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Site-Selective Alkyl Dehydrogenation of a Coordinated Acylphosphine Ligand

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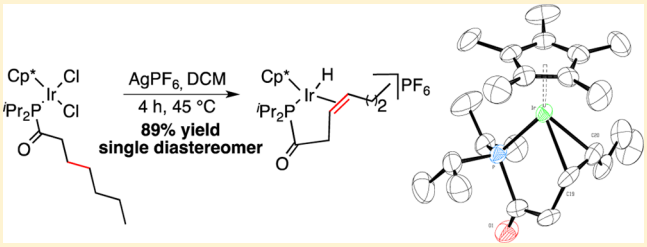
Supporting Information

ABSTRACT: Regio- and stereoselective alkane dehydrogenation is a difficult challenge in organometallic chemistry. Intermolecular reactions of this type typically produce numerous olefin stereo- and regioisomers. Herein, we report our initial investigations into the intramolecular dehydrogenation of a datively bound alkyl ligand, demonstrating the first example of a site-selective dehydrogenation of an unactivated acyclic alkyl group. The alkyl group is located on an acylphosphine ligand that is coordinated to a Cp^*IrCl_2 monomer. A mechanistic proposal, guided by the isolation of a dimeric iridium complex and supported by computational results, is also described.



INTRODUCTION

Achieving selectivity in the preparation of organic molecules is one of the many challenges facing synthetic chemists. To meet the challenge of developing selective C−H activation reactions, many groups have prepared exquisite metal complexes wherein selectivity is controlled via the ancillary ligands on the metal center.[1−8] The genesis of this selectivity can also emanate from substrate-controlled reactions, which are also mediated by a metal complex. Much of this selectivity has revolved around allylic[9−11] or aromatic C−H bonds.[12,13] Selectivity in reactions of acyclic alkanes is more challenging to achieve because of the lack of inherent functionality and the high temperatures typically required to activate sp^3 C−H bonds.[14]

Another challenge in organic chemistry is that of employing renewable resource materials in the synthesis of platform chemicals. Biomass provides excellent sources of carbohydrates, lignin, and fatty acids; however, most research programs focus on the conversion of carbohydrates or lignin to value-added chemicals. Fatty acids are likely avoided because of their lack of initial functionality and the difficulty to activate C−H bonds in a selective fashion. We hypothesized that we could develop a site-selective dehydrogenation of unactivated alkyl groups by employing modified fatty acids that are able to covalently bind to the metal center and allow the formation of a single alkene. Not only would a successful reaction prove that the site-selective dehydrogenation of an unactivated acyclic alkane is possible, but it would also promote the use of renewable resource materials in chemical synthesis.

Most dehydrogenation studies involving alkanes focus on intermolecular processes. Despite the development of a multitude of efficient catalysts,[15−18] there are no reports of a truly site-selective system that does not produce isomeric products. Rather than focus on the intermolecular reaction, we explored employing directing groups to attain selectivity in intramolecular alkyl dehydrogenations. The use of directing groups to assist in intramolecular alkane dehydrogenations is not a new concept.[19] Numerous metal complexes have been shown to activate a C−H bond on a coordinated ligand, and this C−H activation event typically leads to a stable, cyclometalated complex. Other C−H activation events that do not stop at the cyclometalated complex are less prominent. Results from a number of laboratories that have reported this chemistry are shown in Chart 1.[20−31]

The examples in Chart 1 represent a range of complexes that have undergone alkane or cycloalkane dehydrogenation of a coordinated ligand. Most of these ligands are strongly basic and sterically hindered. The steric bulk crowding the metal center situates the C−H bond closer to the metal so activation of the inert bond is more facile.[32] *More importantly, these examples illustrate that the only reported intramolecular acyclic desaturations are alkyl groups that do not have any potential selectivity issues, as any C−H bond will provide the same complex.* A single intermolecular example by Arndtsen and Bergman reported the selective dehydrogenation of pentane to 1-pentene.[33]

RESULTS AND DISCUSSION

Rather than employ highly basic ligands, the lesser known acylphosphines were employed as ligands.[34] Initially, we thought to employ less basic ligands so that the coordinated ligand and olefin would be easier to exchange with an additional ligand and, hence, allow the possibility for catalyst turnover. We were intrigued by the limited employment of these types of ligands in transition metal catalysis, as well as the ability to directly incorporate fatty acids as starting materials to prepare the ligand. Ligand preparation was facile, starting from the

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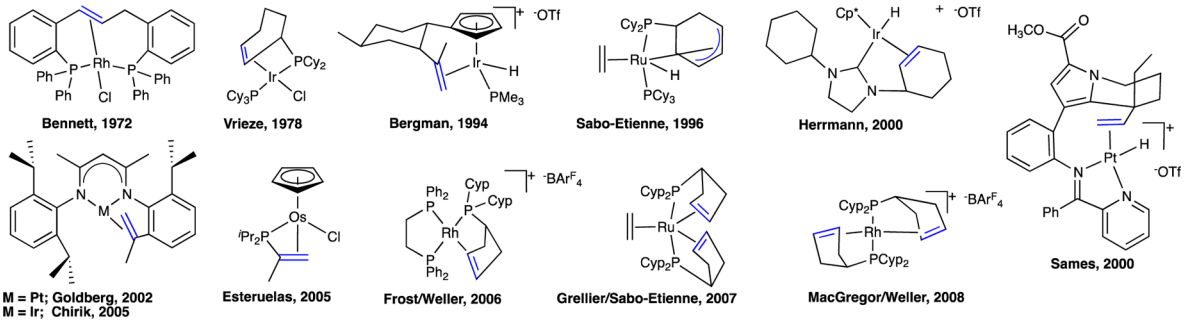
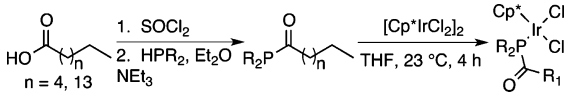
Chart 1. Previous Examples of Intramolecular Alkane Dehydrogenation Reactions



corresponding saturated carboxylic acids (**1**–**5**) (Scheme 1). Because of the lack of basicity in the phosphine, the electron-rich Cp* (1,2,3,4,5-pentamethylcyclopentadienyl) ligand was chosen to provide electron density to the complex. Reaction of the corresponding acylphosphine with $[Cp^*IrCl_2]_2$ provided the desired complexes (**6**–**10**) in excellent yields.

Scheme 1. Preparation of Acylphosphines and Corresponding Complexes

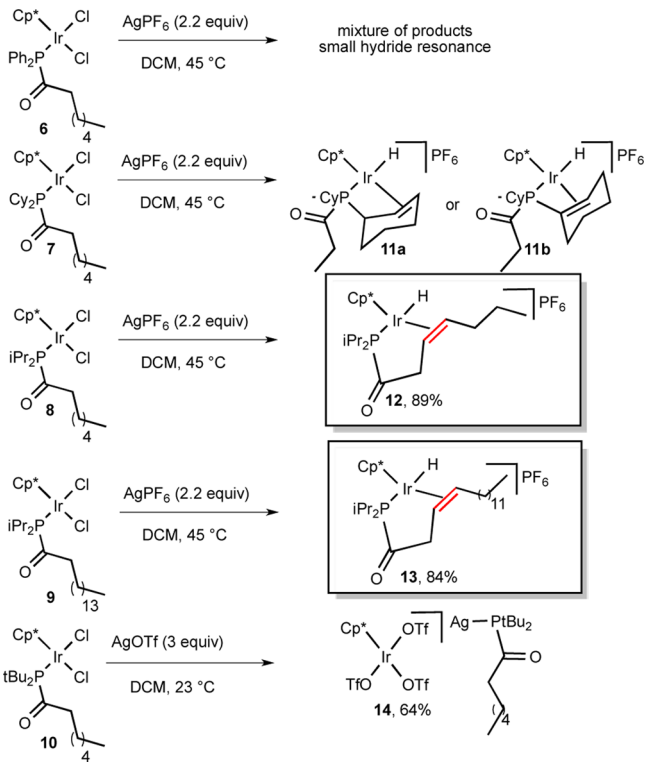


1; R = Ph; n = 4; 97% y.
2; R = Cy; n = 4; 93% y.
3; R = iPr; n = 4; 95% y.
4; R = iPr; n = 13; 95% y.
5; R = tBu;n = 4; 95% y.

6; R = Ph; R_1 = -$(CH_2)_4CH_3$; 90% y.
7; R = Cy; R_1 = -$(CH_2)_4CH_3$; 83% y.
8; R = iPr; R_1 = -$(CH_2)_4CH_3$; 97% y.
9: R = iPr; R_1 = -$(CH_2)_{13}CH_3$; 99% y.
10; R = tBu;R_1 = -$(CH_2)_4CH_3$; 85% y.

The reactivity of these iridium complexes was then investigated (Scheme 2). Complex **6** reacted with $AgPF_6$ (silver hexafluorophosphate) at 45 °C in CH_2Cl_2, giving a complex spectrum containing a small iridium hydride resonance. The reaction of dicyclohexylphosphine complex **7** at 45 °C with $AgPF_6$ in CH_2Cl_2 gave a single C–H activation product in which the cyclohexyl ring on the phosphine was dehydrogenated. Two-dimensional ^{1}H NMR spectroscopic experiments did not absolutely verify the position of the double bond in the ring. To confirm C–H activation occurred on the cyclohexyl ring and not on the alkyl chain, we prepared a deuterated acylphosphine-ligated iridium complex of **2** and submitted this complex to the same reaction conditions. The hydride signal was still observed in the ^{1}H NMR spectrum (−16.4 ppm, d, $J_{1H\text{-}31P}$ = 32.4 Hz, 1H), confirming that a C–H bond on the cyclohexyl ring of the phosphine was activated. This type of C–H activation reaction on the tricyclohexylphosphine ligand has been previously reported (Chart 1).[22,25,26,28,31,33] When the acylphosphine complex containing isopropyl groups (**8**) was reacted with $AgPF_6$ at 45 °C, complex **12** was formed in 89% yield, as determined by ^{1}H NMR spectroscopy. Submitting the fatty acid acylphosphine complex **9** to the same reaction conditions similarly gave a single complex (**13**) in 84% yield. In the ^{1}H NMR spectra of **12** and **13**, resonances displaying a single coordinated alkene, as well as an iridium hydride, were observed. This result differs from the only other site-selective example by Bergman,[33] because we form an internal olefin, which are less favorable in alkane dehydrogenation reactions than terminal C–H bonds. Interestingly, we have previously reported that the di-*tert*-butylacylphosphine complex (**10**) provided the novel anionic complex **14** in the presence of AgOTf at ambient temperature.[35]

Scheme 2. Reactivity of Ir-Acylphosphine Complexes



To confirm the assignment of complex **12**, an X-ray quality crystal was grown by layering a CH_2Cl_2 solution of the isolated complex with diethyl ether, followed by cooling to −30 °C. An ORTEP diagram of the obtained X-ray structure of the unsaturated ligand complex **12** is shown in Figure 1. The C_{19}–C_{20} bond distance was found to be 1.402(9) Å, indicating a C=C double bond. The hydride ligand was not located by the X-ray analysis; however, a signal in the hydride region of the ^{1}H NMR spectrum displayed a doublet at δ −17.2. This resonance became a singlet upon ^{31}P decoupling of the ^{1}H NMR spectrum. An iridium hydride stretch was also observed in the IR spectrum at 2182 cm^{-1}. Moreover, the sum of the bond angles around the iridium center (352°) indicated distorted tetrahedric coordination, as opposed to a trigonal planar geometry, and thus provided additional evidence for the presence of an iridium hydride.[27] Using density functional theory (see Supporting Information), computational studies have shown that the isolated olefin complex **12** is the most thermodynamically stable of the four possible alkene products,

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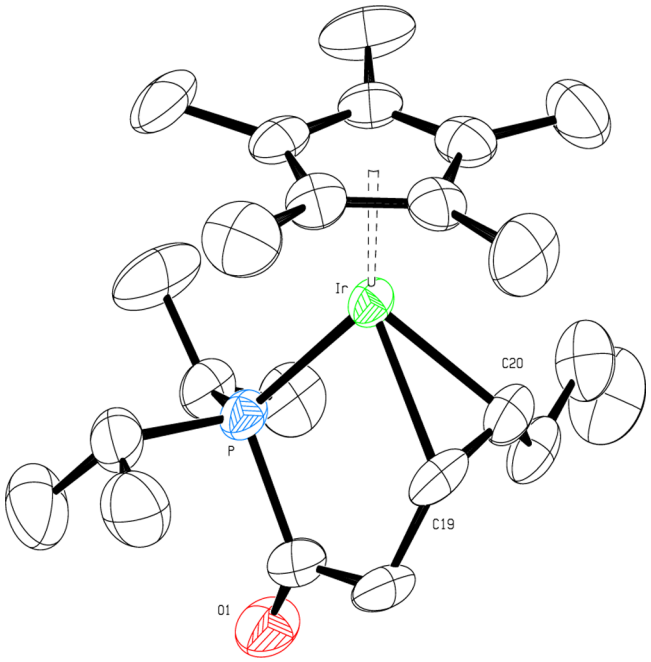

Figure 1. ORTEP diagram of olefin complex **12** with atoms drawn at 50% probability. The hydrogen atoms and the counteranion were omitted for clarity. Selected bond distances and angles: $C_{19}-C_{20}$ = 1.402(9) Å, Ir−P = 2.2570(16) Å, Ir−C_{19} = 2.203(6) Å, Ir−C_{20} = 2.184(6) Å, C═O = 1.213(8) Å, $C_{18}-C_{19}-C_{20}$ = 122.0(6)°.

which could arise from *β*-hydride elimination of a five- or six-membered iridalactone. The *cis*-$\Delta_{3,4}$ alkene product is more stable than the corresponding *trans*-alkene by 3.1 kcal/mol, while also being more stable than the *cis*- or *trans*-$\Delta_{4,5}$ alkene by 4.5 to 5.5 kcal/mol.

To better understand the transformation of complex **8** to the dehydrogenation product **12**, closer inspection of the reaction was undertaken by observing changes in the acylphosphine resonance by ^{31}P NMR spectroscopy (Figure 2). During the initial stages of the reaction, two species were formed with ^{31}P resonances at 50.9 and 61.7 ppm, with the 50.9 ppm resonance being the dominant species. These two species lessened in intensity as two new resonances at 56.7 and 72.3 ppm began to appear. The signal at 72.3 ppm belongs to the monounsaturated olefin complex (**12**). After nearly two hours, the resonances at 50.9 and 61.7 ppm were no longer present, and the major species observed were at 56.7 and 72.3 ppm. During the final stages of the reaction, the resonance at 56.7 ppm disappears, and the product (**12**) at 72.3 ppm became the only major signal remaining in the ^{31}P spectrum. Throughout the course of the reaction, additional resonances from 10 to −30 ppm were observed due to hydrolysis of the hexafluorophosphate anion. The major hydrolysis product formed in the crude reaction was PO_2F_2, which was confirmed by resonances in the ^{19}F and ^{31}P NMR spectra: −80.6 ppm (d, $J_{19F-31P}$= 976 Hz) and −15.9 ppm (t, $J_{19F-31P}$ = 976 Hz), respectively. The hydrolysis of the hexafluorophosphate anion was previously reported to occur in other late transition metal complexes.[36,37]

The conversion of complex **8** to **12** was also monitored by ^{1}H NMR spectroscopy (Figure 3). These experiments revealed that an iridium hydride species formed prior to formation of the olefin product **12**. While isolation and full characterization of this species has remained elusive, we believe that this hydride may be associated with the unknown signal observed at 56.7 ppm in the ^{31}P NMR spectrum. Currently, we speculate that the signal at 56.7 ppm corresponds to the iridacycle formed after the initial C−H activation (**19**, Scheme 4, vide infra).

Although the isolation of the product that gives rise to the resonance at 56.7 ppm in the ^{31}P NMR spectrum is still ongoing, we were able to isolate and crystallize the species observed at 50.9 ppm in the ^{31}P NMR spectrum during the reaction between complex **8** and $AgPF_6$ in CH_2Cl_2 at 45 °C. This complex was determined to be the unusual dimeric iridium complex **15**, which is bridged by the carbonyl of the acylphosphine ligand (Ir−O═C bond length is 2.148(4) Å). This structural determination arose from X-ray crystallographic analysis of a single crystal of the isolated complex (Figure 4). Interestingly, some batches of this isolated dimeric complex contained trace amounts of another unknown complex that resonates at 61.7 ppm in the ^{31}P NMR spectrum. Cooling the bridged carbonyl dimer **15** to −80 °C did not favor one resonance over the other (50.9 vs 61.7 ppm), which likely eliminates the two signals from being conformers.

The reactivity of the dimeric complex **15** was examined further (Scheme 3). One equivalent of the diisopropyl acylphosphine ligand **3** was added to a solution of dimer **15**, and the mixture was heated to 45 °C. After two hours at this temperature, a 2.5:1 ratio of the unknown complex (**18**) (61.7 ppm) and the starting dimer (**15**) was measured using ^{31}P NMR spectroscopy. This ratio remained unchanged after 4 h at 45 °C. Interestingly, no olefin product (**12**) was observed in the presence of the added ligand **3**. The addition of ligand provided some evidence that the unknown species contains two

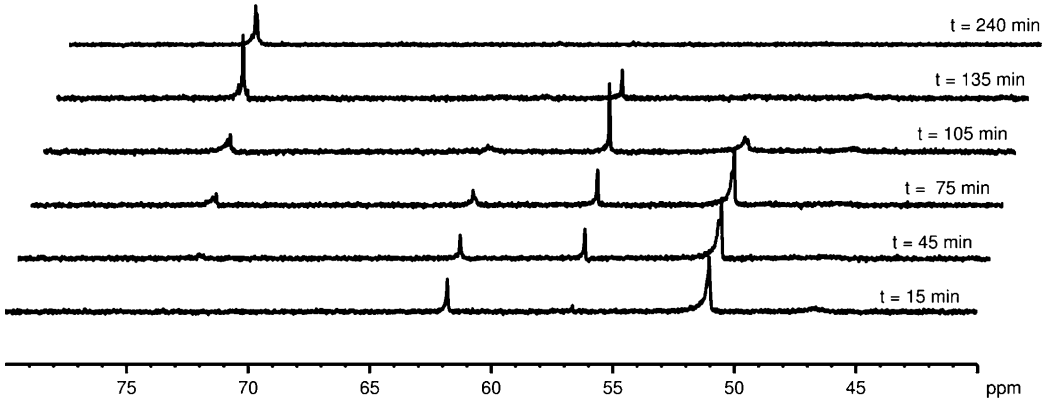

Figure 2. ^{31}P NMR spectra of the reaction of diisopropyl acylphosphine complex **8** and $AgPF_6$ in CH_2Cl_2 at 45 °C.

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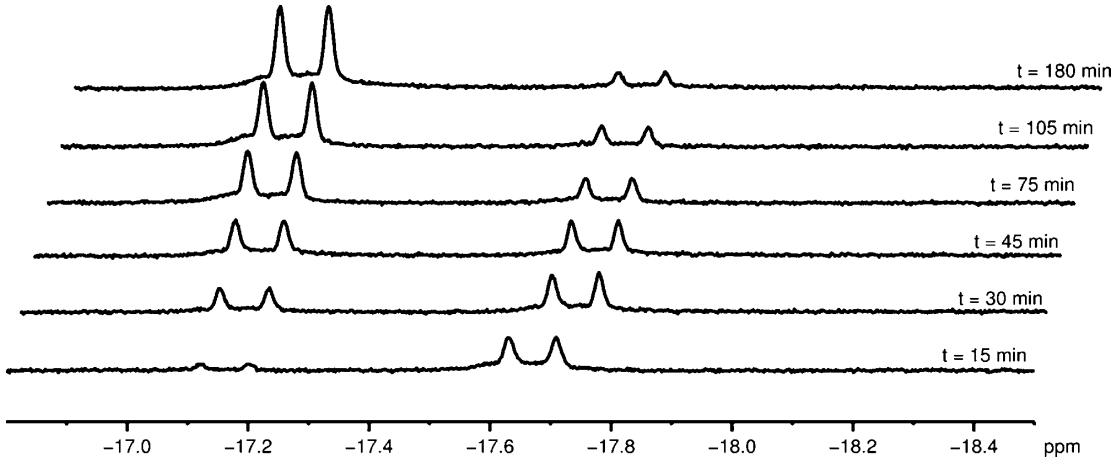
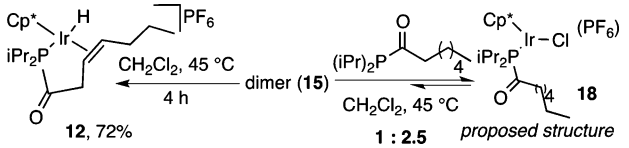


Figure 3. ^{1}H NMR spectra of the reaction of diisopropyl acylphosphine complex **8** and $AgPF_6$ in CH_2Cl_2 at 45 °C.

Scheme 3. Reactivity of Carbonyl Dimer Complex 15

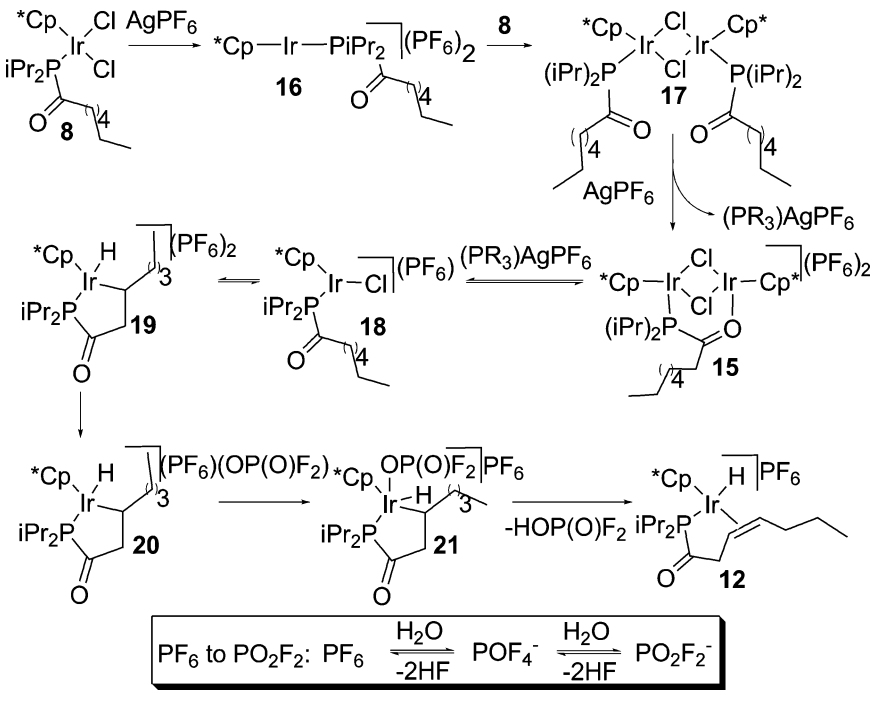


acylphosphine ligands in a dimeric form or that **15** may be cleaved by additional ligand into two equivalents of the monomeric iridium complex [(Cp*Ir(Cl)(**3**)] (**18**, as shown). Once again, using density functional theory, the formation of the monomeric complex from the carbonyl dimer was calculated to be enthalpically favorable. Heating the dimer **15**, without additional ligand in CH_2Cl_2 at 45 °C for 4 h, provided a 72% yield of the monounsaturated olefin complex **12**.

The exquisite selectivity observed in this reaction is most likely due to the geometric constraints afforded by the coordinated acylphosphine ligand. To investigate this, we prepared the analogous complex bearing a hexyl diisopropylphosphine ligand (i.e., no acyl unit for coordination to Ir). When the trialkylphosphine-ligated metal complex was submitted to the reaction conditions, a 1:1 mixture of olefin complexes was obtained. We surmise that the lack of selectivity may arise from the inability of the ligand to form a rigid iridacycle.

The proposed reaction mechanism is described in Scheme 4. The reaction pathways were proposed on the basis of the observations of isolated complexes and from previously mentioned computational data regarding the fate of the isolated dimeric species **15**. The addition of two equivalents of $AgPF_6$ to complex **8** presumably gives the unsaturated cationic iridium (III) complex **16**. Complex **16** reacts with starting material **8** to form the dimeric complex **17**, which can dissociate phosphine and form the bridged carbonyl dimer **15**. We have previously observed that the abstraction of the first chloride of a similar

Scheme 4. Proposed Reaction Mechanism of 8 to 12



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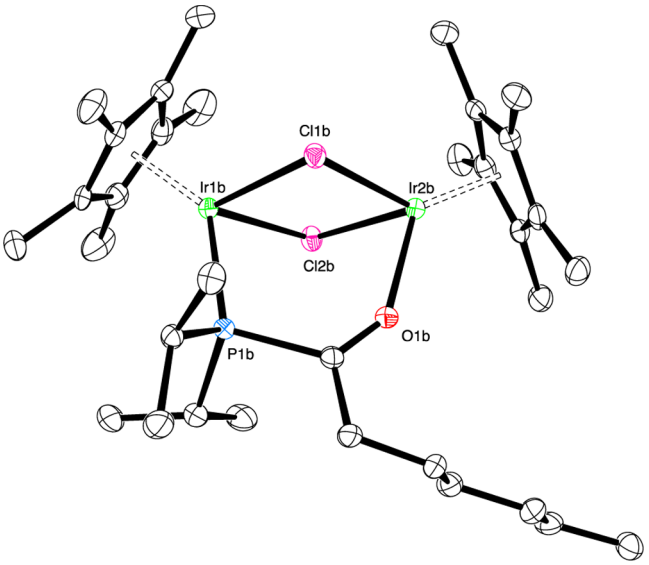

Figure 4. ORTEP diagram of bridged carbonyl dimer **15** with atoms drawn at 30% probability. The hydrogen atoms and the counteranions were omitted for clarity. Selected bond distances: Ir_{1b}–Cl_{1b} = 2.4312(14) Å, Ir_{1b}–Cl_{2b} = 2.4422(14) Å, Ir_{1b}–P_{1b} = 2.3430(14) Å, Ir_{2b}–Cl_{1b} = 2.4209(14) Å, Ir_{2b}–Cl_{2b} = 2.4015(15) Å, Ir_{2b}–O_{1b} = 2.148(4) Å, C═O = 1.231(7) Å.

iridium complex is slower than the second chloride abstraction, hence the remaining starting material **8**. Dimer **15** then collapses into the monomeric three-coordinate iridium species (**18**), and the reaction pathway for this transformation was calculated to be exothermic by 48.4 kcal/mol (Supporting Information). Complex **18** can then form the iridacycle **19** via C–H activation of the alkyl chain. Hydrolysis of hexafluorophosphate to difluorophosphate, followed by elimination of difluorophosphoric acid, and regioselective β-hydride elimination of the alkyl chain would give the olefin complex **12**. The thermodynamics of the reaction mechanism have also been studied computationally, and details are provided in the Supporting Information. The hydrolysis of one of the PF_6 anions was followed by ^{31}P and ^{19}F NMR spectroscopy, which displayed the proposed intermediates to this step. The PF_6 hydrolysis is not believed to be a thermodynamic driving force for the overall transformation because the initial hydrolysis step was calculated to be largely endothermic (Supporting Information).

■ CONCLUSION

In summary, we have demonstrated that the mild, site-selective dehydrogenation of an unactivated alkane is possible with the use of a directing group and occurs in high yields as a single diastereomeric olefin complex. An interesting dimeric iridium complex bridged by a carbonyl group from the acylphosphine ligand was isolated and shown to be a chemically and kinetically competent intermediate in this reaction. A reaction mechanism was proposed using ^{1}H and ^{31}P NMR spectroscopy in concert with computationally calculated reaction pathways. Efforts to further elucidate the reaction mechanism, as well as develop a catalytic variant of this process, are ongoing.

■ EXPERIMENTAL SECTION

General Methods. All manipulations were carried out in an argon atmosphere using standard Schlenk and drybox techniques. The acyl phosphine ligands were prepared in ~95% purity using the previously reported literature procedure.[34] The X-ray crsystal structure and elemental analysis for **12** were obtained for the triflate analogue. The PF_6 anion was quantitatively exchanged by stirring **12** in CH_2Cl_2 with three equivalents of NaOTf. This was necessary to obtain X-ray quality crystals. All solvents were dried over CaH_2 or activated alumina columns. All other commercially obtained reagents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers and are reported relative to TMS. ^{31}P NMR spectra were recorded on Bruker spectrometers and are reported relative to H_3PO_4. ^{19}F NMR spectra were recorded on Bruker spectrometers and are reported relative to trifluoromethyl benzene. High-resolution mass spectra were obtained from the mass spectrometry facility at The Ohio State University. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer.

1-(Diphenylphosphino)heptan-1-one (1). Heptanoyl chloride (160 μL, 1.03 mmol) was added dropwise to a stirring solution of diphenylphosphine (200 mg, 1.07 mmol) and NEt_3 (160 μL, 1.15 mmol) in Et_2O. After stirring for 2 h at ambient temperature the reaction mixture was filtered over a pad of Celite. The filtrate was evaporated to dryness to yield **1** as a yellow oil (300 mg, 97%). ^{1}H NMR (C_6D_6, 400 MHz): δ 7.52 (m, 4H), 7.05 (m, 6H), 2.42 (m, 2H), 1.53 (m, 2H), 1.11 (m, 2H), 1.03 (m, 4H), 0.78 (m, 3H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 400 MHz): δ 223.7 (d, $J_{13C\text{-}31P}$ = 40.5 Hz), 135.2 (d, $J_{13C\text{-}31P}$ = 18.5 Hz), 133.1 (d, $J_{13C\text{-}31P}$ = 7.4 Hz), 129.9, 129.1 (d, $J_{13C\text{-}31P}$ = 8.1 Hz), 45.8 (d, $J_{13C\text{-}31P}$ = 35.3 Hz), 31.9, 29.1, 24.6 (d, $J_{13C\text{-}31P}$ = 4.1 Hz), 22.8, 14.2. ^{31}P NMR (C_6D_6, 160 MHz): δ 13.2. IR (cm^{-1}): 1689 (C═O). HRMS(ESI): calcd for $[M + H]^+$ 299.1559, found 299.1566.

1-(Dicyclohexylphosphino)heptan-1-one (2). Heptanoyl chloride (300 μL, 1.93 mmol) was added dropwise to a stirring solution of dicyclohexylphosphine (384 mg, 1.93 mmol) and NEt_3 (300 μL, 2.15 mmol) in Et_2O. After stirring for 2 h at ambient temperature the reaction mixture was filtered over a pad of Celite. The filtrate was evaporated to dryness to yield **2** as a yellow oil (553 mg, 93%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.58 (m, 2H), 1.95 (m, 2H), 1.71 (m, 10H), 1.55 (m, 2H), 1.27 (m, 10H), 1.23 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 400 MHz): δ 227.2 (d, $J_{13C\text{-}31P}$ = 46.0 Hz), 48.2 (d, $J_{13C\text{-}31P}$ = 34.2 Hz), 32.8, 32.7, 31.9, 31.6, 31.5, 30.3, 30.2, 29.2, 27.8, 27.7, 27.6, 27.5, 26.6, 24.4 (d, $J_{13C\text{-}31P}$ = 4.4 Hz), 22.8, 14.1. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 30.6. IR (cm^{-1}): 1643 (C═O). HRMS(ESI): calcd for $[M + H]^+$ 311.2498, found 311.2522.

1-(Diisopropylphosphino)heptan-1-one (3). Heptanoyl chloride (300 μL, 1.93 mmol) was added dropwise to a stirring solution of diisopropylphosphine (229 mg, 1.93 mmol) and NEt_3 (300 μL, 2.15 mmol) in Et_2O. After stirring for 2 h at ambient temperature the reaction mixture was filtered over a pad of Celite. The filtrate was evaporated to dryness to yield **3** as a yellow oil (423 mg, 95%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.58 (m, 2H), 2.14 (m, 2H), 1.55 (q, J = 7.2 Hz, 2H), 1.27 (m, 6H), 1.12 (m, 12H), 0.87 (t, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz): δ 227.1 (d, $J_{13C\text{-}31P}$ = 45.9 Hz), 48.2 (d, $J_{13C\text{-}31P}$ = 34.0 Hz), 31.9, 29.2, 24.3 (d, $J_{13C\text{-}31P}$ = 4.3 Hz), 22.8, 22.7, 20.9, 20.8, 19.9, 19.8, 14.1. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 38.5. IR (cm^{-1}): 1685 (C═O). HRMS(ESI): calcd for $[M + H]^+$ 231.1872, found 231.1888.

1-(Diisopropylphosphino)hexadecan-1-one (4). Palmitic acid (260 mg, 1.01 mmol) was refluxed in thionyl chloride (10 mL) for 1 h. All the thionyl chloride was then removed in vacuo, and the remaining oil was added dropwise to a stirring solution of diisopropylphosphine (229 mg, 1.93 mmol) and NEt_3 (300 μL, 2.15 mmol) in Et_2O. After stirring for 2 h at ambient temperature the reaction mixture was filtered over a pad of Celite. The filtrate was evaporated to dryness to yield **4** as a yellow oil (342 mg, 95%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.58 (m, 2H), 2.14 (m, 2H), 1.56 (m, 2H), 1.26 (m, 26H), 1.15 (m, 12H), 0.88 (m, 3H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz): δ 227.0 (d, $J_{13C\text{-}31P}$ = 46.2 Hz), 48.3 (d, $J_{13C\text{-}31P}$ = 38.0 Hz), 32.5, 30.3, 30.2, 30.1, 30.0, 29.9, 29.9, 29.8, 24.5 (d, $J_{13C\text{-}31P}$ = 4.5 Hz), 23.2, 23.0, 22.9, 21.2, 21.0, 20.1, 20.0, 14.4. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 38.9. IR (cm^{-1}): 1666 (C═O). HRMS(ESI): calcd for $[M + Na]^+$ 379.3100, found 379.3067.

Hexyldiisopropylphosphine. A Schlenk flask containing chlorodiisopropylphosphine (2.0 g, 13.1 mmol) and Et_2O (15 mL) was

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cooled to −78 °C. An ethereal solution of hexylmagnesium bromide (13.5 mL, 26.3 mmol) cooled to −78 °C was added to the Schlenk flask dropwise with stirring over 20 min via cannula while maintaining the temperature. The mixture was then allowed to warm slowly to ambient temperature over 18 h. Degassed water (∼10 mL) was added slowly to quench any remaining hexylmagnesium bromide. The ethereal layer was then transferred via cannula to a Schlenk flask containing sodium sulfate and equipped with a sintered glass filter and second Schlenk flask. The sodium sulfate was filtered, and the solids were washed with additional Et_2O. The Et_2O was then removed in vacuo, and the crude product was transferred via cannula to a distillation setup. The product was distilled under vacuum (45 °C, 0.5 mmHg) to yield the title compound as a colorless oil (1.07 g, 40%). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.59 (m, 2H), 1.52 (m, 2H), 1.38 (m, 2H), 1.28 (m, 6H), 1.08 (d, J = 7.1 Hz, 3H), 1.05 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.6 Hz), 1.01 (d, J = 7.1 Hz), 0.89 (m, 3H). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 32.0, 31.7 (d, J = 11.6 Hz), 28.7 (d, $J_{13C\text{-}31P}$ = 18.8 Hz), 23.9, 23.8, 23.1, 22.3 (d, $J_{13C\text{-}31P}$ = 19 Hz), 20.5, 20.34, 19.1, 19.0, 14.3. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 3.08. HRMS(ESI): calcd for [M + H]$^+$ 203.1923, found 203.1930.

[Cp*Ir(Ph$_2$P{heptanoyl})Cl$_2$] (6). To a stirring suspension of [Cp*IrCl$_2$]$_2$ (200 mg, 0.251 mmol) in THF (5 mL) was added **1** (160 mg, 0.536 mmol). The mixture was stirred at ambient temperature for 2 h, and the solvent was then removed under vacuum. The residue was dissolved in Et_2O and cooled to −30 °C to yield **6** as an orange crystalline solid (315 mg, 90%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.60 (t, J = 8.6 Hz, 4H), 7.49 (m, 6H), 2.84 (m, 2H), 1.39 (m, 2H), 1.36 (d, $J_{1H\text{-}31P}$ = 2.2 Hz, 15H), 1.17 (m, 2H), 1.09 (m, 4H), 0.79 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 213.3 (d, $J_{13C\text{-}31P}$ = 14.9 Hz), 135.5 (d, $J_{13C\text{-}31P}$ = 8.9 Hz), 131.5 (d, $J_{13C\text{-}31P}$ = 2.0 Hz), 128.6 (d, $J_{13C\text{-}31P}$ = 11 Hz), 128.1, (d, $J_{13C\text{-}31P}$ = 49.0 Hz), 93.3 (d, $J_{13C\text{-}31P}$ = 2.0 Hz), 46.6 (d, $J_{13C\text{-}31P}$ = 39.3 Hz), 31.9, 28.9, 23.6 (d, $J_{13C\text{-}31P}$ = 2 Hz), 22.2, 14.1, 8.4. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 23.1. IR (cm^{-1}) 1699 (C═O). HRMS(ESI): calcd for [M − Cl]$^+$ 661.1965, found 661.1940. Anal. Calcd for $C_{29}H_{38}Cl_2IrOP$: C, 49.99; H, 5.50. Found: C, 49.69; H, 5.29.

[Cp*Ir(Cy$_2$P{heptanoyl})Cl$_2$] (7). To a stirring suspension of [Cp*IrCl$_2$]$_2$ (100 mg, 0.125 mmol) in THF (5 mL) was added **2** (82 mg, 0.264 mmol). The mixture was stirred at ambient temperature for 2 h, and the solvent was then removed under vacuum. The residue was washed with cold pentane to yield **7** as an orange powder (147 mg, 83%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.90 (m, 2H), 2.64 (m, 4H), 1.82 (m, 6H), 1.72 (m, 2H), 1.65 (m, 2H), 1.53 (m, 2H), 1.47 (d, $J_{1H\text{-}31P}$ = 1.6 Hz, 15H), 1.35 (m, 14H), 0.88 (m, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 216.9 (d, $J_{13C\text{-}31P}$ = 12.8 Hz), 92.2 (d, $J_{13C\text{-}31P}$ = 2.1 Hz), 44.7 (d, $J_{13C\text{-}31P}$ = 31.4 Hz), 37.8, 37.6, 32.0, 31.9, 29.9, 29.1, 28.5, 28.4, 28.3, 28.2, 26.7, 22.8 (d, $J_{13C\text{-}31P}$ = 5.5 Hz), 14.2, 8.5. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 18.3. IR (cm^{-1}): 1670 (C═O). HRMS(ESI): calcd for [M − 2Cl + H]$^+$ 639.3303, found 639.3301. Anal. Calcd for $C_{29}H_{50}Cl_2IrOP$: C, 49.14; H, 7.11. Found: C, 49.27; H, 6.97.

[Cp*Ir(^{i}Pr$_2$P{heptanoyl})Cl$_2$] (8). To a stirring suspension of [Cp*IrCl$_2$]$_2$ (825 mg, 1.04 mmol) in THF (15 mL) was added **3** (500 mg, 2.17 mmol). The mixture was stirred at ambient temperature for 2 h, and the solvent was then removed under vacuum. The residue was washed with cold pentane to yield **8** as an orange powder (1.29 g, 97%). ^{1}H NMR (C_6D_6, 400 MHz): δ 3.14 (m, 2H, ^{i}PrH), 3.05 (m, 2H, αCH_2), 1.67 (quint, J = 7.2 Hz, 2H), 1.56 (d, J = 7.2 Hz, 3H), 1.52 (d, J = 7.2 Hz, 3H), 1.27 (m, 4H), 1.23 (d, $J_{1H\text{-}31P}$ = 1.6 Hz, 15H), 1.19 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 216.8 (d, $J_{13C\text{-}31P}$ = 12.7 Hz) 92.3 (d, $J_{13C\text{-}31P}$ = 2 Hz), 44.9 (d, $J_{13C\text{-}31P}$ = 13.2 Hz, αCH_2), 32.0, 29.0, 26.5 (d, $J_{13C\text{-}31P}$ = 24 Hz), 22.8, 21.7, 21.6, 20.0, 14.1, 8.4. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 25.8. IR (cm^{-1}): 1670 (C═O). HRMS(ESI): calcd for [M − 2Cl + H]$^+$ 559.2676, found 559.2658. Anal. Calcd for $C_{23}H_{42}Cl_2IrOP$: C, 43.94; H, 6.73. Found: C, 44.01; H, 6.70.

[Cp*Ir(^{i}Pr$_2$P{palmitoyl})Cl$_2$] (9). To a stirring suspension of [Cp*IrCl$_2$]$_2$ (150 mg, 0.188 mmol) in THF (5 mL) was added **4** (140 mg, 0.393 mmol). The mixture was stirred at ambient temperature for 2 h, and the solvent was then removed under vacuum. The residue was washed with cold pentane to yield **9** as an orange powder (284 mg, 99%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 3.01 (m, 2H), 2.95 (m, 2H), 1.57 (m, 2H), 1.48 (d, $J_{1H\text{-}31P}$ = 1.6 Hz, 15H), 1.47 (m, 6H), 1.36 (d, J = 7.2 Hz, 3H), 1.33 (d, J = Hz, 3 H), 1.26 (m, 24H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 216.3 (d, $J_{13C\text{-}31P}$ = 12.7 Hz), 91.9 (d, $J_{13C\text{-}31P}$ = 2.4 Hz), 44.5 (d, $J_{13C\text{-}31P}$ = 31.6 Hz), 32.0, 29.6, 29.5, 29.5, 29.4, 29.3, 29.0, 26.1 (d, $J_{13C\text{-}31P}$ = 24 Hz), 26.0, 22.6. 22.4, 21.3, 21.2, 19.7, 13.8, 8.0. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 24.6. IR (cm^{-1}): 1670 (C═O). HRMS(ESI): calcd for [M − 2Cl + H]$^+$ 685.4085, found 685.4046. Anal. Calcd for $C_{32}H_{60}Cl_2IrOP$: C, 50.91; H, 8.01. Found: C, 51.02; H, 7.86.

[Cp*Ir(^{i}Pr$_2$P{hexyl})Cl$_2$]. To a stirring suspension of [Cp*IrCl$_2$]$_2$ (200 mg, 0.25 mmol) in THF (5 mL) was added hexyldiisopropylphosphine (110 mg, 0.54 mmol). The mixture was stirred at ambient temperature for 2 h, and the solvent was then removed under vacuum. The residue was washed with cold pentane to yield the title compound as an orange powder (260 mg, 86%). ^{1}H NMR (C_6D_6, 400 MHz): δ 2.47 (m, 2H), 2.40 (m, 2H), 1.65 (m, 2H), 1.35 (d, $J_{1H\text{-}31P}$ = 1.6 Hz, 15H), 1.27 (m, 6H), 1.20 (d, J = 7.1 Hz, 3H), 1.17 (d, J = 7.3 Hz, 3H), 1.15 (d, J = 7.4 Hz, 3H), 1.11 (d, J = 7.2 Hz, 3H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 92.2 (d, $J_{13C\text{-}31P}$ = 2.4 Hz), 32.0 (d, $J_{13C\text{-}31P}$ = 12.5 Hz), 25.9 (d, $J_{13C\text{-}31P}$ = 35.5 Hz), 25.3, 25.2, 23.1, 20.7 (d, $J_{13C\text{-}31P}$ = 37.4 Hz), 19.5, 19.4, 19.2, 14.3, 9.4. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 3.08. HRMS(ESI): calcd for [M − 2Cl + H]$^+$ 531.2727, found 531.2725. Anal. Calcd for $C_{22}H_{42}Cl_2IrP$: C, 43.99; H, 7.05. Found: C, 44.00; H, 6.95.

[Cp*Ir(^{i}Pr$_2$P{(*Z*)-1-(diisopropylphosphino)hept-3-en-1-one})-H]PF$_6$ (12). Silver hexafluorophosphate (42 mg, 0.17 mmol) and **8** (50 mg, 0.78 mmol) were combined in CH_2Cl_2 (1 mL) and stirred at 40 °C for 4 h. The mixture was then cooled to ambient temperature and filtered through a pad of Celite. The resulting solution was concentrated to ∼0.5 mL, and pentane was added to precipitate a white powder, which was collected by vacuum filtration and dried in vacuo to yield **12** (36 mg, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.42 (t, J = 8.4 Hz, 1H, CH═CH), 3.12 (m, 1H, CH═CH), 2.85 (dd, J = 19.6 Hz, J = 8.8 Hz, 1H, αCH_2), 2.46 (q, J = 6.8 Hz, 2H, ^{i}PrCH), 2.05 (s, 15H), 2.05 (m, 1H, αCH_2), 1.80 (m, 1H, δCH_2), 1.48 (m, 2H), 1.23 (m, 6H), 1.00 (m, 3H), 0.99 (m, 3H), 0.90 (m, 3H), 0.58 (m, 3H), −17.21, (d, $J_{1H\text{-}31P}$ = 32 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 225.7 (d, $J_{13C\text{-}31P}$ = 16.8 Hz), 101.2, 58.5 (CH═CH), 42.5 (CH═CH), 40.4 (d, $J_{13C\text{-}31P}$ = 48.3 Hz, αCH_2), 36.5, 24.7, 23.4 (d, $J_{13C\text{-}31P}$ = 21.2 Hz), 22.6 (d, $J_{13C\text{-}31P}$ = 35.7 Hz), 18.7, 18.1, 16.6, 16.5, 13.8, 9.9. ^{31}P NMR ($CDCl_3$, 160 MHz): δ 72.3 (d, $J_{31P\text{-}1H}$ = 2.9 Hz), 143.8 (sept, $J_{31P\text{-}19F}$ = 713 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −73.3 (d, $J_{19F\text{-}31P}$ = 711 Hz). IR (cm^{-1}): 2182 (Ir−H), 1700 (C═O). HRMS(ESI): calcd for [M − 2Cl + H]$^+$ 557.2520, found 557.2527. Anal. Calcd for $C_{24}H_{41}F_3IrO_4PS$: C, 40.84; H, 5.85. Found: C, 40.65; H, 5.65.

[Cp*Ir(^{i}Pr$_2$P{(*Z*)-1-(diisopropylphosphino)hexadec-3-en-1-one})H]PF$_6$ (13). Silver hexafluorophosphate (75 mg, 0.29 mmol) and **9** (75 mg, 0.099 mmol) were combined in CH_2Cl_2 (1 mL) and stirred at 40 °C for 8 h. The mixture was then cooled to ambient temperature and filtered through a pad of Celite. The resulting solution was concentrated to ∼0.5 mL, and pentane was added to precipitate a white powder, which was collected by vacuum filtration and dried in vacuo to yield **13** (50 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.41 (t, J = 8.4 Hz, 1H, CH═CH), 3.10 (m, 1H, CH═CH), 2.85 (dd, J = 19.4 Hz, J = 8.8 Hz, 1H, αCH_2), 2.46 (q, J = 6.8 Hz, 2H, ^{i}PrCH), 2.06 (s, 15H), 2.06 (m, 1H, αCH_2), 1.79 (m, 1H, δCH_2), 1.43 (m, 2H), 1.25 (m, 24H, CH_2 + CH_3), 1.00 (dd, $J_{1H\text{-}31P}$ = 17.2 Hz, J = 6.8 Hz, 3H), 0.88 (m, 3H), 0.90 (m, 3H), 0.58 (dd, $J_{1H\text{-}31P}$ = 18.4 Hz, J = 6.4 Hz), 3H), −17.2 (d, $J_{1H\text{-}31P}$ = 32 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 225.6 (d, $J_{13C\text{-}31P}$ = 17.2 Hz), 101.2, 58.6 (CH═CH), 42.4 (CH═CH), 40.4 (d, $J_{13C\text{-}31P}$ = 47.6 Hz, αCH_2), 34.5, 32.0, 31.4, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 23.4 (d, $J_{13C\text{-}31P}$ = 21.3 Hz), 22.8, 22.5 (d, $J_{13C\text{-}31P}$ = 35.4 Hz), 18.7, 18.2, 16.6, 16.5, 14.2, 9.9. ^{31}P NMR (CD_2Cl_2, 160 MHz): δ 72.4 (d, $J_{31P\text{-}1H}$ = 5.3 Hz), −143.8 (sept, $J_{31P\text{-}19F}$ = 712 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ −73.3 (d, $J_{19F\text{-}31P}$ = 712 Hz). IR (cm^{-1}): 2188 (Ir−H), 1700 (C═O). HRMS(ESI): calcd for [M − PF_6]$^+$ 683.3929, found 683.3924.

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[(Cp*IrCl)$_2$(^{i}Pr$_2$P{heptanoyl})](PF$_6$)$_2$ (15). Silver hexafluorophosphate (85 mg, 0.336 mmol) and **8** (100 mg, 0.155 mmol) were combined in CH_2Cl_2 (1 mL) and stirred at ambient temperature for 10 min. The mixture was then filtered through a pad of Celite. The resulting solution was concentrated to ∼0.5 mL, layered with Et_2O, and cooled to −30 °C to yield **15** as an orange crystalline solid (83 mg, 85%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 3.11 (td, J = 7.0 Hz, $J_{1H\text{-}31P}$ = 3.5 Hz, 2H, αCH_2), 2.94 (m, 2H, ^{i}PrH), 1.82 (m, 2H), 1.62 (s, 15H), 1.60 (d, $J_{1H\text{-}31P}$ = 2 Hz, 15H), 1.40 (m, 18H, CH_2 + CH_3), 0.93 (m, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 236.1 (d, $J_{13C\text{-}31P}$ = 7.8 Hz), 97.3, 90.5, 50.6 (d, $J_{13C\text{-}31P}$ = 12.8 Hz, αCH_2), 31.5, 30.2 (d, $J_{13C\text{-}31P}$ = 20 Hz), 28.2, 24.8, 22.4, 19.5, 18.5, 13.7, 9.5, 9.0. ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 50.9, 143.8 (sept, $J_{31P\text{-}19F}$ = 710 Hz). ^{19}F NMR (CD_2Cl_2, 376 MHz): δ −73.1 (d, $J_{19F\text{-}31P}$ = 710 Hz). IR (cm^{-1}): 1611 (C═O).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and structural characterization, computational results, and ^{1}H and ^{31}P NMR spectroscopic studies. 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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