

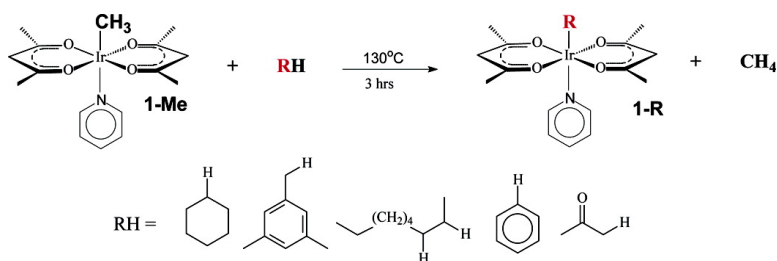
Communication

Alkane C–H Activation and Catalysis by an O-Donor Ligated Iridium Complex

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Alkane C–H Activation and Catalysis by an O-Donor Ligated Iridium Complex

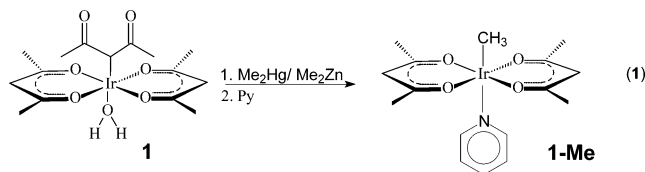
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Catalysts based on the C–H activation reaction show potential for the development of new, selective, hydrocarbon oxidation chemistry.¹ A central consideration in the design of such C–H activation based catalysts is the choice of ligands. The ligands generally acceptable for C–H activation reactions range from C-donor, for example, cyclopentadienyl ligands, to mono- and multidentate P- or N-donor ligands, to chelating NC or PC type ligands.² While O-donor ligands have been utilized with early and late transition metals,³ to our knowledge, well-defined, O-ligated, late transition metal complexes that activate alkane C–H bonds have not been reported. We have been particularly interested in O-ligated, late transition metals as such complexes could exhibit protic and oxidant stability given the lower basicity and higher electronegativity of O as compared to N, C, or P. Another key reason for study is that the electronegativity and “hardness” of O-donor ligands could allow access to higher oxidation states during catalysis that could facilitate the oxidative functionalization reactions of M–R intermediates to functionalized RX products in a catalytic cycle. Given these considerations, it was important to establish whether well-defined, O-ligated late transition metal complexes could activate alkane C–H bonds. Herein, we report a well-defined, O-ligated, late transition metal Ir complex that can activate alkane C–H bonds.

Recently, we demonstrated that the O-ligated complex, Ph-Ir(III)-(acac-O,O)₂(Py) (acac-O,O = η²-O,O-acetylacetonate, Py = pyridine), **1-Ph**, catalyzes the hydroarylation of olefins with arenes to generate alkyl benzenes.⁴ Herein, we report that the Me-Ir(III) derivative, Me-Ir(III)(acac-O,O)₂(Py), **1-Me**, reacts with alkanes (RH) via C–H activation to generate the corresponding alkyl-Ir complexes, **Ir-R** (RH = cyclohexane and *n*-octane). **1-Me** was synthesized from Ir(acac-C³)(acac-O,O)₂(H₂O), **1**, by treatment with (CH₃)₂Hg or (CH₃)₂Zn followed by addition of pyridine, in good yields (70%) as shown in eq 1. Complex **1-Me** is air stable and was fully characterized by ¹H, ¹³C NMR spectroscopy and elemental analysis.



Heating **1-Me** in neat cyclohexane at 130 °C for 3 h yielded the corresponding Ir-cyclohexyl complex, **1-C₆H₁₁**, as shown in eq 2. ¹H NMR analysis of the crude reaction mixture showed that the reaction was essentially quantitative. Complex **1-C₆H₁₁** could be isolated from the reaction mixture and has been fully characterized by ¹H and ¹³C NMR spectroscopy and elemental and X-ray structural analyses. An ORTEP drawing of **1-R** (R = C₆H₁₁) is shown in Figure 1.

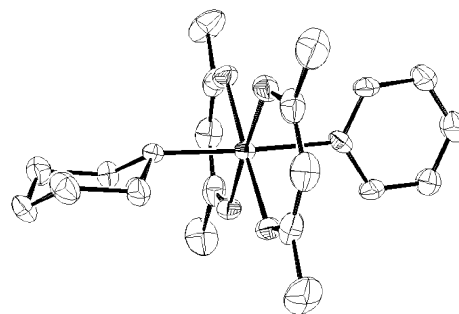
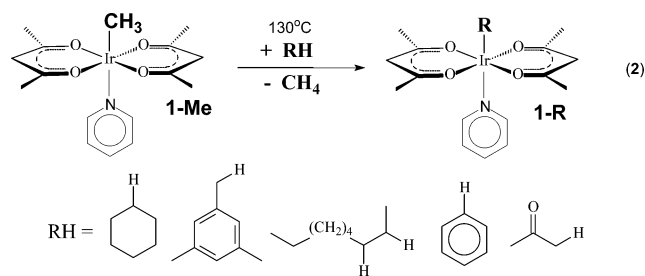


Figure 1. ORTEP drawing of **1-R**, R = cyclohexyl. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1–C4, 2.060(7); Ir1–N1, 2.225(6).

Consistent with the stoichiometry shown in eq 2, when the reaction is carried out in a sealed NMR tube with cyclohexane-*d*₁₂, monodeuterated methane is observed based on gas chromatography–mass spectroscopy (GC–MS) analysis. These observations unambiguously show that complexes based on the O-ligated, (acac-O,O)₂Ir(III) motif can activate alkane C–H bonds. To our knowledge, this is the first well-defined, late-metal, O-donor ligated complex that shows this reactivity for alkane C–H activation.



Other hydrocarbon substrates that react by C–H activation with **1-Me** are shown in eq 2. Thus, heating a solution of **1-Me** in mesitylene at 130 °C for 3 h results in the formation of a single new species. ¹H and ¹³C NMR spectroscopy analysis of the crude mixture in CDCl₃ shows clean formation of the Ir-mesityl, **1-R**, R = mesityl (eq 2), in which only the benzylic C–H bond was activated. The reaction with benzene and acetone cleanly provided the corresponding Ir-phenyl and Ir-acetyl derivatives. These materials have also been isolated and characterized by ¹H, ¹³C NMR spectroscopy and elemental analysis. The reaction with *n*-alkanes, exemplified by *n*-octane, could not be fully characterized, and ¹H and ¹³C NMR spectroscopy shows that several Ir-octyl products (presumably resulting from 1° and 2° C–H bond activation) are produced that could not be separated and quantified.

The alkane C–H activation reactions (eq 2) in the corresponding alkane solvent are retarded by added free pyridine. As shown in Figure 2, a plausible mechanism for the C–H activation from **1-R** can involve initial loss of pyridine, trans to cis isomerization to

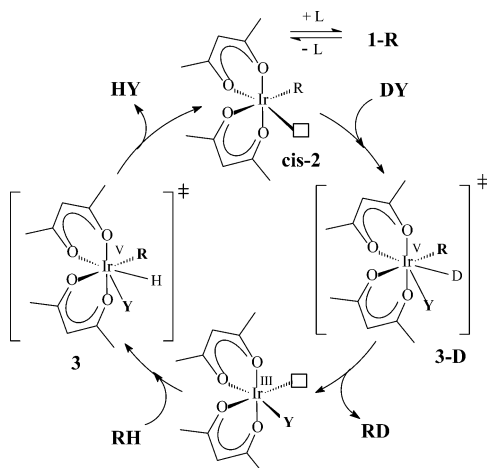


Figure 2. Proposed mechanism for the C–H activation of alkanes and H/D exchange reactions catalyzed by **1-R**.

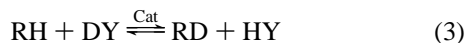
Table 1. H/D Exchange with C_6D_6 Catalyzed by **1-Me**^a

entry no.	substrate	TON ^b	TOF ^b ($\times 10^{-3} s^{-1}$)
1	cyclohexane	240	10
2	methane	123	1.7
3	<i>n</i> -octane	43	2.9
4	benzene	1210	675
5	acetone	72	43

^a All reactions were carried out at 180 °C using **1-Me** as the catalyst (2–20 mM). ^b See Supporting Information for details.

generate a five-coordinate, *cis*-intermediate, *cis*-2, that cleaves alkane C–H bonds via a seven-coordinate oxidative addition intermediate or transition state, **3**, or σ -bond metathesis transition state (not shown).⁵ We are currently carrying out kinetic and theoretical studies of this system to further elucidate the details of these CH activation reactions.

Having established that O-ligated, late-metal complexes can stoichiometrically activate the C–H bonds of alkanes, we have begun to examine the catalytic activity of this class of complexes with hydrocarbons.



Analysis by GC/MS and NMR spectroscopy shows that **1-Me** efficiently catalyzes H/D exchange between C_6D_6 and hydrocarbons, including alkanes, according to eq 3, RH = hydrocarbon, Y = C_6D_5 (Table 1, entries 1–5). These reactions presumably proceed via the catalytic sequence shown in Figure 2. The reactions are clean and no catalyst decomposition is observed, showing that these systems are thermally stable and activate alkane C–H bonds reversibly. ¹H NMR analysis of the crude reaction mixtures after heating shows that the resting state of the catalyst in the reaction with C_6D_6 is **1-Ph-d₅**. Control experiments with added drops of Hg metal (to test for catalysis by reduced metals) show no change in rate. Consistent with the presumption of stoichiometric C–H activation reactions with *n*-octane, ¹³C NMR analysis of the C_6D_6 /*n*-octane reaction mixture after catalysis shows deuterium incorporation into all of the positions of *n*-octane with higher selectivity for the 1° positions.

Consistent with the expected protic stability of O-donor ligands, preliminary results show that **1-Me** is thermally stable (to loss of

the O-ligated acac ligands) in protic media such as D_2O , CH_3CO_2D , and CF_3CO_2D and remains active for C–H activation and catalysis in these media. Thus, reaction of 0.1 mL of mesitylene with 1 mL of CF_3CO_2D containing 10 mM of **1-Me** shows H/D exchange (according to eq 3, Y = CF_3CO_2 , RH = mesitylene) of only the benzylic C–H bonds with a TOF of $\sim 10^{-3} s^{-1}$ at 160 °C. These H/D exchange reactions in protic media are being examined in greater detail.

In summary, we demonstrate that well-defined, late-metal, O-ligated complexes are competent for alkane C–H activation, exhibit high thermal and protic stability, and are efficient catalysts for H/D exchange reactions with alkanes. We are currently investigating the oxidative functionalization of O-donor M–R complexes and new O-donor complexes that activate C–H bonds.

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Supporting Information Available: Synthetic procedures, spectroscopic details for **1-R** (R = Me, C_6H_{11} , mesityl, acetyl), and crystallographic details for the complex **1-C₆H₁₁** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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