

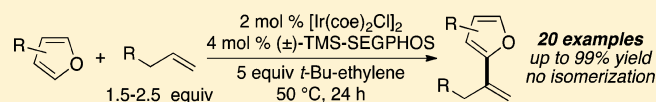
Iridium-Catalyzed Oxidative Olefination of Furans with Unactivated Alkenes

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S Supporting Information

ABSTRACT: The oxidative coupling of arenes and alkenes is an attractive strategy for the synthesis of vinylarenes, but reactions with unactivated alkenes have typically occurred in low yield. We report an Ir-catalyzed oxidative coupling of furans with unactivated olefins to generate branched vinylfuran products in high yields and with high selectivities with a second alkene as the hydrogen acceptor. Detailed mechanistic experiments revealed catalyst decomposition pathways that were alleviated by the judicious selection of reaction conditions and application of new ligands.



INTRODUCTION

The oxidative coupling of arenes with alkenes to generate vinylarenes is an attractive alternative to the Mizoroki–Heck reaction because the oxidative functionalization reaction does not require a functionalized coupling partner.^{1,2} First discovered by Fujiwara and Moritani as a Pd-mediated process³ and later developed into a Pd-catalyzed⁴ coupling of benzene with styrene, this reaction has been reported with a range of arenes,^{5–21} heteroarenes,^{8,22–29} and alkenes.^{30,31} These oxidative olefinations of aryl C–H bonds have the potential to provide, in a single step, access to vinylarenes for further functionalization during the synthesis of complex structures.

However, current couplings of alkenes and arenes in high yield are limited to those of conjugated olefins, such as acrylates,^{1,6,12,16,21,28,30,32–34} acrylonitriles,^{35–38} or styrenes.^{20,26} Olefinations with unconjugated alkenes are rare. Oxidative couplings of arenes with allyl esters^{17,25} have been reported to form mixtures of branched and linear isomers, and directed olefinations of benzamides with isobutylene or cyclopentene occur in low yield and generate large amounts of alkylarene side-products.¹⁹ The olefinations of tolyltriazole *N*-oxide,²⁹ benzothiazole,²⁸ and thiophene²⁵ with 1-octene have been reported, but just one example of each was described, and all formed complex mixtures of products in low yield.

We recently reported the asymmetric addition of heteroaryl C–H bonds across norbornene to form alkylarenes.³⁹ We considered whether this reaction could be modified to form vinylarenes from heteroarenes, such as furans. Polymers of vinylfuran monomers have the potential to serve as biorenewable surrogates for polystyrene;^{40–42} however, furyl-substituted acrylates, which are accessible from known oxidative coupling reactions or aldol condensation reactions, are challenging to polymerize.⁴² In contrast, cationic polymerizations of isopropenylfurans, which are currently prepared by stoichiometric transformations,⁴¹ occur readily.^{40,42}

We report the olefination of furans with unactivated alkenes, including unstrained internal alkenes and propene, to form

branched vinylfurans in excellent yields and with high selectivities with a second alkene as the terminal oxidant. Mechanistic studies indicate that this reaction occurs by turnover-limiting migratory insertion of an alkene into an Ir–C bond, and studies on catalyst speciation explain an unusual kinetic observation: the rate of product formation is greater at lower temperatures than at higher temperatures.

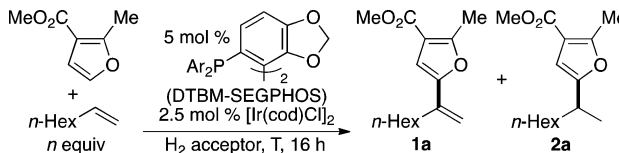
RESULTS AND DISCUSSION

Method Development. The observation of furan olefination stemmed from our recent studies on enantioselective additions of heteroarene C–H bonds to strained bicycloalkenes catalyzed by iridium complexes of DTBM–SEGPHOS (DTBM = 3,5-di-*t*Bu-4-OMe-phenyl; illustrated in Figure 2).³⁹ Selected results gained during the development of the olefination of furans are summarized in Table 1. These results reveal a counterintuitive effect of temperature on the rate and yield.

Reactions of methyl 3-methyl-2-furoate conducted with 1-octene under conditions analogous to those reported for reactions of strained alkenes formed only trace amounts of products from the alkene and the heteroarene at 100 °C (entry 1). Instead, the terminal alkene isomerized to less reactive internal alkene isomers. Conducting the reaction neat with an excess of 1-octene at elevated temperatures led to substantial conversion of the starting material to form the vinylfuran **1a**, rather than alkylfuran **2a** (entry 2). A variety of olefins that could serve as hydrogen acceptors for the oxidative coupling of octene with furan were tested (see the Supporting Information for the full set of compounds tested as hydrogen acceptors). Reactions with vinylsiloxanes as a hydrogen acceptor formed product mixtures with greater ratios of **1a** over **2a** than did reactions conducted in the absence of the additive, but these additives decreased the overall rates and yields of the reactions (entry 3).

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Table 1. Reaction Development for the Iridium-Catalyzed Olefination of Furans^a


entry	temp (°C)	n equiv 1-octene	H ₂ acceptor, (m equiv)	% conv	% 1a	% 2a	ratio 1a/2a
1	100	1.5	inherent 1-octene	<5	2	0	
2	140	6	inherent 1-octene	68	61	7	9
3	140	6	(vinyl-Me ₂ Si) ₂ O, (2)	41	33	2	17
4	50	6	inherent 1-octene	70	64	5	13
5	50	2.5	inherent 1-octene	86	69	17	6
6 ^b	50	2.5	<i>tert</i> -butylethylene, (5)	84	78	6	13

^aYields were determined by GC analysis with dodecane as the internal standard. ^bReaction was conducted with [Ir(coe)₂Cl]₂, rather than [Ir(cod)Cl]₂.

Ultimately, we discovered that reactions conducted at 50 °C occurred with conversions comparable to reactions conducted at 140 °C (entry 4). In addition, isomerization of 1-octene to unreactive isomers was not observed under these conditions; this lack of isomerization eliminated the requirement for reactions to be conducted with a large excess of olefin. Reactions performed with only 2.5 equiv of 1-octene and *tert*-butylethylene (TBE) as a sacrificial hydrogen acceptor generated **1a** in good yield and selectivity.

The effect of temperature on the rate of the reaction was more counterintuitive than was its effect on the yield. The rate of reactions conducted at 50 °C was an order of magnitude greater than that of reactions conducted at 100 °C. This unexpected result merited additional mechanistic study, which aided in the improvement of the catalytic reaction.

Mechanistic Analysis of the Unusual Dependence of Rate on Temperature. Mechanistic data on the catalytic reactions conducted at 50 and 130 °C are summarized in Figure 1 and revealed the origin of the unusual relative rates at high and low temperature. Monitoring of the reactions at 50 and 130 °C by ³¹P NMR spectroscopy showed that the resting state of the catalyst at the two temperatures was different. At 50 °C, the reaction solution was red. At this temperature, the resting state

was shown by NMR spectroscopy and X-ray diffraction to be the Ir(olefin) complex **3** (part a of Figure 1). At 130 °C, the catalytic reaction was colorless, and the resting state was shown by NMR spectroscopy to be the Ir(allyl)(H) complex **4**.

Complex **4** formed from olefin complex **3** within seconds at 130 °C; the rate constant was >10⁻¹ s⁻¹. This rate constant is much greater than that of the catalytic reaction ($k \approx 10^{-4}$ s⁻¹). Thus, we were surprised to observe that the olefination of furan proceeded to 84% conversion after 16 h at 50 °C with only 28% of **3** having decomposed to **4**. These data indicate that the olefination is faster than formation of **4** at 50 °C, whereas the formation of **4** is faster than olefination at 130 °C.

A more detailed view of the effect of temperature on the identity of the resting states was created by performing separate Eyring analyses on the rate constants for formation of **4** from isolated **3** and the olefination of furan catalyzed by **3** (part b of Figure 1). Analysis of the rate of formation of **4** in the temperature range 72–106 °C revealed the following activation parameters: $\Delta H^\ddagger = 22.5$ kcal/mol and $\Delta S^\ddagger = -8$ eu. The small ΔS^\ddagger is consistent with the same composition of the starting complex **3** as for product **4**. The dependence of the rate of formation of complex **4** on temperature is large because of the large enthalpic difference between the ground and transition states.

The activation parameters for the olefination of furan in the temperature range 35–65 °C were $\Delta H^\ddagger = 8.2$ kcal/mol and $\Delta S^\ddagger = -45$ eu. The large, negative entropy suggests that the transition state forms by a combination of the furan and the resting state. The small dependence of the rate of olefination on temperature is due to the small enthalpy of activation. Consistent with our observations, the overlay of the Eyring plots for the competing processes reveals that the furan olefination is faster than the catalyst decomposition at temperatures below 110 °C, whereas formation of complex **4** is faster than olefination at temperatures above 110 °C (part b of Figure 1).

Effect of Ligand on Yield and Selectivity. These mechanistic insights directed the development of new complexes that would disfavor formation of Ir(allyl)(H) intermediates, improve rates of olefination, and increase the selectivity for **1a** over **2a**. We prepared ligands that were less electron-donating than DTBM-SEGPHOS to reduce the rate of allylic C–H activation, more sterically bulky than DTBM-SEGPHOS to prevent formation of Ir dimers, and soluble in the nonpolar reaction media (illustrated in Figure 2). As summarized in Table 2, complexes of SEGPHOS-based ligands

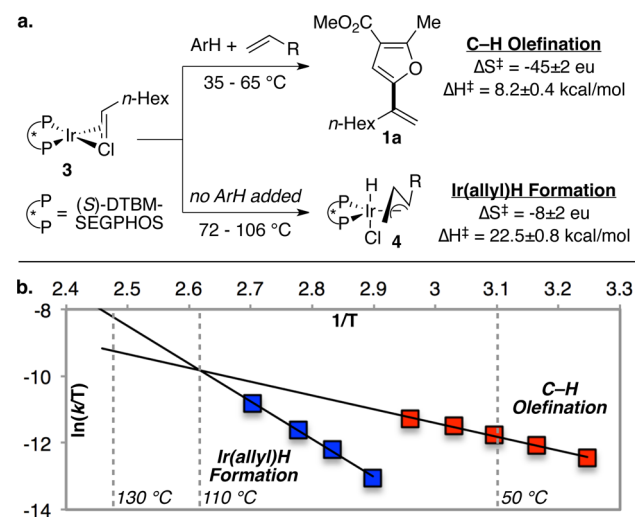


Figure 1. (a) Competing processes: olefination catalyzed by complex **3** (top) and decomposition of **3** to form complex **4** (bottom). (b) Eyring plot of the competing processes.

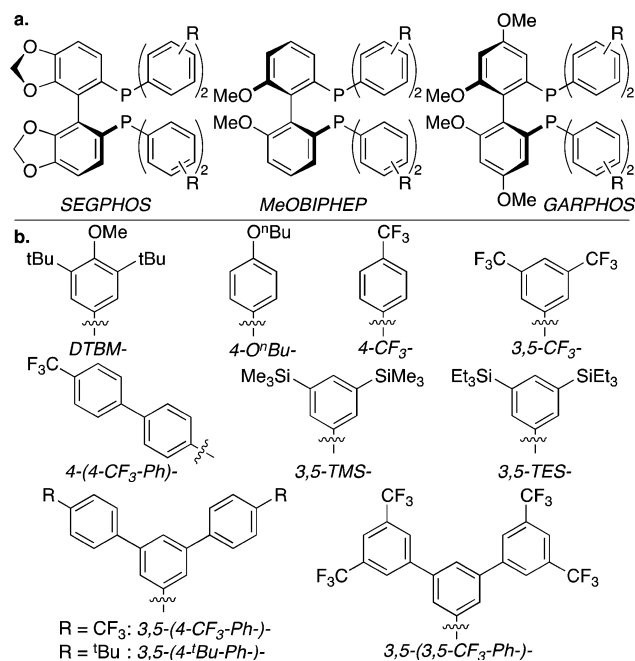


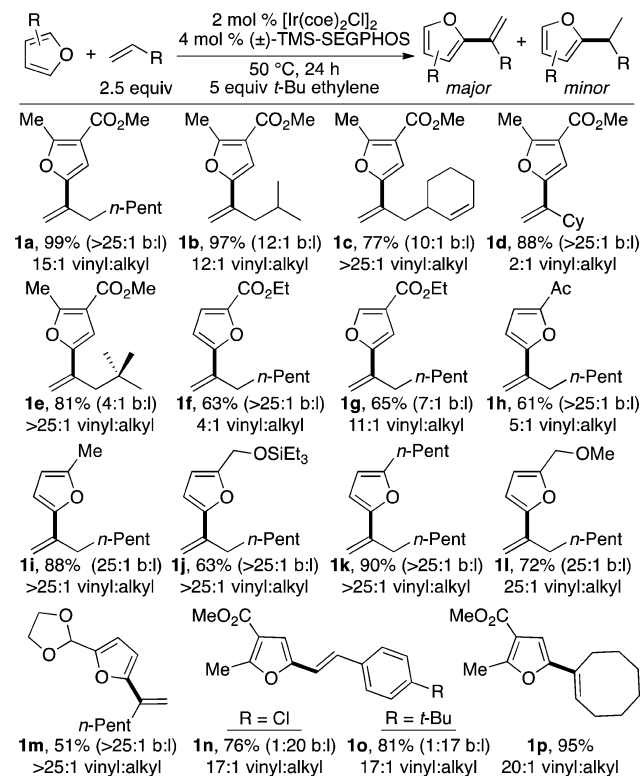
Figure 2. Bisphosphines tested as ligands for the iridium-catalyzed olefination of furans: (a) biaryl-backbones of the tested ligands and (b) aryl groups on phosphorus.

formed more active catalysts than those of analogous biaryl bisphosphine ligands (entries 1–3). Complexes of ligands containing electron-withdrawing substituents were more reactive than those containing electron-donating substituents (entry 5 vs 4); however, additional electron-withdrawing groups led to decreased reactivity, as revealed by a comparison of the reactions catalyzed by complexes of 3,5-bis-CF₃-substituted ligands (entry 6) to those of 4-CF₃-substituted ligands (entry 5). SEGPHOS derivatives with bi- and terphenylarenes formed complexes that generated vinylfuran **1a** with high selectivity over alkyl product **2a**, but in low yield (entries 7–10). High yield, as well as high selectivity for olefination products, was observed for reactions catalyzed by Ir complexes of SEGPHOS derivatives containing 3,5-bis-(trialkylsilyl) arenes (entries 11 and 12). This air-stable TMS-SEGPHOS ligand was prepared as a racemate on the gram scale, forms Ir complexes that are soluble in pentane, and does not readily decompose to analogues of **4** under catalytic

conditions. Thus, we studied olefination reactions under the conditions of entry 11.

Scope of Iridium-Catalyzed Olefination of Furans. The olefination of a range of furans with a variety of alkenes by the procedure just described is illustrated in Chart 1. Branched

Chart 1. Scope of Ir-Catalyzed Olefination of Furans^a



^aReported yields are isolated yields.

vinylfurans formed in high yields with reaction exclusively α to oxygen. These products were formed with good to excellent selectivities over the possible alkylfurans or linear vinylfurans. The resulting 1,1-disubstituted alkenes are kinetic products and do not undergo isomerization to other olefins under these mild conditions. Reactions of furans possessing electron-donating substituents formed products in higher yields and with higher selectivities than did reactions of furans containing electron-

Table 2. Effect of Ligand on the Reaction^a

entry	ligand	substituents on aryl group	% conv	% 1a	% 2a	ratio 1a/2a
1	(S)-Ar-SEGPHOS	DTBM—	84	77	6.5	12
2	(R)-Ar-MeOBIPHEP	DTBM—	54	47	3.3	14
3	(S)-Ar-Garphos	DTBM—	37	30	2.2	14
4	(±)-Ar-SEGPHOS	4-O ⁿ Bu—	16	4.0	0.30	13
5	(±)-Ar-SEGPHOS	4-CF ₃ —	25	19	1.1	17
6	(±)-Ar-SEGPHOS	3,5-CF ₃ —	7	3	0.05	>40
7	(±)-Ar-SEGPHOS	4-(4-CF ₃ -Ph)—	37	37	0.5	>40
8	(±)-Ar-SEGPHOS	3,5-(4-CF ₃ -Ph)—	28	28	0.6	>40
9	(±)-Ar-SEGPHOS	3,5-(4- ⁿ Bu-Ph)—	18	9.0	0.60	15
10	(±)-Ar-SEGPHOS	3,5-(3,5-CF ₃ -Ph)—	39	38	0.9	>40
11	(±)-Ar-SEGPHOS	3,5-TMS—	100	96	4.0	24
12	(±)-Ar-SEGPHOS	3,5-TES—	100	96	3.5	27

^aReactions were conducted following the conditions of entry 6, Table 1. Yields were determined by GC analysis with dodecane as an internal standard.

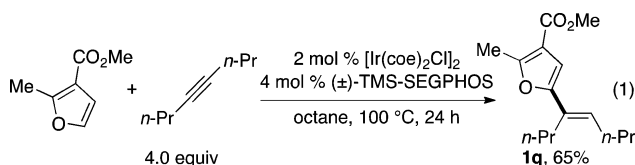
withdrawing groups (**1f** vs **1i**). The reactivity of furan **1a** bearing the combination of electron-donating and electron-withdrawing groups at the C2 and C3 positions, respectively, was more comparable to that of 2-methylfuran **1i** than to that of ethyl 3-furoate **1g**. These data indicate that reactions occurring at the C5 position are more strongly influenced by substitution at the C2 position than at the C3 position of the furan. These observations are also consistent with the greater dienic and lower aromatic character of furans than of analogous pyrroles or thiophenes.⁴³

No coupling products were observed from reactions of the commodity chemical furfural, but derivatives of furfural generated from aldehyde reduction (**1i**), hydrosilylation (**1j**), or protection (**1m**) underwent the Ir-catalyzed olefination to form products in good yields and with high selectivities. These results highlight the compatibility of this process with substrates bearing ester, dioxolane, protected alcohol, and ketone functionality. In addition, reactions of furans with substrates possessing multiple alkenyl moieties occurred selectively at the terminal C–C double bond without isomerization of the internal C–C double bond (**1c**).

Reactions of unactivated α -olefins formed branched vinylfuran products in preference to the linear isomers. Steric bulk in proximity to the reacting olefin led to a decrease in the ratio of branched to linear vinylfuran products (see entries **1a** vs **1b** vs **1e** vs **1d**). Unlike reactions conducted with unactivated alkenes, the reactions of styrenes with furans gave the linear (1,2-substituted) vinylfurans as the major products. Reactions conducted with an electron-deficient (**1n**) or electron-rich (**1o**) styrene both formed the corresponding products in high yields and with high selectivities for the linear products. These results are similar to those of palladium-catalyzed olefinations of furans with styrenes.²⁶ Under these conditions, a benzyl-metal intermediate is generated after C–C bond formation in preference to a terminal alkyl-metal intermediate. The benzyl-palladium or -iridium complexes lead to linear vinylfuran products, and the terminal alkyl-palladium or -iridium complexes, which form from reactions of 1-octene, lead to branched vinylfuran products.

With the exception of cyclooctene, reactions of furans with internal cyclic or acyclic alkenes did not form coupled products. However, *cis*-cyclooctene reacted under the standard conditions to form the conjugated vinylfuran product in high yield (**1p**).

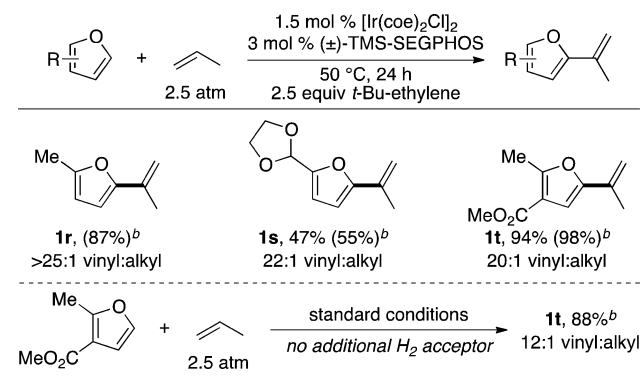
The products that are equivalent to those formed from olefination reactions conducted with internal alkenes can also be formed by the addition of furan C–H bonds across alkynes. Indeed, the same complex that catalyzes the oxidative olefination of furans with alkenes catalyzed the addition of furan C–H bonds across alkynes. For example, the reaction of methyl 2-methyl-3-furoate with 4-octyne occurred at 100 °C to form the addition product as a single *E* isomer (**1q**) from syn addition of the C–H bond across the alkyne (eq 1).



Finally, we assessed whether vinylfurans would form from the most abundant alkenes, propene and ethene. Reactions conducted in TBE as solvent and with 2.5 atm of propene

formed products from the combination of the furan and the alkene in high yield and selectivity, as summarized in Chart 2.

Chart 2. Olefination of Furans with Propene^a



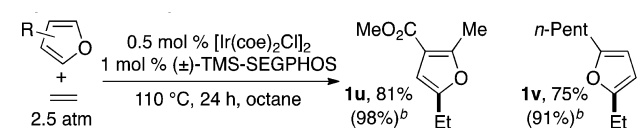
^aReported yields are isolated yields. ^bNMR yield with mesitylene as the internal standard.

This procedure was amenable to reactions of abundant furans that are of interest for biorenewable materials, specifically: 2-methylfuran (**1r**) and protected furfural (**1s**). For reactions of these abundant furans, the hydrogen acceptor TBE is the most expensive component. Thus, we performed the catalytic reaction in the absence of TBE to test if the olefination reaction could be performed with propene as the substrate and oxidant. Reactions conducted in the absence of TBE, with propene as the sole hydrogen acceptor, formed isopropenylfuran **1t** in high yield. In addition, the selectivity for the vinyl product was only slightly lower than that for reactions conducted with added TBE, even though the reaction without TBE contains a lower concentration of the hydrogen acceptor.

Reactions of ethylene occurred with high conversions under conditions that are similar to those for reactions of propene. The absence of allylic protons on the ethylene allowed the reaction to be conducted at elevated temperatures without catalyst deactivation by formation of an allyl complex. Consequently, higher catalyst turnover numbers were achieved for reactions of ethylene than for those of α -olefins. However, reactions of ethylene formed products of hydroarylation exclusively, even with added hydrogen acceptors. No vinylfuran products were observed at low conversion. The origin of this dramatic change in selectivity is unclear. Nonetheless, ethylfuran products were formed in excellent yield with only 1 mol % catalyst under 2.5 atm of ethylene (Chart 3).

Experimental and Computational Evaluation of the Steps Within the Catalytic Cycle. Mechanism of C–C Bond Formation. The carbon–carbon bond in the product could be formed by a range of mechanisms: olefin insertion into an Ir–C bond, nucleophilic attack of the furan onto an alkene that is bound to iridium, or reductive elimination of an aryl vinyl

Chart 3. C–H Bond Additions of Furans to Ethylene^a



^aReported yields are isolated yields. ^bNMR yield with mesitylene as the internal standard.

intermediate. To distinguish among these mechanisms, the geometry of the vinylfuran products from reactions with geometrically defined alkenes was determined. The olefination reaction conducted with (*E*)-octene-*d*₁ would form the (*Z*)-1k-*d*₁ isomer if the reaction occurred by nucleophilic attack onto a metal-bound olefin or by cleavage of a vinyl C–H bond and subsequent C–C reductive elimination (parts d and e of Figure 3), whereas the reaction of (*E*)-octene-*d*₁ would form the (*E*)-

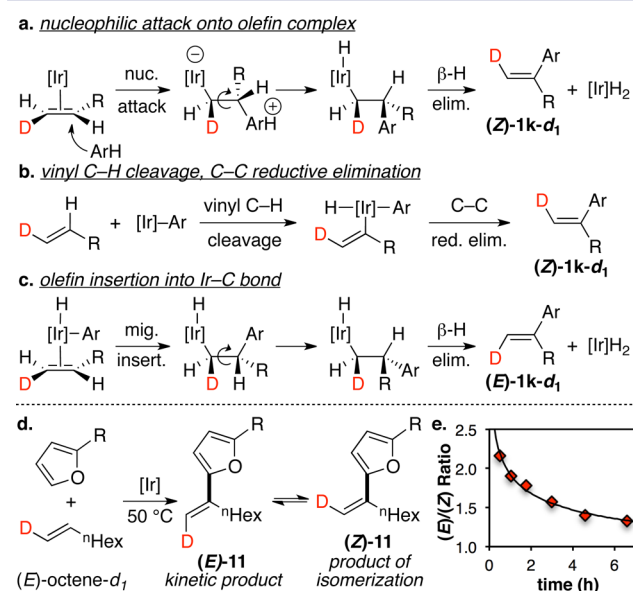


Figure 3. (a, b) Mechanisms that are inconsistent with formation of the observed product. (c) Proposed mechanism for the stereospecific formation of (*E*)-1k-*d*₁. (d) Ir-catalyzed olefination of 2-pentylfuran with (*E*)-octene-*d*₁. (e) Ratio of (*E*)-1k-*d*₁ to (*Z*)-1k-*d*₁ vs time.

1k-*d*₁ isomer if the reaction occurred by insertion of the alkene into a furyliridium bond, followed by stereospecific β -H elimination.

The reaction of 2-pentylfuran with (*E*)-octene-*d*₁ was conducted under the conditions reported in Chart 1 (part a of Figure 3). When the reaction was monitored at low conversions, (*E*)-1k-*d*₁ was the major isomer of the vinylfuran product (part b of Figure 3). These results imply that (*E*)-1k-*d*₁ is the product of the Ir-catalyzed reaction, whereas the *Z* isomer is formed by isomerization of the *E* isomer. The formation of (*E*)-1k-*d*₁ as the kinetic product is inconsistent with a mechanism involving C–C reductive elimination from a vinyl furyl complex or a nucleophilic attack (parts d and e of Figure 3); instead, this result implies that the reaction occurs by a mechanism involving migratory insertion of (*E*)-octene-*d*₁ into an Ir–C bond, followed by stereospecific β -H elimination (part c of Figure 3).

Kinetic Studies of a Representative Catalytic Reaction. Kinetic experiments by the method of initial rates (to 15% conversion) on the reaction of 2-pentylfuran with 1-octene provided insight into the identity of the turnover-limiting step (TLS). The reaction was found to be first-order in catalyst and furan, but the rate of the reaction was independent of the concentration of 1-octene. A comparison of the initial rates for the reaction of 1-octene with 2-pentylfuran and with 2-pentyl-5-deuteriofuran in separate vessels revealed a small kinetic isotope effect (KIE) of 1.4. This small KIE is inconsistent with turnover-limiting cleavage of the C–H bond by a P₂IrCl complex. These kinetic data, and data on the identity of the

resting state (3), suggest that the TLS of the catalytic reaction occurs after cleavage of the C–H bond of furan from an olefin-bound intermediate.

Two catalytic cycles that are consistent with the observed resting state 3 and the empirical rate law are illustrated in Figure 4. In both cycles, the resting-state (complex 3) is

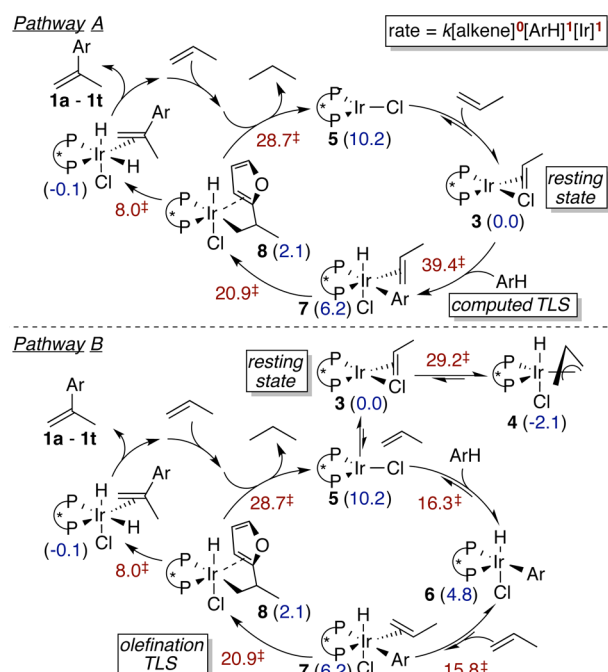


Figure 4. Proposed mechanisms with computed Gibbs free energies of transition states (red) and intermediates (blue) in kcal/mol. Pathway A: mechanism occurs by C–H cleavage at complex 3. Pathway B: mechanism occurs by C–H cleavage at complex 5.

converted to the alkene-ligated aryl hydride complex 7. Turnover-limiting insertion of the alkene of 7 into the Ir-furyl bond then forms alkyridium 8. DFT calculations (vide infra) indicate that this complex contains a stabilizing interaction between the C=C bond of the furyl group and iridium. β -H elimination from this alkyridium intermediate 8 is then followed by dissociation of the vinylfuran product. Finally, hydrogenation of the hydrogen acceptor generates the Ir(I) chloride intermediate, which binds alkene to regenerate complex 3. Complex 3 lies directly on the cycle in pathway A and lies off the cycle in pathway B.

In pathway A, the conversion of resting state 3 to complex 7 occurs by oxidative addition of furan directly to 3 to form 7. In pathway B, the conversion of 3 to 7 occurs by the more circuitous reversible dissociation of the alkene from complex 3 to generate three-coordinate intermediate 5, oxidative addition of the furyl C–H bond to 5 to form furyliridium hydride complex 6, and coordination of propene to 6 to generate 7. Both of these pathways are consistent with our observed reaction orders, isotope effects, and isotopic labeling; however, the two pathways were easily distinguished by computational studies.

Computational Studies. In parallel with the experimental studies, we computed by density functional theory many of the individual steps of the catalytic mechanisms in Figure 4 (see the Supporting Information for details). To simplify these calculations, complexes of the parent SEGPHOS were

computed, rather than complexes of the full DTBM–SEGPPOS ligand. Although the energies of these computed compounds will differ from those of the experimental system because the DTBM–SEGPPOS is more hindered and more electron-donating, the computations provided insight into the stability of intermediates and rates of the elementary steps of the cycle.

The calculations were conducted with the Gaussian 09 package. Geometry optimization was conducted with the M06 functionals with the lanl2dz basis set and ECP for iridium and the 6-31g(d,p) basis set for all other atoms at 298 K. Frequency analysis was conducted at the same level of theory to verify the stationary points to be minima or saddle points and to obtain the thermodynamic energy corrections. Single-point energies were calculated with the M06 functionals with the lanl2tz(f) basis set and ECP for iridium and the 6-311++g** basis set for all other atoms. Solvation was modeled with the IEFPCM.

The computed barriers and Gibbs free energies of intermediates are provided in Figure 4. These computed energies are consistent with reaction by pathway B. The barrier for oxidative addition of furan directly to complex 3 to form 7 in pathway A was computed to be 39.4 kcal/mol at 298 K. The energy of this transition state is higher than the experimental value from the kinetic measurements and is much higher than those for each of the steps computed for reaction by pathway B. Consequently, we conclude that the furan adds to 3 by the multistep sequence in pathway B of Figure 4 to form 8, not by the direct addition in pathway A of Figure 4.

The computed barriers for catalyst decomposition to the most stable species 4 (29.2 kcal/mol) and reductive elimination from 8 to release alkylfuran products (28.7 kcal/mol) also are much higher at 298 K than the highest barrier in the olefination process (20.9 kcal/mol). The relative magnitudes of these barriers are consistent with the experimental observation of complex 3 as the resting state and with the trend in relative rates for olefination vs conversion of the catalyst to the more stable allyl complex. Finally, the computed barriers are also consistent with the relative rates for reductive elimination vs β -hydrogen elimination from the alkyliridium complex 8. Thus, all of our experimental and computational studies are consistent with reaction by pathway B of Figure 4.

CONCLUSIONS

In conclusion, we have reported a rare example of the oxidative olefination of furans with unactivated alkenes to form branched vinylfurans in high yields and with high selectivities. Mechanistic studies, including the observation of faster product formation at lower temperatures, led to the development of new ligands that form complexes capable of catalyzing olefination of a wide range of furans under mild conditions. Efforts to extend the scope of this process to arenes are ongoing.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization of all new compounds including NMR spectroscopy data, kinetic studies, and optimization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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