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Iridium-Catalyzed, Intermolecular Hydroetherification of Unactivated Aliphatic Alkenes with Phenols

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Supporting Information

ABSTRACT: Metal-catalyzed addition of an O−H bond to an alkene is a desirable process because it allows for rapid access to ethers from abundant starting materials without the formation of waste, without rearrangements, and with the possibility to control the stereoselectivity. We report the intermolecular, metal-catalyzed addition of phenols to unactivated α-olefins. Mechanistic studies of this rare catalytic reaction revealed a dynamic mixture of resting states that undergo O−H bond oxidative addition and subsequent olefin insertion to form ether products.

Metal-catalyzed hydrofunctionalization of alkenes offers the potential to control the regioselectivity, diastereoselectivity, and enantioselectivity of the addition process and to form products from readily accessible starting materials without the formation of waste. Metal-catalyzed hydrofunctionalizations also could be more tolerant of auxiliary functionality than acid-catalyzed additions and could occur without the rearrangements that are characteristic of acid-catalyzed additions to alkenes. Hydroamination (the addition of a N−H bond across an unsaturated C−C bond) remains one of the most studied transformations in hydrofunctionalization chemistry,[1] but hydroetherification (the addition of an O−H bond across an unsaturated C−C bond) is much less developed.

The ether products of hydroetherification are more often formed by substitution reactions than addition reactions.[2] The electrophiles in substitution reactions are typically prepared by a multistep sequence that includes oxidation or reduction and functional group interconversion or activation of an alcohol. Moreover, these substitution reactions generate salt byproducts. Alternatively, ethers are formed by acid-catalyzed additions of alcohols to alkenes.[3] However, these additions often require strong acids and high temperatures, form side products from isomerization of carbocationic intermediates, and occur without control of the product stereochemistry. Moreover, acid-catalyzed additions of phenols to alkenes occur with competitive reaction of the alkene at the O−H bond and at an ortho or para C−H bond.[4] Metal-catalyzed hydroetherification would exploit the abundance and stability of alkene starting materials and could overcome many of the limitations of the classical syntheses of ethers.

However, current hydroetherification reactions are limited in scope. Most reported metal-catalyzed hydroetherifications of unsaturated C−C bonds are intramolecular and occur with C−C multiple bonds that are more reactive than those of unactivated alkenes.[5] Cationic gold complexes catalyze the cyclization of allenyl alcohols in high yield with excellent ee, but the reactions do not occur intermolecularly or with monoenes.[6] Likewise, Ir, Pd, Pt, and lanthanide complexes catalyze intramolecular additions of alcohols to alkenes and alkynes, but intermolecular additions to alkenes catalyzed by such complexes are unknown.[7] Intermolecular hydroetherification of allenes with both carboxylic acids and phenols to form allylic ethers has been reported to occur in high yield and ee in the presence of a Rh catalyst, but the reactions do not occur with monoenes.[8] Finally, intermolecular additions of alcohols to unstrained, isolated alkenes have been reported to occur in the presence of triflates of coinage metals.[9] In these cases, the reactions form side products that are characteristic of carbocation intermediates.[10]

Here we report intermolecular, metal-catalyzed additions of phenols to unactivated α-olefins in good yields. The measurable enantioselectivity and lack of reaction in the presence of acid but the absence of the metal show that the iridium complex rather than a proton catalyzes the addition reaction. Mechanistic studies imply that the reaction proceeds by reversible oxidative addition of the O−H bond of the phenol followed by turnover-limiting insertion of the alkene.

We previously showed that the combination of iridium and DTBM-Segphos (DTBM = 3,5-di-*tert*-butyl-4-methoxy) catalyzes the additions of amides to alkenes.[11] On the basis of these studies, we tested combinations of $[Ir(coe)_2Cl]_2$ (coe = cyclooctene) with a series of phosphine, bisphosphine, and chelating nitrogen ligands as catalysts for the addition of 3-methoxyphenol to 1-octene [see the Supporting Information (SI) for studies with various ligands]. Only Ir complexes of (*S*)-DTBM-Segphos led to substantial amounts of ether and enol ether products. Further experiments conducted with (*S*)-DTBM-Segphos as the ligand are summarized in Table 1. Isomerization of the terminal alkene to unreactive internal olefin isomers was observed over the course of the reaction; because internal alkenes are less reactive than terminal alkenes, this isomerization limited the conversion of the alkene to the ether. Reactions conducted with $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) as the iridium precursor with a slight excess of bisphosphine relative to Ir occurred with less alkene isomerization and concomitantly greater product yields than reactions conducted with $[Ir(coe)_2Cl]_2$ as the precursor (entry 2 vs 1).

Several experiments provided strong evidence that the reaction is catalyzed by iridium rather than a proton. The

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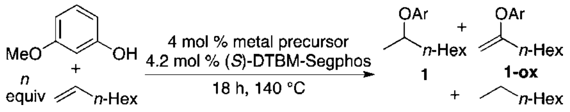
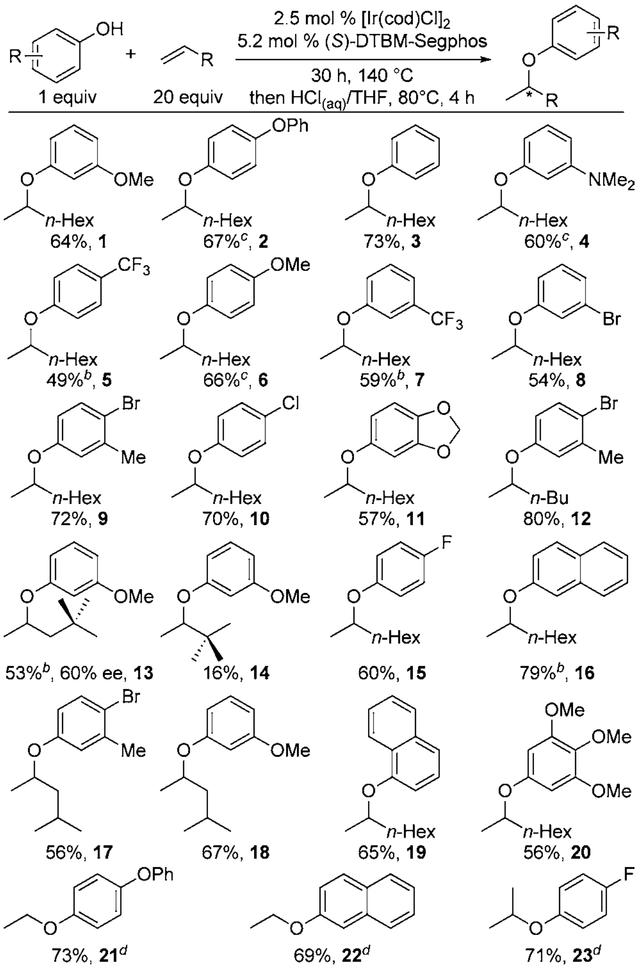
Table 1. Reaction Development for the Ir-Catalyzed Addition of 3-Methoxyphenol to 1-Octene[a]



entry	metal precursor	mol % additive	*n* equiv 1-octene	% 1-octene[b] remaining	% **1**[b]	% **1-ox**[b]
1	$[Ir(coe)_2Cl]_2$	--	10	11	30	4
2	$[Ir(cod)Cl]_2$	--	10	26	46[c]	10
3	--	4% HOTf	10	88	0	0
4	$[Ir(cod)Cl]_2$	17% Bu_3N	10	48	35	6
5	$[Ir(cod)Cl]_2$	4% $AgBF_4$	10	2	68[d]	0
6	$[Ir(cod)_2][BF_4]$	--	10	2	0	0
7	$[Ir(cod)_2][BF_4]$	4% KHMDS	10	5	18	2
8	$[Ir(cod)Cl]_2$	--	5	3	24	5
9	$[Ir(cod)Cl]_2$	--	20	48	60[e]	16
10	$[Ir(cod)Cl]_2$	--	40	64	51[f]	17
11	$[Ir(cod)Cl]_2$	--	80	70	38	20

[a] Reactions were performed with 0.2 mmol of phenol. [b] Determined by GC analysis. [c] 19% ee. [d] 1:1:1 racemic mixture of 2-, 3-, 4-aryloxyoctane. [e] 25% ee. [f] 36% ee.

Chart 1. Ir-Catalyzed Additions of Phenols to α-Olefins[a]



[a] Isolated yields are shown. [b] 40 equiv of alkene relative to ArOH. [c] 10 equiv of alkene relative to ArOH. [d] Conducted in mesitylene solvent.

measurable (albeit modest) enantioselectivity (19–40% ee) rules out alkene hydroetherification catalyzed by a proton alone. No product was detected in reactions conducted in the presence of added HOTf (entry 3), excluding catalysis by a phosphonium salt. When the reaction was conducted with excess Bu_3N relative to iridium (entry 4), which would quench trace acid, the yield was comparable to that in the absence of this additive. Reactions conducted by initial halide abstraction from iridium with $AgBF_4$ led to the formation of a mixture of racemic ether products, consistent with an acid-catalyzed process. Reactions conducted with a cationic Ir precursor and ligand did not yield product (entry 6), but those conducted with a cationic Ir precursor, ligand, and base did form product (entry 7), presumably after generating a neutral Ir complex. A greater fraction of 1-octene versus other isomers was observed for the reaction conducted with 20 equiv of olefin than for reactions conducted with 5 or 10 equiv of olefin and resulted in a 60% yield of **1** (entry 9).

The scope of the Ir-catalyzed addition of phenols to α-olefins using our procedure is summarized in Chart 1. Products containing the phenoxy group at the 2-position of the alkyl chain were formed exclusively with ee's of 8–60%, with the highest values observed for the reactions of alkenes containing steric bulk proximal to the double bond. Upon completion of the reaction, the enol ether products resulting from oxidative etherification of the alkene were hydrolyzed with acid to facilitate isolation of the alkyl aryl ether products. A broad range of functional groups located meta or para to the OH group were compatible with the addition process; the reactions between olefins and phenols containing halides, ethers, and tertiary amines occurred in good yields. Although the reaction of 1-naphthol formed product **19** in good yield, other phenols containing substituents ortho to the OH group did not add to the α-olefin under similar conditions.

The electronic properties of the phenol substituent(s) influenced the reaction conversion and yield. The yields of electron-poor phenols typically were lower than those for electron-rich phenols because a greater amount of alkene isomerization occurred during the reactions of the electron-poor phenols. Complete isomerization of the terminal alkene was observed after 24 h for reactions of 4-CF_3-phenol, while only half of the terminal alkene isomerized during reactions of 4-OMe-phenol. Consequently, reactions of electron-rich phenols conducted with 10 equiv of olefin, rather than 20 equiv as used for a majority of the reactions, formed the addition products in good yields.

The alkene scope of the reaction was also examined. Addition products were not detected from reactions of phenols with olefins containing activated allylic C−H bonds, such as allylbenzene, under our conditions. Rapid isomerization of these terminal alkenes occurred. Alkenes with steric bulk in close proximity to the double bond reacted more slowly than alkenes lacking this property. For example, the reaction of 3,3-dimethyl-1-butene gave **14** in low yield. However, 4,4-dimethyl-1-pentene and 4-methyl-1-pentene did form products **13**, **17**, and **18** in substantial yields. The reactions of phenols with ethylene and propene occurred at an alkene pressure of only 2.5 atm to form ether and enol ether products. Catalyst decomposition was observed upon accumulation of the enol ether during the reactions with ethylene. Nonetheless, the yields of the reactions with these alkenes were higher than those with longer-chain olefins because alkene isomers could not form.

Mechanistic studies were conducted to gain insight into the elementary steps of this unusual process. Kinetic analysis of the addition of 4-fluorophenol to propene was conducted. Initial rates (to 15% conversion) were measured by ^{19}F NMR spectroscopy (see the SI). The reaction was found to be first order in catalyst, zeroth order in alkene, and 0.6 order in 4-fluorophenol.

Monitoring of the reactions by ^{31}P NMR spectroscopy indicated that an unsymmetrical bisphosphine complex persisted throughout the course of the reaction (Figure 1a, spectrum V).

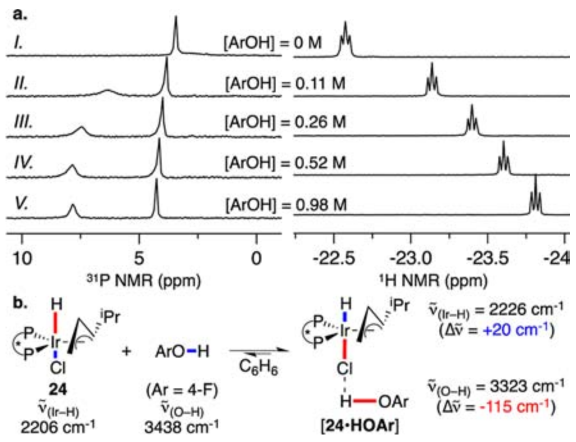


Figure 1. (a) ^{31}P (left) and ^{1}H (right, Ir−H region only) NMR spectra of **24** in the presence of varying concentrations of 4-fluorophenol at 294 K. (b) IR stretching frequencies of the Ir−H and O−H bonds of **24**, free 4-fluorophenol, and [**24**·HOAr].

This observed species was characterized to allow interpretation of the kinetic data. The oxidative addition of O−H bonds to Ir(I) is well-established.[12] However, the addition of 4-fluorophenol to a solution of $[\mathrm{Ir(cod)Cl}]_2$ and DTBM-Segphos in benzene did not form any new species. In contrast, the combination of Ir, ligand, and olefin in the absence of alcohol did react; the original orange solution turned light yellow in 1 h at 294 K. A similar color change was observed at the start of the catalytic reaction. The product of this reaction was shown by NMR spectroscopy to be Ir(allyl)hydride complex **24** (Figure 1a). The hydride and phosphorus NMR resonances of isolated **24** in C_6D_6 (spectra I) did not match those of the species in the catalytic reaction (spectra V). However, the hydride chemical shift in the ^{1}H NMR spectra of solutions of **24** containing various concentrations of 4-fluorophenol (spectra II−V) depended on the phenol concentration, and the ^{1}H and ^{31}P NMR spectra of the solution containing alcohol at a concentration of 1 M matched those of the complex observed in the catalytic reactions (spectra V).

The interaction of the phenol with **24** was investigated by nuclear Overhauser effect NMR spectroscopy (NOESY) and IR spectroscopy (Figure 1b). Metal hydride complexes are known to be hydrogen-bond acceptors. NOE correlations between metal hydrides and alcoholic protons as well as a reduced metal−hydride IR stretching frequency in the presence of an alcohol are commonly observed for systems containing these hydrogen-bonding interactions.[13] In contrast to these characteristics of a M−H·HX interaction, no NOE was observed between the Ir−H resonance of **24** and the OH resonance of 4-fluorophenol. In addition, the IR stretching frequency of the Ir−H bond of **24** in the presence of 1 M 4-fluorophenol was 2226 cm^{-1}, which is 20 cm^{-1} *higher* than in the absence of alcohol, while the O−H stretching frequency of the phenol was 3323 cm^{-1}, which is 115 cm^{-1} lower than in the absence of **24**. These data suggest that the hydrogen-bond acceptor in the [**24**·HOAr] complex is a ligand other than the hydride. The remaining likely hydrogen-bond acceptor in the coordination sphere of **1** is the chloride ligand (Figure 1b). We suggest that the reduced electron donation by the hydrogen-bonded chloride ligand strengthens the Ir−H bond trans to the chloride, accounting for the observed increase in the Ir−H stretching frequency.

The fractions of **24** and [**24**·HOAr] ($\chi_{\mathbf{24}}$ and $\chi_{[\mathbf{24}\cdot\mathrm{HOAr}]}$, respectively) were determined by ^{1}H NMR spectroscopy, and their ratio was consistent with the order of the reaction in phenol. The observed resonance in the Ir−H region of the ^{1}H NMR spectrum (δ_{obs}) is the sum of the fractional contributions of the absolute Ir−H chemical shifts of **24** and [**24**·HOAr] (eq 1). The equilibrium concentrations of the two complexes were determined by measuring δ_{obs} as a function of the concentration of 4-fluorophenol (Figure 2). The value of K_{eq} obtained by fitting the data to eq 2 is 4.4 M^{-1}, and the Ir−H of [**24**·HOAr] resonates at −24.1 ppm. Van't Hoff analysis of the equilibrium constants determined by conducting this experiment at temperatures from 294 to 335 K (see the SI) revealed the following thermodynamic parameters for the equilibrium: $\Delta H^{\circ}_{\mathrm{eq}} = -1.9$ kcal/mol and $\Delta S^{\circ}_{\mathrm{eq}} = -3.5$ eu.[14] From these values, a K_{eq} value of 1.6 M^{-1} at the reaction temperature of 140 °C was calculated; this value of K_{eq} corresponds to a **24**:[**24**·HOAr] ratio of 40:60. Having significant concentrations of both complexes is consistent with the measured fractional order of 0.6 with respect to 4-fluorophenol for the catalytic addition.

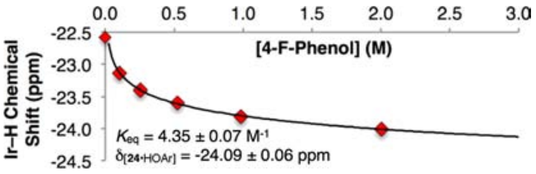


Figure 2. Observed Ir−H chemical shift as a function of 4-fluorophenol concentration in C_6D_6 at 294 K. The black curve is the fit to eq 2.

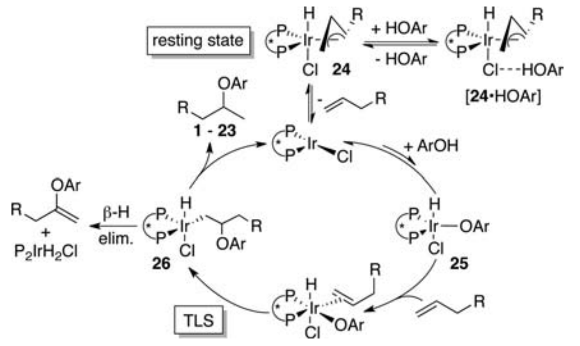
$$\delta_{\mathrm{obs}} = \delta_{\mathbf{24}}\chi_{\mathbf{24}} + \delta_{[\mathbf{24}\cdot\mathrm{HOAr}]}\chi_{[\mathbf{24}\cdot\mathrm{HOAr}]} \tag{1}$$

$$\delta_{\mathrm{obs}} = \frac{\delta_{\mathbf{24}} + \delta_{[\mathbf{24}\cdot\mathrm{HOAr}]}K_{\mathrm{eq}}[\mathrm{ArOH}]_0}{1 + K_{\mathrm{eq}}[\mathrm{ArOH}]_0} \tag{2}$$

A comparison of the initial rates for the addition of 4-fluorophenol and O-deuterated 4-fluorophenol to propene in separate vessels revealed a kinetic isotope effect (KIE) of 1.6. Although greater than unity, this KIE is likely too small to be consistent with turnover-limiting protonolysis or oxidative addition of the O−H bond[6d] but would be consistent with reversible oxidative addition of the alcohol O−H bond to the Ir center prior to a turnover-limiting step. In this case, the product of oxidative addition would be less stable than the catalyst resting state. This conclusion is consistent with the lack of O−H addition product from the reaction of DTBM-Segphos, $[\mathrm{Ir(coe)_2Cl}]_2$, and 4-fluorophenol.

These mechanistic data are consistent with the proposed catalytic cycle shown in Scheme 1. In this mechanism, the (allyl) iridium hydride resting state **24**, which equilibrates with hydrogen-bonded [**24**·HOAr], undergoes C−H bond-forming reductive elimination to release the olefin and form an Ir(I) complex that can undergo reversible, endergonic oxidative addition of the O−H bond of the phenol to form **25**. Subsequent olefin coordination and turnover-limiting insertion into the Ir−O bond forms an alkyl-Ir complex **26**. C−H bond-forming reductive elimination would then release the ether product, whereas β-H elimination from the same intermediate would form the enol ether side product. This mechanism is consistent with

Scheme 1. Proposed Catalytic Cycle



the observed zeroth-order dependence of the rate on the concentration of alkene because the alkene is released and added prior to the turnover-limiting step. This mechanism is also consistent with the fractional-order dependence with respect to the alcohol because a significant fraction of the resting state exists as the alcohol adduct [**24**·HOAr]. The alcohol dissociates and adds prior to the turnover-limiting step of a reaction initiated from [**24**·HOAr].

Several aspects of this mechanism are distinct from those for addition of the N−H bonds of amides to alkenes catalyzed by the combination of $[Ir(coe)_2Cl]_2$ and Segphos.[11] The product of oxidative addition of the amide is the resting state of the catalyst in the hydroamidations of alkenes; the open coordination site of the $L_2IrCl(H)(amide)$ complex formed by oxidative addition is occupied by a second amide. The system for the catalytic additions of phenols lacks a basic component, making the stable 18-electron Ir(III) complex in the system the allyl hydride complex **24** and its phenol adduct [**24**·HOAr]. Consequently, isomerization of the alkene occurs faster during the Ir-catalyzed additions of phenols to alkenes than during the additions of amides to alkenes.

In summary, we have reported a rare example of a metal-catalyzed intermolecular addition of an alcohol to an unactivated alkene. The lack of products from rearrangements and addition of the ortho C−H bond, the measurable enantiomeric excess, the absence of product from phosphonium salts, the lack of an effect of added tertiary alkylamine, and kinetic data that are consistent with the observed species show that the reaction is not purely acid-catalyzed. Instead, it likely occurs by generation of an Ir(I) intermediate via reductive elimination of the observed allyliridium hydride species, followed by reversible O−H bond oxidative addition, turnover-limiting olefin insertion, and product-releasing reductive elimination. Efforts to mitigate olefin isomerization and increase the enantioselectivity of the reaction are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures and additional 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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■ REFERENCES

(1) (a) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795. (b) Hannedouche, J.; Schulz, E. *Chem.—Eur. J.* **2013**, *19*, 4972.

(2) (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 4545. (b) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (c) López, F.; Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 3426. (d) Beletskaya, I. P.; Cheprakov, A. V. *Coord. Chem. Rev.* **2004**, *248*, 2337. (e) Onitsuka, K.; Okuda, H.; Sasai, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1454.

(3) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; p 996.

(4) (a) Ronchin, L.; Quartarone, G.; Vavasori, A. *J. Mol. Catal. A: Chem.* **2012**, *353*, 192. (b) Ronchin, L.; Vavasori, A.; Toniolo, L. *J. Mol. Catal. A: Chem.* **2012**, *355*, 134.

(5) Hintermann, L. *Top. Organomet. Chem.* **2010**, *31*, 123.

(6) (a) Hamilton, G. L.; Kang, E. J.; Mba, M.; Toste, F. D. *Science* **2007**, *317*, 496. (b) Zhang, Z. B.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 283. (c) Wang, Z. J.; Brown, C. J.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 7358. (d) Brown, T. J.; Weber, D.; Gagné, M. R.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2012**, *134*, 9134. (e) Butler, K. L.; Tragni, M.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 5175.

(7) (a) Qian, H.; Han, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 9536. (b) Li, X.; Chianese, A. R.; Vogel, T.; Crabtree, R. H. *Org. Lett.* **2005**, *7*, 5437. (c) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270. (d) Messerle, B. A.; Vuong, K. Q. *Organometallics* **2007**, *26*, 3031. (e) Yu, X.; Seo, S.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7244. (f) Seo, S. Y.; Yu, X. H.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 263. (g) Weiss, C. J.; Marks, T. J. *Dalton Trans.* **2010**, *39*, 6576. (h) Atesin, A. C.; Ray, N. A.; Stair, P. C.; Marks, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 14682.

(8) (a) Kim, I. S.; Krische, M. J. *Org. Lett.* **2008**, *10*, 513. (b) Kawamoto, T.; Hirabayashi, S.; Guo, X.-X.; Nishimura, T.; Hayashi, T. *Chem. Commun.* **2009**, 3528. (c) Koschker, P.; Lumbroso, A.; Breit, B. *J. Am. Chem. Soc.* **2011**, *133*, 20746.

(9) (a) Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2005**, *127*, 6966. (b) Yang, C.-G.; Reich, N. W.; Shi, Z.; He, C. *Org. Lett.* **2005**, *7*, 4553. (c) Hirai, T.; Hamasaki, A.; Nakamura, A.; Tokunaga, M. *Org. Lett.* **2009**, *11*, 5510.

(10) For a discussion of the parallels between intermolecular O−H bond additions to unactivated alkenes catalyzed by metal triflates and Brønsted acids, see: (a) Li, Z.; Zhang, J.; Brouwer, C.; Yang, C.-G.; Reich, N. W.; He, C. *Org. Lett.* **2006**, *8*, 4175. (b) Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. *Org. Lett.* **2006**, *8*, 4179.

(11) Sevov, C. S.; Zhou, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 11960.

(12) (a) Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681. (b) Blum, O.; Milstein, D. *J. Organomet. Chem.* **2000**, *593−594*, 479. (c) Dorta, R.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *124*, 188. (d) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **2002**, *124*, 11456. (e) Schaub, T.; Diskin-Posner, Y.; Radius, U.; Milstein, D. *Inorg. Chem.* **2008**, *47*, 6502.

(13) (a) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429. (b) Lee, J. C.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.

(14) The small negative value of ΔS°_{eq} is consistent with an equilibrium between a self-associated phenol and [**24**·HOAr], as would be expected in the nonpolar organic solvent benzene.