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# Novel bis-acac-O,O–Ir(III) catalyst for anti-Markovnikov, hydroarylation of olefins operates by arene CH activation†

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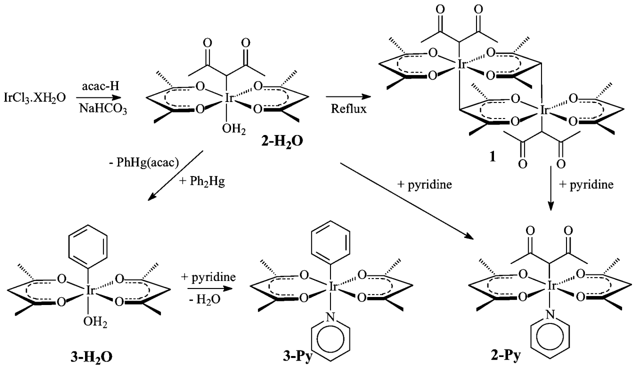
**A novel, thermally stable, homogeneous Ir catalyst for the anti-Markovnikov, hydroarylation of olefins is shown to operate by arene CH activation *via* the formation of a bis-acac-O,O phenyl–Ir(III) species.**

Recently we reported the binuclear complex, [Ir(μ-acac-O,O,C$^3$)(acac-O,O)(acac-C$^3$)]$_2$, **1**, that catalyzes the only reported example of anti-Markovnikov, hydroarylation of unactivated olefins by unactivated arenes to produce saturated alkyl arenes.[1] To account for the anti-Markovnikov regioselectivity, it was presumed that the active catalyst was a homogeneous Ir species that catalyzed reaction by arene C–H bond activation (rather than *e.g.*, by carbocations intermediates) but no mechanistic work has been reported to confirm these possibilities. It is important to understand the basis of operation of this catalyst as the reactivity is unique and knowledge of the composition of the active catalyst and reaction mechanism could provide the basis for developing new classes of catalysts for regio and stereoselective C–H and C–C bond forming reactions. In contrast to this system, reported systems that catalyze reactions between olefins and arene C–H bonds typically generate unsaturated, rather than saturated products.[2] Herein, we report the first evidence that the active catalyst is a thermally stable, homogeneous, bis-acac-O,O–Ir(III) species and the reaction proceeds *via* arene CH activation to generate a bis-acac, phenyl–Ir(III) intermediate that has been observed and characterized.

The initial catalysis was observed with the dinuclear Ir complex **1**.[1] To examine the possibility that a mononuclear Ir complex formed from **1** was the active catalyst we sought to synthesize and examine the reactivity of stable, mononuclear bis-acac-O,O–Ir(III) complexes. Interestingly, we have found that the new mononuclear complex,**2-H$_2$O**, Scheme 1,[3] can be isolated in 45% yield as an initially formed species during the reported synthesis of **1**.[4] To examine the possibility that the acac ligands may be thermally labile at the typical conditions for catalysis, 150–200 °C for 2 h, we examined the reaction kinetics and thermal stability of **2-Py**, Py = pyridine (the limited solubility of **2-H$_2$O** and **1** in neat benzene complicated studies). Attesting to the thermal stability of the bis-acac-O,O–Ir(III) motif, refluxing **2-Py** with mixtures of benzene and/or neat acetic acid, hexafluoroacac or 2-methylacetylacetone for several hours led only to exchange of the γ-C bonded acac ligand (acac-C$^3$) but no exchange or loss of the bis-acac-O,O bonded ligands. The reaction mixtures remained homogeneous and only bis-acac-O,O–Ir(III) species were observed.

To further determine if the dinuclear Ir species **1** or a mononuclear Ir species was the active catalyst we compared the catalytic hydroarylation activity of **1** and the mononuclear species **2-Py** and **2-H$_2$O**. As can be seen in Table 1, entries 1–3, the mononuclear complexes are both active catalysts with **2-H$_2$O** being as active as the dinuclear species, **1**, while **2-Py** is less active. Importantly, both complexes gave identical linear to branched (L:B) product ratios compared to **1** in the hydrophenylation of propylene. This strongly indicates that the same active catalytic species (albeit at different concentrations to account for the differences in rate) is formed from **1**, **2-H$_2$O** or **2-Py**. The lower rate of **2-Py** relative to **2-H$_2$O** and **1** is consistent with the better ligating properties of pyridine and the possibility that the active catalytic species is a mononuclear, bis-acac-O,O–Ir(III) species formed by dissociation of **1** or ligand loss from **2-H$_2$O** or **2-Pyr**. As expected, the addition of pyridine decreases the rate of catalysis with **1**, **2-H$_2$O** and **2-Py**.[5]

Consistent with the possibility that the active catalyst is a mononuclear bis-acac-O,O–Ir(III) species, the calculated catalyst TOF is independent of the amount of added **2-Py** (Table 1, entries 3–5). Assuming equilibrium between a mononuclear and dinuclear Ir species and that only one of these species is the active catalyst, this constant TOF would only be expected if either all the added complex remains mononuclear or all is converted to a dinuclear species. These results, coupled with the observation that **2-Py** is stable with respect to the formation of dinuclear species at elevated temperatures in benzene show that it is unlikely that dinuclear Ir species are the active catalysts. Supporting this, we have also observed that treatment of **1** with ethylene at moderate pressures leads to the formation of a



**Scheme 1** Synthesis of mononuclear bis-acac-O,O–Ir(III) complexes.

**Table 1** Results from the hydrophenylation of propylene catalyzed by bis-acac-O,O–Ir(III) complexes[a]

| Entry | Complex | Additive | [Complex] mmol | TOF[b] ($\times 10^{-4}$ s$^{-1}$) | L:B[c] ratio |
|---|---|---|---|---|---|
| 1 | **1** | — | 5 | 110 | 61:39 |
| 2 | **2-H$_2$O** | — | 5 | 100 | 61:39 |
| 3 | **2-Py** | — | 5 | 24 | 61:39 |
| 4 | **2-Py** | — | 10 | 22 | 61:39 |
| 5 | **2-Py** | — | 30 | 22 | 61:39 |
| 6 | **3-Py** | — | 5 | 32 | 61:39 |
| 7 | **3-H$_2$O** | — | 5 | 130 | 61:39 |
| 8 | **3-Py** | Acac-H | 5 | 15 | 61:39 |
| 9 | **3-Py** | H$_2$O | 5 | 36 | 61:39 |

[a] All reactions were carried out at 0.96 MPa of propylene in neat benzene at 180 °C and for 30 min. [b] TOF = [mols of product]/([mols of added **2-Py**].Reaction time). [c] Mole ratio of linear to branched products.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org.suppdata/cc/b2/b208680h/

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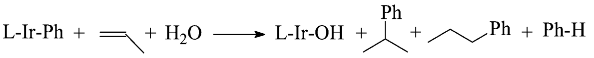
mononuclear bis-acac-O,O–Ir(III) species which we speculate is the ethylene complex, **2-$C_2H_4$**.

To determine whether the hydroarylation occurred by benzene C–H activation to generate phenyl–Ir intermediates, we examined the reaction mixture for phenyl–Ir complexes. NMR analysis of crude reaction mixtures resulting from reaction of benzene and propylene, catalyzed with 5 mol% **2-Py**, after removal of volatiles, led to the detection of the phenyl–Ir(III) species, Ir(Ph)(acac-O,O)$_2$(pyridine), **3-Py**, in ~65% yield based on added **2-Py**. The identity of this material has been confirmed by comparison with the independently synthesized and fully characterized complex, **3-Py**, prepared as shown in Scheme 1.[3] The identical material is also formed when catalysis is carried out with **2-$H_2O$**, followed by addition of pyridine and isolation.

To confirm that bis-acac-O,O, phenyl–Ir(III) species were involved in the catalysis, the catalytic activity of **3-Py** and the related complex, **3-$H_2O$** (both prepared by independent syntheses, Scheme 1)[3] were examined as hydroarylation catalysts. As can be seen in Table 1, **3-Py** (entry 6) was found to be as active as **2-Py** (entry 3) while **3-$H_2O$** (entry 7) was found to be slightly *more* active than **1** or **2-$H_2O$**. Critically, these bis-acac-O,O, phenyl–Ir(III) complexes also gave the same L : B ratios of hydroarylation products with propylene strongly indicating that the same catalytic species are involved starting from **2** or **3**. The efficient reaction of **3-Py** seemed to indicate that neither γ-C bonded acac (present in complexes **1** and **2**) nor water (present in **2-$H_2O$**) was essential to catalysis. To further confirm this, we explicitly examined the effect of added free acetylacetone (acac-H) and water on the catalytic activity of **3-Py** in dry benzene/olefin mixtures. As can be seen in Table 1, (entries 8 and 9) neither added acac-H nor water has any effect on the reaction rate or product selectivity of **3-Py**.[6]

To provide additional evidence for the intermediacy of a bis-acac-O,O, phenyl–Ir(III) species in the catalytic, hydrophenylation of olefins, the stoichiometric reaction of **3-Py** and **3-$H_2O$** with propylene in mesitylene,[7] saturated with water to provide a H source as shown in eqn. (1), was examined. This led (based on added phenyl–Ir complex) to the formation of benzene (33%) and n-propylbenzene (40%) and isopropylbenzene (27%). Importantly the ratio of propylbenzene products was in the same L : B ratio (~61 : 39) as observed in the catalytic hydrophenylation of propylene catalyzed by **1**, **2-$H_2O$**, **2-Py**, **3-$H_2O$** or **3-Py**. The identity of the Ir products in eqn. (1) were not confirmed but it is presumed that a bis-acac-O,O–Ir(III) hydroxyl species is formed.



$$\text{L-Ir-Ph} + \text{propylene} + H_2O \longrightarrow \text{L-Ir-OH} + \text{isopropylbenzene} + \text{n-propylbenzene} + \text{Ph-H} \quad (1)$$

The results above, along with the initially noted high catalytic stability and reaction reproducibility[1a] support the conclusion that the catalysis proceeds by arene CH activation *via* a thermally stable, homogeneous, mononuclear, bis-acac-O,O aryl–Ir(III) species. While we cannot completely rule out other possibilities, such as Ir(I) species or slippage of the spectator $\eta^2$-acac-O,O ligands to an $\eta^1$-acac ligand that is O or C bound, we believe that formation of such species are not consistent with the complete lack of exchange of the bis-acac-O,O ligands with free acac-H at elevated temperatures or in the presence of acids. Additionally, the relatively low level of inhibition by olefins[1] would not be expected with an Ir(I) species as the active species.[8]

Interestingly, if the catalysis is based on Ir(III) rather than an Ir(I) species, an important question is how the arene C–H bond is activated. Our initial speculation[1b] of an electrophilic substitution mechanism by a 5-coordinate, cationic Ir(III) species formed by dissociation of the anionic, γ-C bonded acac (acac-$C^3$) was based on early results that implicated that the γ-C bonded acac-$C^3$ ligand of **1** was essential to catalytic activity. However, as no such plausible anionic leaving group can be invoked for catalysis by **3-Py** in dry, neat benzene it is unlikely that an electrophilic mechanism *via* cationic 5-coordinate Ir(III) species is involved. Instead, we now favor the mechanism shown in Fig. 1, where arene C–H activation and product formation occur in the same step from a *cis*, bis-acac-O,O, arene, phenethyl Ir(III) species, **4**, that generates the product by either oxidative addition to a C–H bond of the coordinated arene to generate a seven coordinate Ir(V) intermediate, **5**, or by a sigma-bond metathesis transition state. In light of the recent precedent by Bergman for the involvement of seven coordinate, Ir(V) intermediates in C–H activation reactions with Ir(III),[9] we are biased toward the oxidative addition pathway and are carrying theoretical calculations to distinguish between the two possibilities. We have no evidence for the proposed *cis*-isomerization but this is reasonable given the requirement for an olefin insertion step.

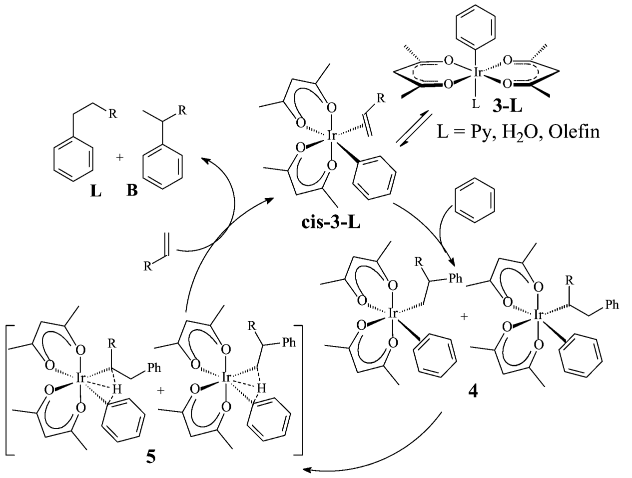


**Fig. 1** Proposed CH activation reaction mechanism for hydroarylation of olefins by a bis-acac,O,O–Ir(III) species.

Work is continuing on delineating additional details of the reaction mechanism, understanding the molecular basis for the uniqueness of the acac-O,O ligands and designing improved catalysts. A unique aspect of this catalysis is the complete lack of any olefinic products that could result by β-hydride elimination from intermediates **4** or **5**. As developing strategies to design catalysts that disfavor such β-hydride eliminations would be important, we are investigating the synthesis and chemistry of the phenethyl intermediate, **4**, to determine if such species are formed and why olefins products are not produced.

## Notes and references

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3 See supporting material for syntheses of new complexes in Scheme 1.

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5 Pyridine is inert to the hydroarylation reaction. Exchange can be observed between pyridine-$d_5$ and **3-Py**.

6 As a result of more detailed studies, added water, rather than accelerating catalysis by **1** as reported earlier,[1a] has now been found to have little effect on the rate of catalysis by **1** or **2**. This result is consistent with the proposed CH activation reaction mechanism.

7 Mesitylene is an inert solvent that supports the hydroarylation catalysis. The arene CH bonds of mesitylene are not activated.

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