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Study of Intermediates in Iridium−(Phosphoramidite,Olefin)-Catalyzed Enantioselective Allylic Substitution

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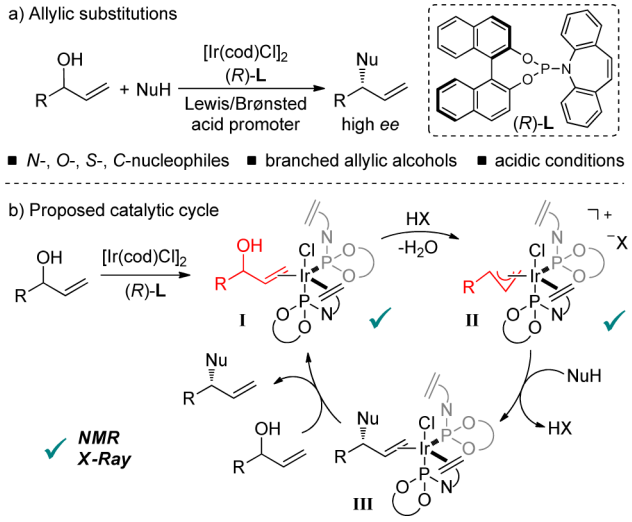
Supporting Information

ABSTRACT: Experimental mechanistic studies of iridium-catalyzed, enantioselective allylic substitution enabled by (phosphoramidite,olefin) ligands are reported. (η^2-Allylic alcohol)iridium(I) and (η^3-allyl)iridium(III) complexes were synthesized and characterized by NMR spectroscopy as well as X-ray crystallography. The substrate complexes are catalytically and kinetically competent to be intermediates in allylic substitutions of branched, racemic allylic alcohols with various nucleophiles. In addition, we have identified an off-cycle pathway involving reversible binding of molecular oxygen to iridium, which contributes to the air tolerance of the catalyst system.

Iridium-catalyzed allylic substitutions have emerged as versatile methods for the enantioselective formation of carbon−carbon and carbon−heteroatom bonds.[1] These processes are characterized by preferential attack of nucleophiles at the more substituted terminus of unsymmetrical allylic electrophiles, complementing the regioselectivity generally observed with palladium.[2] Following Takeuchi's[3] and Helmchen's[4] seminal reports on iridium-catalyzed allylic substitution in 1997, a variety of chiral ligands have been shown to induce enantiocontrol.[5] The best-studied catalyst system, however, relies on Feringa's phosphoramidites,[5f] the use of which in iridium-catalyzed allylic amination was first described by Hartwig.[6] This catalyst system typically employs linear allylic carbonates as substrates along with iridacyclic catalysts[7] and operates under alkaline conditions.[8]

Our laboratory has been studying and developing iridium catalysts derived from (phosphoramidite,olefin) ligand **L**, which allows direct enantio- and regioselective substitution of easily accessible branched, racemic allyl alcohols in the presence of a variety of acid promoters (Scheme 1a).[9] The iridium−**L** catalyst system is remarkably tolerant of oxygen and water, enabling operationally simple execution. While the mechanisms by which the iridacyclic complexes of Hartwig and Helmchen operate have been studied in detail,[10−12] no such experimental studies have been reported to date for the Ir−(P,olefin) system. However, Sunoj has recently disclosed a detailed computational study.[13] Herein we report the isolation and characterization of (η^2-allylic alcohol)iridium(I) and (η^3-allyl)iridium(III) complexes and demonstrate their competence as intermediates in a variety of catalytic reactions, giving products in yields and selectivities that match those observed for the in situ-generated catalyst originally reported.

Scheme 1. Ir−(P,olefin)-Catalyzed Allylic Substitutions



Previous studies have established the mechanism of allylic substitutions with a variety of palladium[2] and iridium[10−12] catalysts. In light of this precedent, our own studies were guided by the proposed catalytic cycle shown in Scheme 1b. Accordingly, coordination of allylic alcohol to iridium gives η^2 complex **I**, which undergoes acid-promoted oxidative addition to furnish (η^3-allyl)iridium(III) species **II**. Nucleophilic attack on the allyl fragment affords product complex **III**, and subsequent displacement of the product by allylic alcohol completes the catalytic cycle.

We first set out to examine whether adducts of allylic alcohols, iridium, and ligand **L**, such as substrate complex **I**, could be formed and spectroscopically observed. We found that combining 2 equiv of (*R*)-**1**, 0.5 equiv of $[Ir(cod)Cl]_2$, and 2 equiv of ligand (*R*)-**L** led to a well-defined species in solution as determined by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). Its characterization was facilitated by removal of the released 1,5-cyclooctadiene and uncomplexed (*R*)-**1**. Precipitation with pentane gave a powder whose $^{31}P\{^1H\}$ NMR spectrum displayed the same signals as observed in the initial experiment. The formation of (η^2-allylic alcohol)iridium(I) complex (*R*,*R*,*R*)-**2** was evidenced by two doublets in the $^{31}P\{^1H\}$ NMR spectrum at δ = 114.1 and 106.4 ppm ($^2J_{P-P}$ = 27.1 Hz), indicating two inequivalent phosphorus donors at the iridium center. In particular, the upfield shifts of the vinyl protons in the ^1H

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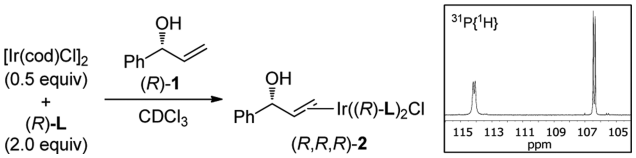
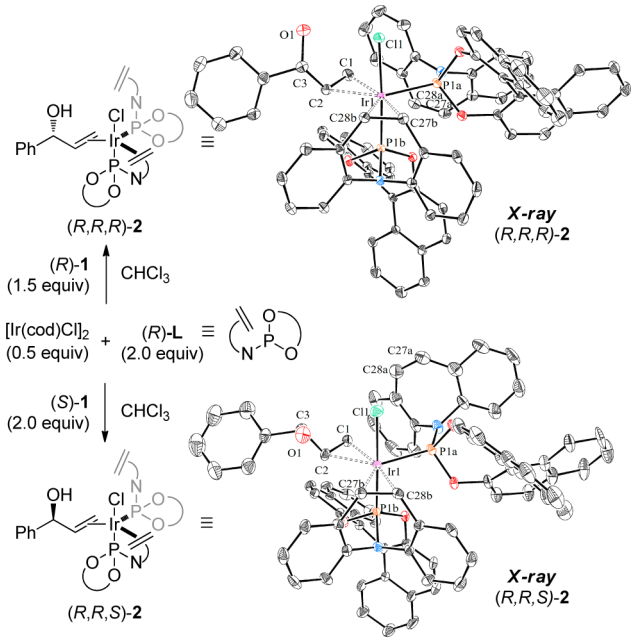
Scheme 2. NMR Experiment Showing Coordination of Allyl Alcohol (*R*)-1 to Iridium



NMR spectrum (δ = 3.53, 2.35, and 1.66 ppm) provide evidence for η^2 coordination of the terminal olefin in (*R*)-**1** to iridium. Consistent with the η^2 hapticity for (*R*)-**1**, the ^{13}C NMR spectrum displayed upfield resonances for the olefinic carbons (δ = 63.8 and 28.5 ppm).

The solid-state structure of (*R*,*R*,*R*)-**2** confirmed the NMR assignment and revealed coordination of one phosphoramidite ligand in bidentate (η^2-κP) fashion, whereas the other (P,olefin) ligand is bound solely through phosphorus (Scheme 3).

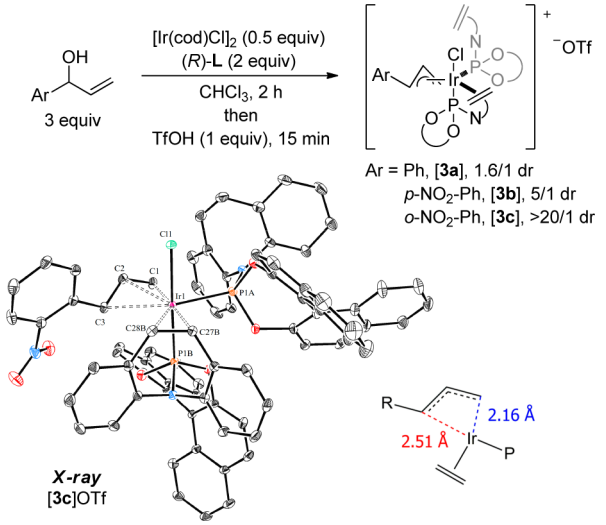
Scheme 3. Synthesis and X-ray Structures of (η^2-Allylic alcohol)iridium(I) Complexes (*R*,*R*,*R*)-2 and (*R*,*R*,*S*)-2[15]



Complex (*R*,*R*,*R*)-**2** adopts a distorted trigonal bipyramidal geometry in which the equatorial loci are occupied by the terminal olefin of (*R*)-**1**, P1A, and the olefin of the chelating phosphoramidite ligand; P1B and chloride reside in the axial positions. The bond of the equatorial phosphorus to iridium (Ir1−P1A, 2.3272(9) Å) is longer than that of the axial P (Ir1−P1B, 2.1917(9) Å). The coordinated olefin of the ligand (C27B−C28B, 1.425(5) Å) and that of the allyl alcohol (C1−C2, 1.425(6) Å) are elongated compared with those of the uncoordinated olefin (C27A−C28A, 1.338(6) Å) and free ligand (*R*)-**L** (C23−C32, 1.350(11) Å; Figure S14), indicating significant back-bonding. Interestingly, the dibenzazepine nitrogen atom undergoes a hybridization change from sp^2 in the monodentate ligand to sp^3 in the bidentate ligand.[14] The diastereomeric complex (*R*,*R*,*S*)-**2** was prepared analogously from allyl alcohol (*S*)-**1**. The spectroscopic features of (*R*,*R*,*S*)-**2** are similar to those of complex (*R*,*R*,*R*)-**2**, and its solid-state structure is also a distorted trigonal bipyramid (Scheme 3). The main structural differences compared with its diastereomer are the orientation of the azepine moiety and the spatial disposition of the allylic alcohol C−O bond in relation to the substrate olefin (C1−C2−C3−O1, 3.4(5)° in (*R*,*R*,*R*)-**2** vs −127.0(7)° in (*R*,*R*,*S*)-**2**). Notably, the solid-state structures of (*R*,*R*,*R*)-**2** and (*R*,*R*,*S*)-**2** closely resemble the lowest-energy structures of the allylic alcohol complexes predicted by Sunoj's computational study.[13]

We then examined the reactions of the allylic alcohol complexes with acid on the premise that (η^3-allyl)iridium(III) complexes might be formed and observed. Following treatment of (*R*,*R*,*R*)-**2** in $CDCl_3$ with triflic acid, two new species were observed in a 1.6/1 ratio by $^{31}P\{^1H\}$ NMR spectroscopy (δ = 105.4 and 66.5 ppm ($^2J_{P-P}$ = 31.6 Hz); δ = 101.9 and 69.9 ppm ($^2J_{P-P}$ = 25.0 Hz)), and HRMS analysis showed a major peak at *m*/*z* 1359.2788, corresponding to $[M]^+$ of the allyl complex. We suspected that the novel species were two diastereomeric *endo*- and *exo*-(η^3-allyl)iridium(III) complexes. Remarkably, treatment of (*R*,*R*,*S*)-**2** with acid also led to the same two diastereomers in identical ratio. Thus, either enantiomer of the allylic alcohol leads to the same mixture of (η^3-allyl)iridium(III) species. If oxidative addition proceeds with inversion of configuration, our observations are consistent with rapid isomerization of the two diastereomeric allyl complexes.[16] The (η^3-allyl)iridium(III) complexes could also be synthesized directly without prior isolation of (η^2-allylic alcohol)iridium(I) intermediates, as shown in Scheme 4. This procedure enabled the synthesis of several (η^3-allyl)iridium(III) complexes bearing various allyl groups.

Scheme 4. Synthesis of (η^3-Allyl)iridium(III) Complexes and X-ray Structure of [3c]OTf[15]



The putative *endo*/*exo* ratio in these was dependent on the electronic and steric properties of the arene substituents. Thus, the *o*-nitro substrate formed complex [**3c**]OTf as a single diastereomer (>20/1 dr) as indicated by $^{31}P\{^1H\}$ NMR analysis (δ = 104.7 and 62.1 ppm ($^2J_{P-P}$ = 32.2 Hz)). The ^{13}C NMR spectrum of [**3c**]OTf displayed the resonance belonging to the terminal CH_2 of the allyl group at δ = 33.0 ppm, providing evidence against a σ-bound allyl Ir−CH_2 moiety since these typically appear at lower chemical shifts.[17] After several unsuccessful attempts to crystallize enantiomerically pure [**3c**]OTf, crystals suitable for X-ray diffraction were grown from the racemate obtained by mixing [**3c**]OTf and its

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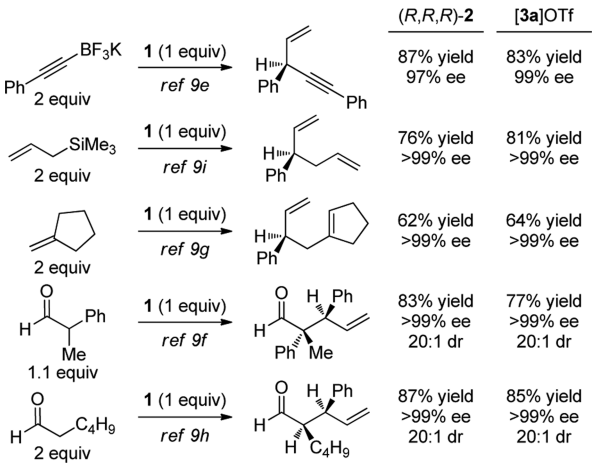
enantiomer in equimolar amounts.[18] The solid-state structure of [**3c**]OTf is shown in Scheme 4 and allowed assignment of the major diastereomer as *exo*-[**3c**]OTf. $^{31}P-^{1}H$ HOESY and $^{31}P-^{1}H$ COSY experiments confirmed the *exo* configuration as the major diastereomer in solution (Figure S5).[19] It is important to note that outer-sphere attack on this intermediate would lead to the minor product enantiomer. Thus, the high enantioselectivities observed would be explained either by isomerization prior to nucleophilic attack or an inner-sphere mechanism. Additional experiments will be required to determine the detailed course of events. Complex [**3c**]OTf adopts a severely distorted six-coordinate octahedral geometry with the allyl group, the phosphorus atom of the nonchelating **L**, and the olefin of the chelating **L** in one plane. The phosphorus atom of the chelating ligand and the chloride lie apically with respect to this plane. The bond from the benzylic carbon of the allyl fragment to iridium is 0.35 Å longer than that from the terminal carbon (Ir1−C1, 2.161(3) Å; Ir1−C3, 2.508(3) Å). Such a difference is unusually large for it to be attributed solely to the trans influence of the phosphoramidite and olefin ligands.[20] Considering the spatial environment about the iridium, the elongated bond may also stem from an allyl plane deflection due to steric hindrance between the allyl's arene fragment and the ligand's azepine moiety. Although the terminus with the longer metal−carbon bond has been proposed to be more electrophilic,[21] Hartwig's recent studies have established that Ir−C bond lengths do not govern regioselectivity in allylic substitutions involving triphenylphosphite as a ligand.[10g] Additional data will therefore be needed to clarify the influence of Ir−C bond lengths on the regioselectivity of the (P,olefin) catalyst system.

To evaluate the catalytic competence of the isolated complexes, (*R,R,R*)-**2** and [**3a**]OTf were employed as catalysts in a number of our published methods, as shown in Scheme 5.

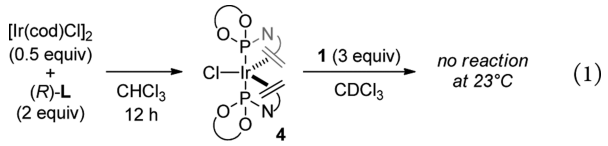
Scheme 5. Allylic Substitution Reactions Catalyzed by (*R,R,R*)-2 and [3a]OTf[a]



[a](*R,R,R*)-**2** and [**3a**]OTf were employed as catalysts with the reported catalyst loadings. See the Supporting Information for experimental details.

The yields and selectivities observed with the isolated complexes as catalysts match our previous observations,[9] establishing that (*R,R,R*)-**2** and [**3a**]OTf are catalytically competent in a broad range of reactions. Furthermore, the allylation of **1** with allyltrimethylsilane was monitored, establishing the kinetic competence of (*R,R,R*)-**2** and [**3a**]OTf to be intermediates in the catalytic cycle (Figure S8).

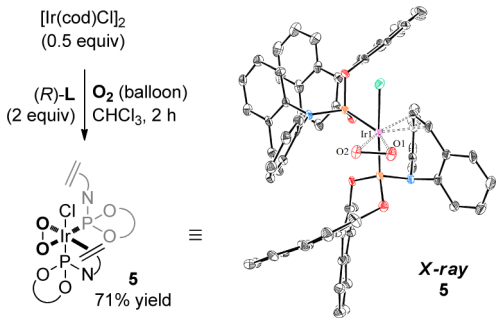
When allylation experiments were monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy, a singlet resonance at δ = 141.1 ppm indicated the presence of a minor species. The same species had also been observed to slowly form upon dissolution of (η^2-allylic alcohol)iridium(I) complexes in the absence of substrate to function as an additional ligand. Indeed, the complex associated with this resonance was synthesized independently from $[Ir(cod)Cl]_2$ and 2 equiv of (*R*)-**L** and was identified as **4**, in which both ligands bind in bidentate fashion (eq 1; the solid-state structure of **4** is shown in Figure S12).[22]



Importantly, treatment of complex **4** with an excess of allylic alcohol **1** in $CDCl_3$ did not lead to formation of the allylic alcohol complexes **2** at room temperature (eq 1). This observation indicates that the allylic alcohol substrate does not displace the olefin of the iminostilbene portion of the ligand in **4**. In our published procedures,[9] $[Ir(cod)Cl]_2$ and ligand **L** are combined in solvent and stirred for 15 min prior to addition of allylic alcohol and nucleophile. An important corollary of the above observation is that when the reactions are conducted with in situ-generated catalyst, it is best to include substrate from the outset (Figure S8) in order to avoid slow formation of **4** (Figure S7).

The Ir/(*R*)-**L** catalyst system is remarkably tolerant of oxygen and moisture. Indeed, some reactions can be carried out in mixed organic−aqueous media,[9d] and generally no special precautions are needed to exclude air. In this regard, we were curious to examine the effect of oxygen on the catalyst system. Stirring a solution of 0.5 equiv of $[Ir(cod)Cl]_2$ and 2 equiv of (*R*)-**L** in $CHCl_3$ saturated with oxygen followed by precipitation with Et_2O gave a solid, which we characterized as oxygen adduct complex **5** on the basis of analysis by NMR spectroscopy and X-ray diffraction (Scheme 6). The solid-state structure of complex **5**

Scheme 6. Synthesis and X-ray Structure of 5[15]



revealed side-on binding of dioxygen in which the two oxygen atoms are approximately equidistant to iridium (Ir1−O1, 2.027(6) Å; Ir1−O2, 2.028(6) Å). The average O−O distance of 1.465(8) Å, while longer than that in O_2 (1.21 Å), is comparable to that in the oxygen adduct of Vaska's complex (1.47 Å)[23] and corresponds closely to that in O_2^{2-} (1.49 Å).[24] Accordingly, the iridium center in **5** can be described as six-coordinate with a formal oxidation state of III.

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Reversible binding of molecular oxygen to low-valent iridium complexes has been known since Vaska's pioneering studies,[25] and treatment of **5** with allyl alcohol *rac*-**1** (15 equiv) in $CDCl_3$ indeed resulted in the formation of a 1:1 mixture of **2** and **5**. Furthermore, complex **5** also catalyzed the allylation of **1** with allyltrimethylsilane at a decreased rate (Figure S8). This experiment underscores the robustness of the catalyst system, since iridium can re-enter the catalytic cycle upon oxygen dissociation.

In summary, we have isolated and characterized key complexes relevant to the catalytic cycle of iridium-catalyzed allylic substitution involving (P,olefin) ligand **L**, including substrate–iridium complexes, namely, (η^2-allylic alcohol)iridium(I) and (η^3-allyl)iridium(III). Two practical consequences emanate from this work: the catalyst is optimally prepared in situ in the presence of allyl alcohol, and the robustness of the iridium catalyst system stems in part from reversible dioxygen binding. These results form the basis of in-depth studies currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12421.

Experimental procedures and characterization data (PDF)
Crystallographic data for (*R*,*R*,*R*)-**2**, (*R*,*R*,*S*)-**2**, [**3c**]OTf, **4**, **5**, and (*R*)-**L** (CIF)

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Notes

The authors declare no competing financial interest.

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(19) Crystals of [**3c**]OTf were dissolved at −78 °C in CD_2Cl_2, and an NMR spectrum was acquired at −70 °C. The spectrum matches the low-temperature NMR spectrum of amorphous [**3c**]OTf (Figure S4).

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