/D exchange that is proposed to proceed via CH activation with a Ru−OH complex. In ongoing efforts, we are examining the extension of this chemistry to the discrete hydroxo, phenoxo, and *tert*-butoxo complexes as well as to the CH activation of alkanes. To complete the catalytic cycle in Figure 1B, we are also developing non-free radical reactions for the oxidation of M−R bonds to metal−alkoxo complexes.

In summary, we demonstrate that the air, protic, and thermally stable O-donor alkoxo complexes, (acac-O,O)$_2$Ir(OMe)(L), **2-L**, L = Py and CH$_3$OH, react in stoichiometric CH activation reactions with benzene to generate the corresponding phenyl complex, **3**, with co-generation of methanol in high yield. To our knowledge this is the first example of such an intermolecular CH activation reaction with a metal−alkoxo complex.

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Supporting Information Available: Synthetic procedures and experimental details as well as the crystallographic data for **2-CH$_3$OH** and **2-Py** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) This is readily evident from the distinctive singlet resonance for ^{13}CH$_3$OH(D).

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