# **ORGANOMETALLICS**

# Cyclohexane-Based Phosphinite Iridium Pincer Complexes: Synthesis, Characterization, Carbene Formation, and Catalytic Activity in Dehydrogenation Reactions

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# **Supporting Information**

**ABSTRACT:** Metalation of two cyclohexane-based phosphinite pincer ligands, *cis*-POCyPO (4) and *trans*-POCyPO (5) (POCyPO = {1,3-bis-[(di-*tert*-butylphosphinito]cyclohexane}<sup>-</sup>), is reported. In line with previously published results (*Dalton Trans.* 2009, 8626, DOI: 10.1039/B910798C), ligand 4 undergoes aromatization to give benzene-based complex (POCOP)IrHCl (3) at high temperatures in the presence of [Ir(COD)Cl]<sub>2</sub>. However, here we present the isolation of carbene complex (POCyOP)=IrCl (6) which is an intermediate in the aromatization process; upon reaction with H<sub>2</sub>, 6 can be readily transformed to the corresponding hydridochloride 8. Metalation of *trans*-POCyOP ligand 5 gives hydridochloride 13 which only upon further heating can be converted



to the corresponding carbene 14. A mechanistic study of hydrogenation of carbene 6 is reported, as well as interesting ambient temperature CO-induced C–H activation in  $\beta$ -position of 6, a process that under other circumstances takes place around 200 °C. The cis complex (POCyOP)IrHCl (8), upon activation with base, revealed moderate activity in transfer dehydrogenation of cyclooctane (144 turnover numbers (TON)), while the performance of trans analog 13 was much better (up to 1684 TON). Carbene complex 6 and *in situ* generated 14 demonstrated promising activity in acceptorless dehydrogenation of alcohols, presumably operating via a novel metal–ligand cooperation type mechanism. Some of the alcohol dehydrogenations generated large amounts of polystyrene.

# INTRODUCTION

Transition metal pincer complexes constitute a research area of great interest due to the combination of high stability and tunabilty of electronic and steric properties of the ligands, giving rise to remarkable catalytic activity in many reactions.<sup>1</sup> In particular, iridium pincer complexes are efficient catalysts for dehydrogenation of alkanes, heterocycles, alcohols, and ammonia-boranes.<sup>3</sup> The majority of systems studied are arene-based PCP<sup>4</sup> and POCOP<sup>5</sup> type complexes; some recent developments include hybrid PCOP,<sup>6</sup> POCN,<sup>7</sup> and POCSP,<sup>8</sup> as well as CCC<sup>9</sup> pincer compounds. At the same time, complexes with an sp<sup>3</sup> carbon in the central position only recently have begun to attract considerable attention, despite being synthesized three decades ago during the pioneering studies by Shaw.<sup>10</sup> These compounds are believed to be somewhat more electron-rich compared to their arene  $C_{sp^2}$  counterparts, which may, for example, facilitate oxidative addition.<sup>11</sup> Another interesting feature of aliphatic pincers is their ability to form reactive C = M carbene complexes via  $\alpha$ -hydrogen<sup>10</sup> or even  $\alpha$ alkyl elimination.<sup>12</sup> Such reactivity patterns are responsible for many interesting transformations including  $C_{sp}^{3}$ -H- $C_{sp}^{3}$ -H bond coupling,<sup>13</sup>  $C_{sp}^{3}$ - $C_{sp}^{3}$  bond cleavage,<sup>12,13</sup> H<sub>2</sub>,<sup>10,14</sup> H<sub>2</sub>O,<sup>15</sup> and N<sub>2</sub>O<sup>16</sup> activation, but in contrast, the  $\alpha$ - $C_{sp}^{3}$ -H unit may also decrease the thermal stability. Thus, we previously found

that under typical conditions used for benchmark transfer dehydrogenation of cyclooctane (COA) precatalyst (PCyP)-IrHCl (1) suffered severely from decomposition and gave only 50 turnovers,<sup>17</sup> much fewer than the values obtained for corresponding arene-based analogues 2 and 3 (Chart 1).<sup>18</sup>

Chart 1. Ir Pincer Complexes Used for Dehydrogenation Reactions and Phosphinite Ligands in This Work



However, Brookhart reported<sup>19</sup> that a triptycene-based (PC<sub>sp</sub><sup>3</sup>P)Ir complex which lacks labile  $\alpha$ - and  $\beta$ -hydrogens demonstrated a very high activity (2820 turnover numbers (TON)) under the same conditions, indicating a good potential for (PC<sub>sp</sub><sup>3</sup>P)Ir systems. Later, the same framework was shown to be active for dehydrogenation of ethers.<sup>20</sup> Gelman designed

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an efficient (PC<sub>sp</sub>;P)Ir dibenzobarrelene based catalyst for acceptorless dehydrogenation of alcohols working through a metal–ligand cooperation;<sup>21</sup> a somewhat related design was used by Iluc as a catalyst for alkane dehydrogenation but with a more limited success.<sup>22</sup>

Most reported  $(PC_{sp}^{3}P)Ir$  compounds belong to the phosphine family of catalysts, with methylene linkers in the pincer arm. Inspired by the enhancement of the catalytic activity upon CH2-for-O substitution within the arene-based PCP pincer ligand to give the POCOP one,<sup>18</sup> we have been interested in synthesizing aliphatic phosphinite (POC<sub>sp</sub><sup>3</sup>OP)Ir complexes for some time. Initial attempts to metalate phosphinite cyclohexyl based ligand 4 under conditions similar to those used for its phosphine counterpart led to aromatization of the ligand and formation of benzene-based complex 3, and only with nickel has cyclometalation been successful.<sup>2</sup> Complexation of an acyclic aliphatic ligand with an Ir precursor afforded the corresponding pincer complex in low yield,<sup>24</sup> but it was very prone to thermal metal mediated ligand decomposition and, unsurprisingly, revealed no activity in catalytic dehydrogenation of COA.<sup>17</sup> This latter result is well in line with a report by Zargarian,<sup>25</sup> who noted facile decomposition of some acyclic POC<sub>sp</sub><sup>3</sup>OP type nickel complexes by C-O bond rupture and is likely related to an inherent fragility of this type of ligands.

We thus returned to the cyclohexane-based ligands and here report a more thorough study of complexation of cis ligand 4 and its trans counterpart 5 with iridium. We show that under certain conditions the complete aromatization of the ligand can be prevented to give the desired aliphatic phosphinite iridium pincers in the form of  $(POC_{sp}{}^{2}OP)$ =IrCl carbenes or  $(POC_{sp}{}^{3}OP)Ir(H)Cl$  hydrido-chlorides. The presence of an  $\alpha$ - $C_{sp}{}^{3}$ -H unit is probably responsible for the thermal instability of hydrido-chloride complexes, still their activity in dehydrogenation of COA can be fairly high under certain conditions. However, the  $\alpha$ - $C_{sp}{}^{3}$ -H group can be successfully used to organize a novel catalytic cycle for dehydrogenation of alcohols.

#### RESULTS AND DISCUSSION

Metalation and Aromatization of Cis Aliphatic Pincer Ligand 4. Mixing ligand 4 with  $[Ir(COD)Cl]_2$  at room temperature results in the formation of several soluble species, structures of which could not be reliably determined from NMR spectra. After heating this mixture in a closed flask at 110–120 °C for several hours, compounds 6 and 7 are observed as predominate species in ca. 1:1.5 ratio; both were isolated as pure compounds using column chromatography (Scheme 1). Complex 6 reveals a singlet at 179.2 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, as well as resonances from -O-CHat -1.21 ppm and from C=Ir at 235.9 ppm in the <sup>1</sup>H and  $^{13}C{^{1}H}$  NMR spectra, respectively, which are very characteristic for a carbene moiety.<sup>10,13–15</sup> This is the first example of a carbene complex derived from an aliphatic pincer phosphinite





ligand, and the structure of 6 was confirmed using X-ray crystallography (Figure 1), revealing a shorter C–Ir distance



Figure 1. Molecular structure of carbene complex 6 (left) and hydrido-chloride 8 (right). Selected bond distances (Å) and angles (deg) of 6, Ir1–C1 1.86(1), Ir–Cl 2.403(4), P–Ir–P 163.8(1), and those of of 8, Ir1–C1B 2.024(7), Ir–Cl 2.4017(18), P–Ir–P 160.23(6).

and a more acute P-Ir-P angle than those of the related phosphine complexes synthesized by Shaw and Piers (C1–Ir 1.86(1) vs  $2.006(4)^{10}$  and  $1.899(7)^{14}$  Å; P–Ir–P 163.8(1) vs  $168.1(1)^{10}$  and 167.81(7),<sup>14</sup> correspondingly). Complex 7 is characterized by a singlet at 159.5 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and reveals <sup>1</sup>H and <sup>13</sup>C signals corresponding to a nonmetalated ligand, in addition to two hydrides at -32.89 and -33.27 appearing as triplets of doublets due to mutual H-H coupling as well as coupling to two equivalent P nuclei. We thus formulate 7 as [(POCyHOP)\*Ir(H)<sub>2</sub>Cl]<sub>n</sub>; HRMS and DOSY NMR measurements argue for a dimeric composition. Based on previously reported structures for complexes of 4 and related ligands with other metals,<sup>26</sup> we propose the structure of 7 as depicted in Scheme 1. Along with these two complexes, small amounts of other compounds are present in solution prior to chromatography, one of which is hydrido-chloride (POCyOP)IrHCl 8 (identified by comparison with an independently prepared sample, see below). It seems reasonable that cyclometalation of 4 produces complex 8 which extrudes a molecule of dihydrogen to give carbene 6.

The mixture of **6** and 7 is fairly stable at the temperature of refluxing toluene. Upon raising the temperature to 160-180 °C, some 7 is gradually converted to **6**; at the same time **6** slowly transforms into aromatic complex **3**. Thus, after several hours at that temperature, the NMR yield of **6** passes through a maximum of 70–75%. At 200 °C, complex **3** is formed almost exclusively within a few hours. In contrast to the phosphine analogue (PCyP)IrHCl (1), no olefin or diene<sup>13</sup> intermediates could be detected during the formation of **3** from **4**. It is likely that COD from [Ir(COD)Cl]<sub>2</sub> serves as a hydrogen acceptor during this process; as we reported previously for **1**,<sup>13</sup> aromatization does not proceed to complexes are heated in a sealed vessel.

**Hydrogenation of Carbene 6.** At ambient temperature, carbene complex 6 reacts with hydrogen to give several species characterized by broad resonances in <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra. After ca. 3 days, this mixture is converted into a single product, namely, hydrido-chloride complex 8, which demonstrates a <sup>31</sup>P{<sup>1</sup>H} NMR signal at 170.0 ppm as well as a <sup>1</sup>H NMR hydride resonance at -40.37 (td, <sup>2</sup>J<sub>PH</sub> = 12.4 Hz, <sup>3</sup>J<sub>HH</sub> = 3.1 Hz), cf. Scheme 2. The molecular structure of 8 is given in Figure 1. The cyclohexane unit adopts a chair conformation





and is somewhat disordered due to an inverted configuration of ca. 40% of the molecules; therefore, bond lengths and angles within this part of the structure should be treated with caution. Compared to 1, 8 reveals the expected lowering of the P-Ir-P angle (160.28(5) vs  $166.74(5)^{\circ}$ ) and shortening of the C-Ir distance (2.048 vs 2.094(5) Å). Although the hydride position(s) could not be located with certainty, there is electron density in the Fourier map in positions where the hydride should be found. Most probably the conformation is anti with respect to the  $\alpha$ -hydrogens in the two conformations, respectively; the H-H coupling constant of 3.1 Hz is similar to that of the phosphine analog 1 (3.0 Hz) and supports this conclusion. Interestingly, the same stereochemical result (anti addition) was observed by Shaw for hydrogenation of the related phosphine carbene complex; 10b it is thus evident that addition of  $H_2$  to 6 is not just a simple syn addition of  $H_2$  to Ir or along the C=Ir bond. In order to get some mechanistic insight into the process, we performed a VT NMR study of the interaction of 6 with  $H_2$ . Complex 6 does not react with  $H_2$  at temperatures below the -40 °C required to make sharp NMR signals, so we quickly warmed the J. Young NMR tube charged with a solution of **6** in toluene- $d_8$  and  $H_2$  to room temperature and then inserted it into the spectrometer precooled to -80°C. This sequence was repeated several times.

Along with nonreacted **6**, three compounds were detected by NMR spectroscopy. One intermediate demonstrates NMR signals that are very similar to those of **8**, namely, a doublet at 171.3 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (high-field hydride is not decoupled) and a hydride peak at -46.5 ppm (t, <sup>2</sup>J<sub>PH</sub>  $\approx$  13 Hz). We thus propose that this compound is a close analog of **8** but with syn orientation of  $\alpha$ -C–H and Ir–H bonds, cf.

Scheme 3. Upon warming, the signals of 8-syn are broadened, but above 0 °C begin to become more sharp again; at room temperature, they are observed as moderately broad singlets at 170.7 and -45.54 ppm in the  ${}^{31}P{}^{1}H{}$  and  ${}^{1}H$  NMR spectra, correspondingly. After several hours at room temperature, only signals from 8-syn and 8 (henceforth called 8-anti) were observed in the reaction mixture, indicating that the two other intermediates are formed at some early stage of hydrogenation and are further converted to 8-syn as the kinetic and 8-anti as the thermodynamic products. The second intermediate demonstrated a broadened signal at 178.9 ppm in the  $^{31}P{^{1}H}$  NMR spectrum and a broadened triplet at -48.25 ppm (t,  ${}^{2}J_{\rm PH} \approx 13$  Hz) in the  ${}^{1}$ H NMR spectrum; given the almost equal probability of H<sub>2</sub> attack from both sides of P1-P2- $\alpha$ -C-Ir plane, it is reasonable to propose that this compound is an axially metalated analog of 8-syn, 8-syn-axial (in 8-anti and 8-syn, equatorial positions are metalated), resulting from an attack of  $H_2$  on the same side as the >CH-O or  $\beta$ -hydrogens (*cis-* $\alpha$ -H). The third detected compound was characterized by a <sup>31</sup>P{<sup>1</sup>H} NMR signal at 160.6 ppm and a resonance in the <sup>1</sup>H NMR spectrum appearing as an apparent quintet at -13.90 ppm. In addition, a broad signal at -2.55 ppm in the <sup>1</sup>H NMR spectra was observed, always integrating as 2:1 versus the hydride.

We thus propose that this broad signal corresponds to a coordinated molecule of dihydrogen, and the quintet-like pattern from the hydride is a coinciding triplet of triplets resulting from coupling with two equivalent P nuclei and the H<sub>2</sub> unit with similar *J* of around 14 Hz; the structure of this complex is formulated as 9 (see Supporting Information for a longer discussion of its NMR characterization). Upon heating, the signals from intermediates 8-syn-axial and 9 are broadened and at ca. -20 °C cannot be distinguished from the baseline. At room temperature, a very broad phosphorus signal is observed at ca. 174.1 ppm (without detectable hydride), which we interpret as a weighted-average resonance from 8-syn-axial and 9. The position of the signal is much closer to that of 8-syn-axial which likely reflects the disfavored coordination of H<sub>2</sub> at



<sup>a</sup>Compounds observed by NMR spectroscopy are marked with frames. Calculated energies are given in Figure 2.

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higher temperatures. The overall mechanism of hydrogenation is thus depicted on Scheme 3. It is likely that the reaction begins with the formation of complexes with dihydrogens A-1 and A-2, which undergo oxidative addition (B-1 and B-2) and subsequent migration of hydrogen ( $\alpha$ -insertion) to give 8-syn and 8-syn-axial; the latter is in equilibrium with 9. How are 8syn-axial and 8-syn now transformed into 8-anti? During our previous studies of the dihydride complex (PCyP)IrH<sub>2</sub>, we found that it undergoes H/D exchange between Ir-H and  $\alpha$ -C-H positions.<sup>27</sup> Experimental and computational studies also revealed that (PCyP)IrH<sub>2</sub> is prone to rapid reversible demetalation of both equatorial and axial positions, which is responsible for the observed H/D scrambling. It seems reasonable that a similar mechanism may be involved in the isomerization of 8-syn-axial and 8-syn into 8-anti. Overall this mechanism of reaction between 6 and  $H_2$  was corroborated by DFT calculations giving reasonable barriers as opposed to the direct H<sub>2</sub> addition to the carbene (TS3) which gives prohibitively high barriers, cf. Figure 2. Note that 8-syn-axial



**Figure 2.** Calculated free energy barriers for  $H_2$  attack cis and trans to  $\beta$ -hydrogens of **6** (at room temperature). Structures are given in Scheme 3.

slightly more favorably adds an  $H_2$  molecule with formation of 9, compared to the action of 8-syn, which explains the lack of observation of 8-syn( $H_2$ ) at low temperature. Finally, a computational search of the potential energy surface for the transformation of the 8-syn species to 8-anti shows that it is extremely complicated with a large number of isomers and conformers, and we were unable to establish a certain mechanism. It seems clear, though, that the fully demetalated species (as seen for the hydrides)<sup>27</sup> is high in energy and that involved intermediates and transition states involve partially broken Ir–C and Ir–H bonds.

With these result in hand, we attempted the synthesis of complex 8 directly from ligand 4 under  $H_2$  pressure. Unfortunately, instead of 8, a mixture of unidentified compounds was formed, none of which could be properly characterized.

**CO-Induced C–H Activation.** Carbene complex **6** readily reacts with 1 atm of CO with a simultaneous formation of isomeric adducts **10a** and **10b** (ca. 1:0.8 ratio) which are likely formed via CO attack on Ir from the *trans-* or *cis-β-*H side, cf. Scheme 4. These complexes are unstable. At ambient temperature, they undergo further transformations character-ized *in situ* by NMR and IR spectroscopy. Two very similar sets of signals were observed; thus,  ${}^{31}P{}^{1}H{}$  NMR spectrum revealed two peaks at 182.45 and 182.40 ppm. Carbon signals at 214.3 and 212.0 ppm were assigned as C=Ir, while those at





187.35 and 187.09 were assigned as Ir–CO moieties. In the IR spectra, C–O stretching vibrations were observed at 1961 and 1968 cm<sup>-1</sup>. After ca. 0.5 h, a new AB system (156.82 and 155.86 ppm  ${}^{2}J_{\rm PP}$  = 325.4 Hz, ca. 8%) appeared in the  ${}^{31}{\rm P}\{{}^{1}{\rm H}\}$  NMR spectrum. The new compound, **11a**, was also unstable and was never a major component in the mixture, but we managed to identify most of its  ${}^{1}{\rm H}$  and  ${}^{13}{\rm C}$  signals.

Specifically, the chemical shift of a hydride (-8.49 ppm), apparent t,  ${}^{2}J_{P1H} = {}^{2}J_{P2H} = 16.3$  Hz) points to the trans position being occupied by a high-field ligand like CO. Complex 11a was further transformed into 11b (this does not exclude that some of the 11b may be formed directly from 10b). After reaction overnight, the 10ab/11a/11b ratio was around 1:1:2, and after a few days, 11b became the sole product in the solution. An AMX system in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **11b** points to a desymmetrized structure (high-field hydride is not decoupled); the presence of <sup>13</sup>C NMR signals in the olefin region (154.5 and 127.5 ppm) which reveal a resolvable C-H coupling with the hydride unambiguously point to migration of one of the  $\beta$ -hydrogens to Ir with formation of a C–C double bond. A hydride resonance at -17.96 appears as a doublet of doublets; such chemical shifts are typical for a hydride trans to a weak-field ligands like Cl (for instance, -18.7 ppm for phosphine complex (PCyP)IrH(CO)Cl).<sup>28</sup> In agreement, a  ${}^{2}J_{CH}$  of 4 Hz between Ir–H and CO indicates a mutual cis arrangement of these ligands.<sup>29</sup> Because of the diequatorial substitution of the cyclohexane ring with  $-OP^tBu_2$ , the  $\beta$ hydrogens occupy axial positions and can only approach Ir from the cis- $\beta$ -H side, with a resulting syn arrangement of the remaining >C-H(-O-) bond and Ir-H, as drawn for 11a and 11b.

In solution, **11b** slowly loses HCl, and after 2 weeks, it is fully converted to 16-electron Ir(I) carbonyl complex **12**. Isomerizations similar to the transformation of **11a** to **11b** were previously observed by us<sup>28</sup> and others<sup>30</sup> for carbonyl-hydrido-chloride pincer complexes.

A more interesting process from a mechanistic point of view is the formation of **11a** from **10a**, which is a CO-induced C–H activation.<sup>31</sup> In principle, one can think of this process as a  $\beta$ elimination, which can be facile for the more flexible acyclic aliphatic backbone.<sup>32</sup> In the bulky and rigid pincer framework, a simple  $\beta$ -elimination is probably much more difficult which is manifested in the fact that for **6** the isomerization into olefin forms has a high barrier and takes hours at temperatures above 180 °C. A possible explanation for the effect of CO coordination is found in the calculated Ir–Cl bond, which is fairly long for **10a** (2.57 Å) and **10b** (2.55 Å). Possibly, this leads to partial or complete dissociation of the chloride giving a buildup of some positive charge on Ir, thereby facilitating the elimination (see the Supporting Information for more details). Metalation and Aromatization of Trans Aliphatic Pincer Ligand 5. Similar to the case of 4, addition of  $[Ir(COD)Cl]_2$  to a solution of 5 resulted in formation of several unidentified compounds. However, refluxing the reaction mixture in toluene provided mainly hydrido-chloride complex 13, which was isolated by crystallization. Compound 13 revealed an AMX pattern with some roof effect (173.28 and 169.23 ppm,  ${}^2J_{PP} = 366.2 \text{ Hz}$ ) in the  ${}^{31}P{}^{1}H{}$  NMR spectrum in agreement with a nonsymmetrical structure; a hydride resonance was observed at -39.37 with  ${}^3J_{H-IrH} = 2.8 \text{ Hz}$ , consistent with a mutual anti arrangement of  $\alpha$ -C-H and Ir-H bonds. The crystal structure of 13 suffers from disorder in the cyclohexane unit, but the trans orientation of the  $-OP({}^{t}Bu)_2$ groups can clearly be seen in both components (Figure 3).



Figure 3. Molecular structures of trans pincer complexes 13 (left) and 15 (right, half of the asymmetric unit). Selected bond distances (Å) and angles (deg) of 13, Ir–C1B 1.998(14), Ir–C1A 2.101(13), Ir–C1 2.417(2), P–Ir–P 160.61(7), and those of 15, C1–Ir1 2.076(5), C21–Ir2 2.077(5), P1–Ir1–P2 152.23(5), P3–Ir2–P4 153.54(5).

Some ligand decomposition was always observed during the metalation; in one experiment, possibly because of traces of methanol left from crystallization, it was sufficient enough to change the Ir/5 ratio and produce dinuclear complex 15 as the major product. Fortunately, the crystal structure of 15 was not disordered and allowed some conclusions about the geometry of pincer complexes with trans phosphinite ligands, cf. Figure 3. Two crystallographically independent molecules revealed  $\alpha$ -C-Ir distances of 2.07 and 2.08 Å and P-Ir-P angles of 152.2 and 153.5°. The cyclohexyl ring adopts a twisted-boat conformation in contrast to related cis systems where the chair conformation is usually preferred. Although the hydride was not located in the Fourier map, the position of other atoms unambiguously points to an anti arrangement with respect to the  $\alpha$ -C-H. Heating 13 at 180 °C leads to formation of carbene complex 14, which has a characteristic carbene peak in the <sup>13</sup>C NMR spectrum at 236.0 ppm. A number of very small unidentified hydride peaks were detected by NMR during this transformation, indicating that a complicated process occur as described above for cis-ligand 4. Further heating at even higher temperatures leads to aromatization and formation of complex 3. Reactions are described in Scheme 5.

Some Remarks about Aromatization of Cyclohexane-Based Phosphine and Phosphinite Pincer Ligands. We previously reported the aromatization of phosphine complex  $1.^{13}$  At temperatures around 200 °C, a carbene complex as well as olefin and diene complexes were formed, which upon further heating were converted to benzene-based complex 2. The presence of a hydrogen acceptor was essential for the completion of the reaction; otherwise, the mixture of compounds mentioned above was formed.

Scheme 5. Metallation and Aromatization of trans Aliphatic Pincer Ligand 18



Aromatization of phosphinite ligands 4 and 5 is quite similar to the one for phosphine analog, but has some important differences. Thus, carbene complexes 6 and 14 are formed at temperatures significantly lower than those required for isomerization into olefin forms (roughly around 200 °C for all compounds) as major products; at the same time, the yield of the phosphine based carbene never exceeded 10% because of further transformations. We attribute this difference to a tightening effect resulting from the CH<sub>2</sub>-for-O substitution, which is seen as a decrease of P–Ir–P angles and shorter  $\alpha$ -C– Ir distances, compared to the phosphine counterpart. The shorter distance apparently lowers the barrier for  $\alpha$ -hydrogen elimination, a key step for the formation of carbene compounds. It therefore can be concluded that for phoshinite ligands the carbene chemistry should be more important or even predominating compared to that for similar phosphine frameworks (see also the catalytic part). Neither olefin nor diene intermediates were observed during aromatization of 4 and 5, likely indicating their rapid conversion to complex 3 at the conditions required for their formation.

**Catalytic Dehydrogenation of Alkanes.** A benchmark reaction which is used for testing catalytic activity of iridium pincer complexes is transfer dehydrogenation of cyclooctane in the presence of *tert*-butylethylene (TBE) (Scheme 6).

Scheme 6. Catalytic Transfer Dehydrogenarion of Cyclooctane



Common conditions which most of the literature refer to include 3030/3030/1 COA/TBE/cat. ratio and temperatures around 200 °C. If the corresponding hydrido-chloride complex is used as catalyst, then 1 equiv of base, typically <sup>t</sup>BuONa, is required to generate active species. Cis complex 8 demonstrated only moderate catalytic activity with TON 144, which can be compared to arene-based (PCP)Ir (2, TON 230)<sup>18</sup> and (POCOP)Ir (3, TON 1512 according to the original report;<sup>5a</sup> 1730-1918 in our hands)<sup>17,33</sup> and therefore was not studied any further. Trans complex 13 however showed a fairly good TON of 1223 under the same conditions. Bearing in mind that thermal decomposition of catalytically active species was a problem for phosphine complex 1, we gradually decreased the temperature to 150 °C and then to 120 °C. This was accompanied by an increase in the turnover numbers at the cost of reaction rate. Subsequently raising the temperature indicated that after 32 h at 150 °C there is almost no activity (Table 1, entries 3 and 4), but after the same time at 120 °C, some

Table 1. Transfer Dehydrogenation of Cyclooctane by Iridium Pincer Complexes

catalyst	conditions [ $T$ (°C); $t$ (h)]	COA/TBE/cat	TON
8	200; 16	3030/3030/1	144
13	200; 16	3030/3030/1	1223
13	150; 32	3030/3030/1	1253
13	150; 32 + 180; 3	3030/3030/1	1365
13	120; 32	3030/3030/1	1388
13	120; 32 + 180; 3	3030/3030/1	1684
13	120; 32 + 180; 3	20000/5000/1	3238
	catalyst 8 13 13 13 13 13 13 13	catalystconditions $[T (°C); t (h)]$ 8200; 1613200; 1613150; 3213150; 32 + 180; 313120; 3213120; 32 + 180; 313120; 32 + 180; 313120; 32 + 180; 3	catalyst         conditions [T (°C); t (h)]         COA/TBE/cat           8         200; 16         3030/3030/1           13         200; 16         3030/3030/1           13         150; 32         3030/3030/1           13         150; 32         3030/3030/1           13         150; 32 + 180; 3         3030/3030/1           13         120; 32         3030/3030/1           13         120; 32 + 180; 3         3030/3030/1           13         120; 32 + 180; 3         3030/3030/1           13         120; 32 + 180; 3         20000/5000/1

catalyst remained in active form (Table 1, entries 5 and 6). The highest TON thus obtained was 1684. Interestingly, the formation of COD was detected in this experiment giving a ca. 84:16 COE/COD ratio. In a diluted solution containing 20 000/5000/1 COA/TBE/cat., the turnover number went up to 3238, consistent with a less pronounced inhibition by olefins. For comparison, the best catalyst reported to date demonstrated a TON of 5901 with 6000/6000/1 COA/TBE/cat.<sup>8</sup>

Catalytic Dehydrogenation of Alcohols. Acceptorless alcohol dehydrogenation is a promising way to produce hydrogen from liquid organic substrates and also a valuable tool for green oxidation and green synthesis of amides, acetals, lactams, and many other classes of compounds when combined with coupling reactions.<sup>3b,34</sup> Inspired by the facile oxidative addition of hydrogen to carbene 6 and regeneration of the latter upon heating, we reasoned that  $(PC_{sp}{}^{3}P)Ir$  systems may offer something that their aromatic  $(PC_{sp}{}^{2}P)Ir$  analogs cannot: a possibility of metal-ligand cooperation, where a related reaction sequence would lead to the dehydrogenation of alcohols. An obvious problem could be the competing aromatization of the carbene compounds; in order to circumvent such reactivity, we decided to take neat alcohols as the reaction media to maximize probability of the reaction between carbene and alcohol. When cis carbene complex 6 was heated with benzyl alcohol at 190 °C in a 4000/1 ratio, a complete conversion of the substrate was observed with formation of benzylbenzoate, benzaldehyde, and some amount of unidentified products (Table 2). Corresponding hydridochloride 8 can be used with virtually the same result; we thus used more accessible trans complex 13 instead of carbene 14. The activity of the latter compounds was found to be very similar to that of 6/8. With secondary substrate 1-phenylethanol, the reaction was much less clean and produced more byproducts than desired acetophenone; decreasing the temperature to 175 °C improved the yield of the ketone. The byproducts from the 190 °C experiment were precipitated and subjected to elemental analysis, which, together with the presence of very broad NMR signals in the aliphatic and aromatic regions suggested that these byproducts have the

composition  $(-CH_2(Ph)CH-)_n$ , i.e., polystyrene. We assume that at lower temperatures similar byproducts are formed. The olefin region of the reaction mixture was almost free from <sup>1</sup>H NMR signals, which probably means that polystyrene was formed via dehydration rather than polycondensation. Pure 1phenylethanol is not readily dehydrated at the specified temperatures, so metal catalysis seems reasonable. While these side reactions are undesired for the purpose of H<sub>2</sub> and/ or carbonyl compounds production, they may have a standalone interest toward bioalcohols functionalization, particularly the use of alcohols to give polymers.<sup>35</sup>

Unfortunately, other tested alcohols demonstrated very low conversions around 10–15%. We speculate that a benzylic  $\beta$ -hydrogen (upon coordination of the oxygen) may be important for the present systems and the low conversion of aliphatic alcohols may be related to slower transfer of this hydrogen to Ir which opens up the way for competing deactivating processes.

To test the possibility of HCl loss from 8/13 and formation of 14-electron (PCP)Ir active species, common for dehydrogenation of alkanes, we performed a control experiment using aromatic (POCOP)IrHCl complex 3 and 1-phenylethanol at 190 °C, but less than 1% of acetophenone was detected indicating that this hypothesis can be rejected. In this respect, it should be noted that in the absence of base, hydrido-chloride 8 (and therefore carbene 6) is not active in the dehydrogenation of alcohols by 6 is principally different from the traditional one operating for alkanes. A possible catalytic cycle is depicted on Scheme 7. An alcohol reacts with the

Scheme 7. Possible Catalytic Cycle for Dehydrogenation of Alcohols by Carbene 11



carbene by oxidative addition of the O–H bond to Ir, followed by hydrogen migration to the  $\alpha$ -carbon. Subsequent  $\beta$ -

Table 2. Acceptorless Alcohol Dehydrogenation by Aliphatic Phosphinite Iridium Pincer Complexes

entry	catalyst	substrate	conditions $[T (^{\circ}C); t (h)]$	conversion (%)	yield <sup>a</sup>
1	6	PhCH <sub>2</sub> OH	190; 16	>99	PhCHO 20%, PhCOOBn 68%
2	13	PhCH <sub>2</sub> OH	190; 16	>99	PhCHO 13%, PhCOOBn 60%
3	6	PhCH(OH)CH <sub>3</sub>	190; 16	>99	PhCOCH <sub>3</sub> 29%, PS 71%
4	6	PhCH(OH)CH <sub>3</sub>	175; 48	>99	PhCOCH <sub>3</sub> 52%
5	6	Су-ОН	190; 16	12	b
6	6	1-octadecanol	190; 16	16	Ь

"When the sum of the yields is less than 100%, the rest corresponds to condensation/polymerization products. PS = polystyrene. "A mixture of several unidentified compounds was formed.

elimination leads to hydrido-chloride 8, which eliminates hydrogen and regenerates carbene 6. No active species could be characterized during reaction, and further studies are required to elucidate the details of the mechanism.

A very important feature related to the mechanism is the compatibility of carbenes **6/14** with primary alcohols. In this respect, it should be noted that seemingly all (PCP)Ir pincers that can somehow form unsaturated 14-electron species are more or less prone to decarbonylation of primary alcohols<sup>29b,36</sup> due to the high binding energy of CO to electron-rich Ir, making catalytic dehydrogenation of such alcohols trouble-some. This limitation is probably relevant to all complexes for which the catalytic cycle at least partially resembles the one for dehydrogenation of alkanes (specifically, involving removal of HCl from the corresponding (PCP)IrHCl complexes), although for secondary alcohols the catalytic activity can be very high.<sup>29b,36a,37</sup> At the same time, catalysts which work via a cooperative type of mechanism are much less prone to decarbonylation.<sup>21</sup>

# CONCLUSIONS

In summary, we have presented the synthesis, characterization, and catalytic activity of aliphatic phosphinite iridium pincer complexes and their derivatives. While under certain conditions cyclohexane-based phosphinite pincer ligands apparently decompose, they can be successfully metalated to give moderately robust iridium complexes. The thermal stability of these compounds and their derivatives is lower compared to that of the arene-based counterparts, but some of them (such as trans complex 13) still demonstrated good catalytic activity for dehydrogenation of alkanes, higher than that for aromatic phosphine complex 2 and only slightly lower than that for aromatic phosphinite complex 3. Because of facile  $\alpha$ -elimination reactions, the chemistry of the ligands reported here is dominated by carbene formation rather than the formation of reactive 14-electrons species as observed for many similar iridium pincer complexes. The  $\alpha$ -elimination is probably facilitated by the compartively short  $\alpha$ -C-Ir distances. On the one hand, this may open up for specific decomposition pathways which are likely responsible for the low activity of cis complex 8 in the dehydrogenation of alkanes, but on the other hand, the possibility of  $\alpha$ -elimination may also provide reactivity patterns that are unavailable for arene-based compounds. We argue that such metal-ligand cooperative pattern is responsible for the catalytic dehydrogenation of alcohols by carbene 6, hydrido-chloride 13, and related compounds. An excellent activity was observed in acceptorless dehydrogenation of benzylic alcohol and good for 1-phenylethanol, but aliphatic alcohols revealed low conversions. Of particular interest is the ability of these complexes to transform alcohols into polymers formally derived from the corresponding olefin.

# EXPERIMENTAL SECTION

**General Considerations.** All manipulations were conducted under an inert gas atmosphere using standard Schlenk, high-vacuum line, and glovebox techniques unless otherwise stated. All solvents were distilled under vacuum from Na/benzophenone except for  $CH_2Cl_2$  which was distilled under vacuum from calcium hydride. Hydrocarbon deuterated solvents were distilled under vacuum from Na/benzophenone. Cyclooctane was washed with  $H_2SO_4$  until it was nearly colorless, dried, and distilled under vacuum from calcium hydride. *tert*-Butylethylene was distilled under vacuum from calcium hydride. Alcohols for catalytic experiments were used as received except for degassing. NMR spectra were recorded on a Varian Unity INOVA 500 MHz or Bruker Avance 400 MHz instruments. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in parts per million and referenced to the signals of deuterated solvents. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are reported relative to external 85% solution of phosphoric acid. In some <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra decoupling of high-field hydride ligands was incomplete or totally absent; in the latter case, coupling constants are indicated in the text. Assignments of signals were typically confirmed using 2D spectra; where such spectra are lacking or do not provide reliable assignment, several possible options are listed. IR spectra were recorded on a Bruker Alpha spectrometer. Elemental analyses were performed by H. Kolbe Microanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Ligand 4 has been synthesized before,<sup>26b</sup> and a slightly modified procedure was used as described in the Supporting Information. In the characterization, the following numbering was applied:



Synthesis of Trans POCyOP Ligand 5. *trans*-1,3-Cyclohexanediols were separated from the cis/trans mixture using the method of Aoyama and co-workers.<sup>38</sup> Starting from trans diol (0.220 g, 1.894 mmol), 60% NaH in paraffin (0.159 g, 3.977 mmol, 2.1 equiv) and di*tert*-butylchlorophosphine (0.79 mL, 4.167 mmol, 2.2 equiv) ligand 5 was obtained in almost quantitative yield using the same procedure as for 4. The product exhibited ca. 95% purity by NMR spectroscopy and was used without further purification. A sample for elemental analysis was additionally recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH.

<sup>1</sup>H NMR (500 MHz, toluene- $d_8$ ) δ 4.05–3.99 (m, 2H, >CH–O–), 1.89 (br s, 1H, Cy–H), 1.67–1.46 (overlapping, m, 4H), 1.39–1.24 (m, 2H, Cy–H), 1.11 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.0 Hz, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.08 (d, <sup>3</sup>*J*<sub>PH</sub> = 11.0 Hz, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 0.95–0.87 (m, 1H, Cy–H). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene- $d_8$ ) δ 155.07 (br s). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>O<sub>2</sub>P<sub>2</sub>: C, 65.32; H, 11.46. Found C, 65.63, H, 11.78.

Metalation of Ligand 4 and Synthesis of Carbene 6 and Complex 7. A Straus flask was charged with POCyOP ligand 4 (0.550 g, 1.360 mmol), [Ir(COD)Cl]<sub>2</sub> (0.457 g, 0.680 mmol), and 15 mL of toluene inside a nitrogen atmosphere glovebox. The flask was sealed, fully immersed into an oil bath, and heated at 120 °C overnight. The volatiles were removed in vacuum, and the residue was extracted with hexane until the extract became pale yellow. The solutions were combined, evaporated, and chromatographed on alumina using benzene-hexane 1:1 mixture as eluent. The green fraction was collected, evaporated, and dried under vacuum to give 6 (0.294 g, 34%) as a dark greenish powder. The residue from the extraction was suspended in a small amount of hexane, the solid particles were allowed to sediment, and the mother liquor was decanted. This procedure was repeated several times. The resulting solid material was dried under vacuum to give 7 (0.277 g, 32%) as a yellow powder. When only 6 is desired, the temperature may be raised to 170  $^{\circ}$ C, which improves the isolated yield of 6 up to 55%.

Characterization of **6**. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.57–1.53 (m, overlapping, 2H, 3H<sub>A</sub> and 5H<sub>A</sub>), 1.51 (vt, 18H,  $|^{3}J_{PH} + {}^{5}J_{PH}| = 14.0$  Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (vt, 18H,  $|^{3}J_{PH} + {}^{5}J_{PH}| = 13.7$  Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.25 (apparent qd, 2H,  $J_{HH} = 12.4$  Hz,  $J_{HH} = 4.4$  Hz, 3H<sub>B</sub> and 5H<sub>B</sub>), 0.98 (apparent qd, 2H,  $J_{HH} = 13.2$  Hz,  ${}^{3}J_{HH} = 3.4$  Hz, 4H<sub>A</sub>), 0.92–0.86 (m, 1H, 4H<sub>B</sub>), -1.21 (dd of vt, 2H,  ${}^{3}J_{HH} = 11.8$  Hz,  ${}^{3}J_{HH} = 5.8$  Hz,  ${}^{13}J_{PH} + {}^{4}J_{PH}| = 5.8$  Hz, 2H and 6H).  ${}^{13}C{}^{14}$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  235.85 (t,  ${}^{2}J_{PC} = 4.3$  Hz, 1C), 106.39 (vt,  ${}^{2}J_{PC} + {}^{3}J_{PC}| = 13.8$  Hz, 2C and 6C), 41.47 (vt,  ${}^{1}J_{PC} + {}^{3}J_{PC}| = 23.0$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 40.14 (vt,  ${}^{1}J_{PC} + {}^{3}J_{PC}| = 24.8$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.16 (vt,  ${}^{2}J_{PC} + {}^{4}J_{PC}| = 7.0$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.93 (vt,  ${}^{2}J_{PC} + {}^{4}J_{PC}| = 6.8$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 27.43 (vt,  ${}^{3}J_{PC} + {}^{4}J_{PC}| = 4.0$  Hz, 3C and 5C), 20.88 (s, 4C). <sup>31</sup>P{}^{1}H NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ 

179.2 (s). Anal. Calcd for  $C_{22}H_{44}ClIrO_2P_2:$  C, 41.93; H, 7.04. Found C, 42.21, H, 7.44.

Characterization of 7. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.08–4.00 (m, 2H, 2H and 6H), 2.76–2.72 (m, 1H, 1H<sub>A</sub>), 2.05–2.00 (m, 2H, 3H<sub>A</sub> and 5H<sub>A</sub>), 1.54–1.48 (m, overlapping, 3H, 1H<sub>B</sub> + 4H<sub>A</sub> + 4H<sub>B</sub>), 1.47–1.43 (m, 36 H, 4 C(CH<sub>3</sub>)<sub>3</sub>), 1.14–1.04 (m, 2H, 3H<sub>B</sub> and 5H<sub>B</sub>), -32.89 (td, 1H, <sup>2</sup>J<sub>PH</sub> = 10.4 Hz, <sup>2</sup>J<sub>HH</sub> = 8.1 Hz, Ir–H), -33.27 (td, 1H, <sup>2</sup>J<sub>PH</sub> = 10.7 Hz, <sup>2</sup>J<sub>HH</sub> = 8.1 Hz, Ir–H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  77.91 (s, 1C), 41.90 (br s, 1C), 41.71 (apparent td, *J* = 14.3 Hz, *J* = 8.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 33.10 (s, 3C and 5C), 29.41 (vt, <sup>1</sup><sup>2</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>] = 6.0 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.35 (vt, <sup>1</sup><sup>2</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>] = 5.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 21.16 (s, 4C). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  159.49 (s). NMR spectra in THF-*d*<sub>8</sub> are given in the Supporting Information. Anal. Calcd for C<sub>44</sub>H<sub>96</sub>Cl<sub>2</sub>Ir<sub>2</sub>O<sub>4</sub>P<sub>4</sub>: C, 41.66 H, 7.63. Found C, 42.16, H, 6.99. HRMS: Calcd for C<sub>44</sub>H<sub>96</sub>ClIr<sub>2</sub>O<sub>4</sub>P<sub>4</sub> ([M - Cl]<sup>+</sup>): 1233.5206. Found: 1233.5211. NMR signals for a single (POCyHOP)\*Ir(H)<sub>2</sub>Cl unit are reported, since the number of units cannot be derived from integration.

Synthesis of Hydrido-Chloride Complex 8. A J. Young NMR tube was charged with carbene 6 (0.020 g, 0.032 mmol) inside a nitrogen atmosphere glovebox, followed by vacuum-transfer of 0.7 mL of C<sub>6</sub>D<sub>6</sub>. The tube was refilled with 1 atm of H<sub>2</sub> and left for 3 days at room temperature, after which NMR spectroscopy indicated that complex 8 was the only product in the solution. The volatiles were evaporated and the residue was dried in vacuum to give 8 as a yellow powder in quantitative yield. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 3.15 (apparent td, 2H,  ${}^{3}J_{HH} = 10.4$  Hz,  ${}^{3}J_{HH} = 3.6$  Hz, 2H and 6H), 2.62 (td, 1H,  ${}^{3}J_{HH} = 10.4$  Hz,  ${}^{3}J_{H-IrH} = 3.1$  Hz, 1H), 1.98–1.92 (m, 2H,  $3H_A$  and  $5H_A$ ), 1.59–1.54 (m, 1H,  $4H_A$ ) 1.38 (vt, 18H,  $|{}^3J_{PH} + {}^5J_{PH}| =$ 13.8 Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (d, 18H,  $|{}^{3}J_{PH} + {}^{5}J_{PH}| = 14.0$  Hz, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.20–1.12 (m, 2H, 3H<sub>B</sub> and 5H<sub>B</sub>), 1.06–0.96 (m, 1H,  $4H_B$ ), -40.37 (td,  ${}^{2}J_{PH}$  = 12.4 Hz,  ${}^{3}J_{H-IrH}$  = 3.1 Hz, 1H, Ir-H). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  88.73 (vt,  $|^{2}J_{PC} + {}^{3}J_{PC}| = 9.6$  Hz, 2C and 6C), 43.54 (dt,  ${}^{2}J_{CH}$  = 6.2 Hz,  ${}^{2}J_{PC}$  = 2.0 Hz, 1C), 40.46 (vt,  $|{}^{1}J_{PC} + {}^{3}J_{PC}| = 26.8 \text{ Hz}, C(CH_{3})_{3}), 40.04 \text{ (vt, } |{}^{1}J_{PC} + {}^{3}J_{PC}| = 23.5 \text{ Hz},$  $C(CH_3)_3$ , 32.45 (t,  $|{}^{3}J_{PC} + {}^{4}J_{PC}| = 10.6$  Hz, 3C and 5C), 28.25 (vt,  $|{}^{2}J_{PC} + {}^{4}J_{PC}| = 6.6$  Hz,  $C(CH_3)_3$ ), 27.96 (vt,  $|{}^{2}J_{PC} + {}^{4}J_{PC}| = 6.0$  Hz,  $C(CH_3)_3$ ), 22.36 (s, 4C).  ${}^{31}P{}^{1}H$  NMR (202 MHz,  $C_6D_6$ )  $\delta$  170.0 (d,  ${}^{2}J_{PH}$  = 12.4 Hz). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClIrO<sub>2</sub>P<sub>2</sub>: C, 41.80; H, 7.33. Found C, 41.96, H, 7.47.

**Reaction of Carbene 6 with CO.** A J. Young NMR tube was charged with carbene 6 (0.019 g, 0.030 mmol) inside a nitrogen atmosphere glovebox, followed by vacuum-transfer of 0.7 mL of  $C_6D_6$ . The tube was refilled with 1 atm of CO accompanied by a simultaneous color change from dark greenish to yellow. Compounds **10a** and **10b** were initially the only products of reaction and were characterized by NMR spectroscopy. The low stability of **10a** and **10b** requires high concentration in order to get reasonably good <sup>13</sup>C and 2D spectra. Subsequently, **11a** and **11b** were formed, and after several days, **11b** was the only product in the solution. Complex **11a** was never formed as a major product, but the majority of its NMR signals were reliably identified. After 2 weeks there was complete conversion of **11b** into **12**, which was obtained by evaporation of the volatiles in almost quantitative yield.

Characterization of **10a**. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.61–2.57 (m, 2H, 2H and 6H), 1.71 (overlapping, 3H<sub>A</sub> and 5H<sub>A</sub>), 1.50 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.38 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.17 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.38 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.17 (overlapping, 4H<sub>A</sub>), 0.91 (overlapping, 3H<sub>B</sub> and 5H<sub>B</sub> + 4H<sub>B</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 214.31 (t, <sup>2</sup>J<sub>PC</sub> = 7.8 Hz, 1C), 187.35 (t, <sup>2</sup>J<sub>PC</sub> = 3.5 Hz, Ir–CO), 99.78 (vt, <sup>12</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>| = 12.6 Hz, 2C and 6C), 43.58 (vt, <sup>11</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>| = 25.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 38.81 (t, <sup>11</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>| = 27.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 33.02 (vt, <sup>13</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>| = 4.4 Hz, 3C and 5C), 29.61 (vt, <sup>12</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>| = 4.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.36 (vt, <sup>12</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>| = 6.2 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 20.37 (s, 4C). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ 182.45 (s).

*Characterization of* **10b**. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 2.90–2.85 (m, 2H, 2H and 6H), 1.76 (overlapping, 3H<sub>A</sub> and 5H<sub>A</sub>), 1.52 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (overlapping, 18H, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.26 (overlapping, 3H<sub>B</sub> and 5H<sub>B</sub>), 0.91 (overlapping, 4H<sub>B</sub>). <sup>13</sup>C{<sup>1</sup>H}

NMR (126 MHz,  $C_6D_6$ )  $\delta$  211.99 (t,  ${}^2J_{PC}$  = 7.7 Hz, 1C), 187.09 (t,  ${}^2J_{PC}$  = 3.8 Hz, Ir–CO), 99.77 (vt,  ${}^2J_{PC}$  +  ${}^3J_{PC}$ | = 12.6 Hz, 2C and 6C), 42.56 (vt,  ${}^{1}J_{PC}$  +  ${}^{3}J_{PC}$ | = 26.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 40.27 (vt,  ${}^{1}J_{PC}$  +  ${}^{3}J_{PC}$ | = 26.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 31.63 (vt,  ${}^{1}J_{PC}$  +  ${}^{4}J_{PC}$ | = 3.2 Hz, 3C and 5C), 29.18 (vt,  ${}^{1}J_{PC}$  +  ${}^{4}J_{PC}$ | = 7.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 27.83 (vt,  ${}^{1}J_{PC}$  +  ${}^{4}J_{PC}$ | = 6.0 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 20.96 (s, 4C).  ${}^{31}P{}^{1}H$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  182.40 (s).

*Characterization of* **11a.** <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.15–4.11 (m, 1H, 2H), 2.07 (overlapping, 5H<sub>A</sub>), 1.94 (overlapping, 5H<sub>B</sub>), 1.89 (overlapping, 3H<sub>A</sub>), 1.53 (overlapping, 4H<sub>B</sub>), 1.5 (overlapping, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.42 (overlapping, 2 C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (overlapping, 3H<sub>B</sub>), 1.20 (overlapping, 4H<sub>B</sub>), -8.49 (apparent t, 1H, <sup>2</sup>J<sub>P1H</sub> = <sup>2</sup>J<sub>P2H</sub> = 16.3 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 180.12 (m, Ir–CO), 148.08 (m, 6C), 111.11 (m, 1C), 86.73 (d, <sup>2</sup>J<sub>PC</sub> = 3.7 Hz, 2C), 29.45 (dd, <sup>2</sup>J<sub>PC</sub> = 3.5 Hz, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 29.27 (dd, <sup>2</sup>J<sub>PC</sub> = 3.5 Hz, <sup>4</sup>J<sub>PC</sub> = 1.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 23.34 (dd, <sup>3</sup>J<sub>PC</sub> = 6.0 Hz, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, 5C). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ 156.82 and 155.86 ppm (AB system, <sup>2</sup>J<sub>PP</sub> = 325.4 Hz).

Characterization of **11b**. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ )  $\delta$  4.99 (apparent ddt, 1H, J = 10.0 Hz, J = 5.1 Hz, J = 2.6 Hz, 2H), 2.16–2.12 (m, 2H, 5H<sub>A</sub> + 5H<sub>B</sub>), 2.12–2.07 (m, 1H, 3H<sub>A</sub>), 1.64 (d, 9H,  $^3J_{PH} = 14.7$  Hz,  $C(CH_3)_3$ ), 1.58 (d, 9H,  $^3J_{PH} = 14.6$  Hz,  $C(CH_3)_3$ ), 1.55–1.52 (m, 1H, 4H<sub>A</sub>), 1.38–1.34 (m, 1H, 4H<sub>B</sub>), 1.26–1.20 (m, 1H, 3H<sub>B</sub>), 1.17 (d, 9H,  $^3J_{PH} = 13.9$  Hz,  $C(CH_3)_3$ ), 1.12 (d, 9H,  $^3J_{PH} = 13.8$  Hz,  $C(CH_3)_3$ ), -17.96 (dd,  $^2J_{P1H} = 14.9$  Hz,  $^2J_{P2H} = 12.2$  Hz, 1H).  $^{13}C{^{1}H}$  NMR (126 MHz,  $C_6D_6$ )  $\delta$  179.88 (apparent q,  $^2J_{P1C} = ^2J_{P2C} = ^2J_{CH} = 4.0$  Hz, Ir–CO), 154.49 (apparent dt,  $^2J_{PC} = 7.2$  Hz,  $^3J_{PC} = ^3J_{CH} = 1.6$  Hz, 6C), 127.5 (m, 1C), 88.09 (d,  $^2J_{PC} = 6.5$  Hz, 2C), 44.20 (dd,  $^1J_{PC} = 12.9$  Hz,  $^3J_{PC} = 8.2$  Hz,  $C(CH_3)_3$ ), 43.74 (dd,  $^1J_{PC} = 15.1$  Hz,  $^3J_{CH} = 2.2$  Hz,  $C(CH_3)_3$ ), 30.00 (dd,  $^2J_{PC} = 4.4$  Hz,  $^4J_{PC} = 0.9$  Hz,  $C(CH_3)_3$ ), 29.57 (d,  $^3J_{PC} = 11.0$  Hz, 5C), 20.66 (s, 4C).  $^{31}P{^{1}H}$  NMR (202 MHz,  $C_6D_6$ )  $\delta$  168.16 (dd,  $^2J_{PP} = 310.5$  Hz,  $^2J_{PH} = 14.9$  Hz), 161.68 (dd,  $^2J_{PP} = 310.5$  Hz,  $^2J_{PH} = 12.2$  Hz).

Characterization of **12**. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.58–4.52 (m, 1H, 2H), 2.36–2.28 (m, 2H, 5H<sub>A</sub> + 5H<sub>B</sub>), 2.17–2.11 (m, 1H, 3H<sub>A</sub>), 1.70–1.59 (m, 1H, 4H<sub>A</sub>), 1.39–1.32 (overlapping, m, 36H, 4 C(CH<sub>3</sub>)<sub>3</sub>), 1.28–1.18 (overlapping, m, 2H, 3H<sub>B</sub> + 4H<sub>B</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>) δ 199.23 (apparent t, <sup>2</sup>J<sub>P1C</sub> = <sup>2</sup>J<sub>P2C</sub> = 5.3 Hz, Ir–CO), 161.54 (apparent t, <sup>2</sup>J<sub>P1C</sub> = <sup>2</sup>J<sub>P2C</sub> = 7.3 Hz, 6C) 153.49 (dd, <sup>2</sup>J<sub>PC</sub> = 8.4 Hz, <sup>3</sup>J<sub>PC</sub> = 8.2 Hz, 1C), 88.45 (dd, <sup>2</sup>J<sub>PC</sub> = 5.9 Hz, <sup>3</sup>J<sub>PC</sub> = 5.0 Hz, 2C), 41.62–41.27 (overlapping, 2 C(CH<sub>3</sub>)<sub>3</sub>), 40.20 (X part of ABX, |<sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>| = 25.9 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 39.49 (X part of ABX, |<sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>| = 8.8 Hz, 3C), 28.85 (X part of ABX, |<sup>2</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>| = 7.4 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.51–28.36 (m, overlapping, 2 C(CH<sub>3</sub>)<sub>3</sub>), 28.28 (X part of ABX, |<sup>2</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub>| = 10.6 Hz, SC), 20.85 (s, 4C). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, C<sub>6</sub>D<sub>6</sub>) δ 155.40 and 154.32 ppm (AB system, <sup>2</sup>J<sub>PP</sub> = 305.5 Hz).

Metalation of Trans Ligand 5 and Synthesis of Complex 13. A Straus flask was charged with 5 (0.134 g, 0.331 mmol),  $[Ir(COD)Cl]_2$  (0.111 g, 0.165 mmol), and 7 mL of toluene inside a nitrogen atmosphere glovebox. The flask was sealed, fully immersed into an oil bath and heated at 120 °C for 8 h. The volatiles were removed in vacuum, the residue was dissolved in a minimum amount of hexane at 120  $^\circ\text{C}\textsc{,}$  and the flask was allowed to stay overnight at room temperature. The mother liquor was decanted, and the residue was washed with a small amount of cold hexane to give 13 (0.089 g, 43%) as dark red crystals of XRD quality. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  3.91–3.85 (m, 1H, 2H or 6H), 3.43 (apparent td, 1H,  ${}^{3}J_{\rm HH}$  = 11.6 Hz,  ${}^{3}J_{HH} = 4.8$  Hz, 2H or 6H), 3.15 (apparent td,  ${}^{3}J_{HH} \approx {}^{3}J_{HH} \approx 10.8$ Hz,  ${}^{3}J_{H-IrH} = 2.8$  Hz, 1H, 1H), 1.97–1.91 (m, 1H, 3H<sub>A</sub> or 5H<sub>A</sub>), 1.46– 1.43 (overlapping, 1H, 3H<sub>A</sub> or 5H<sub>A</sub>), 1.45-1.41 (overlapping, 1H,  $4H_A$ ), 1.40–1.33 (overlapping, m, 36H, 4  $C(CH_3)_3$ ), 1.27–1.22 (overlapping, 1H, 4H<sub>B</sub>), 1.23-1.18 (overlapping, 1H, 3H<sub>B</sub> or 5H<sub>B</sub>), 1.12-1.04 (m, 1H,  $3H_B$  or  $5H_B$ ), -39.37 (dd,  ${}^2J_{PH} = 13.9$  Hz,  ${}^2J_{PH} =$ 

11.1 Hz,  ${}^{3}J_{H-IrH} = 2.8$  Hz, 1H, Ir–H).  ${}^{13}C{}^{1}H$  NMR (126 MHz,  $C_6D_6$ )  $\delta$  88.82 (dd,  ${}^{2}J_{PC} = 5.1$  Hz,  ${}^{3}J_{PC} = 2.0$  Hz, 2C or 6C), 83.02 (dd,  ${}^{2}J_{PC} = 7.8$  Hz,  ${}^{3}J_{PC} = 1.6$  Hz, 2C or 6C), 42.37 (dd,  ${}^{1}J_{PC} = 14.5$  Hz,  ${}^{3}J_{PC} = 6.9$  Hz,  $C(CH_3)_3$ ), 40.63 (dd,  ${}^{1}J_{PC} = 18.2$  Hz,  ${}^{3}J_{PC} = 6.3$  Hz,  $C(CH_3)_3$ ), 40.46 (dd,  ${}^{1}J_{PC} = 17.3$  Hz,  ${}^{3}J_{PC} = 6.1$  Hz,  $C(CH_3)_3$ ), 37.83 (dd,  ${}^{1}J_{PC} = 25.8$  Hz,  ${}^{3}J_{PC} = 6.3$  Hz,  $C(CH_3)_3$ ), 37.0 (d of apparent t,  ${}^{2}J_{CH} = 5.5$  Hz,  ${}^{2}J_{PIC} = {}^{2}J_{P2C} = 1.4$  Hz, 1C), 28.69–28.60 (m, overlapping, 2  $C(CH_3)_3$ ), 28.51 (dd,  ${}^{2}J_{PC} = 4.9$  Hz,  ${}^{4}J_{PC} = 1.2$  Hz,  $C(CH_3)_3$ ), 28.37 (dd,  ${}^{2}J_{PC} = 5.0$  Hz,  ${}^{4}J_{PC} = 1.2$  Hz,  $C(CH_3)_3$ ), 26.34 (d,  ${}^{3}J_{PC} = 11.6$  Hz, 3C or 5C), 25.65 (d,  ${}^{2}J_{PC} = 6.6$  Hz, 3C or 5C), 17.64 (s, 4C).  ${}^{31}P{}^{1}H$  NMR (202 MHz,  $C_6D_6$ )  $\delta$  173.28 (dd,  ${}^{2}J_{PP} = 366.2$  Hz,  ${}^{2}J_{PH} = 13.9$  Hz), 169.23 (dd,  ${}^{2}J_{PP} = 366.2$  Hz,  ${}^{2}J_{PH} = 11.1$  Hz). Anal. Calcd for  $C_{22}H_{46}$ ClIrO<sub>2</sub>P<sub>2</sub>: C, 41.80; H, 7.33. Found C, 42.02, H, 7.43.

**Synthesis of Complex 14.** A J. Young NMR tube was charged with complex 13 (0.016 g, 0.025 mmol) and 0.7 mL of toluene-*d*<sub>8</sub> inside a nitrogen atmosphere glovebox. The tube was heated on an oil bath at 180 °C for 24 h, the volatiles were evaporated, and the residue was dried in vacuum to give 14 as brown powder in almost quantitative yield. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.57–1.50 (overlapping, 2H, 3H<sub>A</sub> and 5H<sub>A</sub>), 1.52 (vt, 18H,  $|^{3}J_{PH} + {}^{5}J_{PH}| = 14.0$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.44 (vt, 18H,  $|^{3}J_{PH} + {}^{5}J_{PH}| = 13.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.28–1.21 (m, 2H, 3H<sub>B</sub> and 5H<sub>B</sub>), 0.98–0.87 (m, 2H, 4H<sub>A</sub> + 4H<sub>B</sub>), -1.20 (dd of vt,  ${}^{3}J_{HH} = 11.5$  Hz,  ${}^{3}J_{HH} = 5.6$  Hz,  ${}^{13}J_{PH} + {}^{4}J_{PH}| = 5.6$  Hz, 2H, 2H and 6H).  ${}^{13}C{}^{1}H{}$  NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 236.03 (t,  ${}^{2}J_{PC} = 4.3$  Hz, 1C), 106.35 (vt,  ${}^{12}J_{PC} + {}^{3}J_{PC}| = 13.8$  Hz, 2C and 6C), 41.32 (vt,  ${}^{14}J_{PC} + {}^{3}J_{PC}| = 23.2$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 39.98 (vt,  ${}^{11}J_{PC} + {}^{3}J_{PC}| = 25.0$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.97 (vt,  ${}^{12}J_{PC} + {}^{4}J_{PC}| = 7.0$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.74 (vt,  ${}^{12}J_{PC} + {}^{4}J_{PC}| = 6.8$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 20.68 (s, 4C).  ${}^{31}P{}^{1}H{}$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>) δ 179.48 (s). Anal. Calcd for C<sub>22</sub>H<sub>44</sub>ClIrO<sub>2</sub>P<sub>2</sub>: C, 41.93; H, 7.04. Found C, 42.14, H, 6.86.

Formation of Compound 15. The experiment was conducted in a way similar to synthesis of complex 13 described above, starting from POCyOP ligand (0.521 g, 1.288 mmol) and [Ir(COD)Cl]<sub>2</sub> (0.433 g, 0.644 mmol). After crystallization, in addition to dark red crystals of 13 (0.191 g, 23%), large yellow crystals of 15 (0.255 g, 41% based on Ir) were obtained, which were separated manually. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ )  $\delta$  4.17 (td, 1H,  ${}^{3}J_{HH}$  = 7.3 Hz,  ${}^{3}J_{HH}$  = 3.1 Hz, -CH= CH- in COD), 4.13-4.10 (m, 1H, -CH=CH- in COD), 4.07-4.00 (overlapping, 2H, -CH=CH- in COD + 2H), 3.95 (td, 1H,  ${}^{3}J_{HH} = 7.3 \text{ Hz}, {}^{3}J_{HH} = 3.3 \text{ Hz}, -CH=CH- \text{ in COD}), 3.30-3.24 \text{ (m,}$ 1H, 6H), 2.59 (dd, 1H,  ${}^{3}J_{HH} = 11.6$  Hz,  ${}^{3}J_{HH} = 8.1$  Hz, 1H), 2.17–2.00 (m, 4H,  $-CH_2-$  in COD), 1.92–1.84 (m, 1H, 5H<sub>A</sub>), 1.73 (d, overlapping, 9H,  ${}^{3}J_{PH}$  = 12.6 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.72 (d, overlapping, 9H,  ${}^{3}J_{\rm PH} = 12.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.58–1.53 (m, 1H, 3H<sub>A</sub>), 1.43 (d, 9H,  ${}^{3}J_{\rm PH}$ = 12.7 Hz,  $C(CH_3)_3$ , 1.41–1.34 (overlapping, 1H, 3H<sub>B</sub>), 1.37–1.31 (overlapping, 1H, 4H<sub>A</sub>), 1.36 (d, 9H,  ${}^{3}J_{PH} = 12.7$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 1.24– 1.07 (overlapping, 6H,  $-CH_2$ - in COD + 5H<sub>B</sub> + 4H<sub>B</sub>), -27.11 (dd,  ${}^{2}J_{\rm PH}$  = 16.9 Hz,  ${}^{2}J_{\rm PH}$  = 12.1 Hz, 1H, Ir–H).  ${}^{13}C{}^{1}H$  NMR (126 MHz,  $C_6D_6$ )  $\delta$  88.46 (apparent t,  ${}^2J_{P1C} = {}^2J_{P2C} = 2.7$  Hz, 6C), 83.99 (dd,  ${}^2J_{PC}$ = 8.7 Hz,  ${}^{3}J_{PC}$  = 2.7 Hz, 2C), 61.88 (s, C=C in COD), 61.85 (s, C= C in COD), 61.74 (s, C=C in COD), 61.27 (s, C=C in COD), 44.27 (dd,  ${}^{1}J_{PC} = 9.6$  Hz,  ${}^{3}J_{PC} = 8.3$  Hz,  $C(CH_{3})_{3}$ ), 41.52 (dd,  ${}^{1}J_{PC} =$ 13.8 Hz,  ${}^{3}J_{PC} = 8.7$  Hz,  $C(CH_{3})_{3}$ ), 40.43 (dd,  ${}^{1}J_{PC} = 20.9$  Hz,  ${}^{3}J_{PC} = 5.0$ Hz,  $C(CH_3)_3$ , 39.88 (dd,  ${}^{1}J_{PC} = 29.3$  Hz,  ${}^{3}J_{PC} = 4.3$  Hz,  $C(CH_3)_3$ ), 32.78 (br s, 1C), 32.13 (s,  $-CH_2$ - in COD), 32.04 (s,  $-CH_2$ - in COD), 31.78 (s, -CH<sub>2</sub>- in COD), 31.75 (s, -CH<sub>2</sub>- in COD), 30.21 (d,  ${}^{2}J_{PC} = 4.5 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.83 (dd,  ${}^{2}J_{PC} = 5.2 \text{ Hz}$ ,  ${}^{4}J_{PC} = 1.1 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.55 (d,  ${}^{2}J_{PC} = 4.0 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.55 (d,  ${}^{3}J_{PC} = 4.0 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 27.63 (d,  ${}^{3}J_{PC} = 10.8 \text{ Hz}$ , SC), 26.83 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz}$ , C(CH<sub>3</sub>)<sub>3</sub>), 29.63 (d,  ${}^{3}J_{PC} = 10.6 \text{ Hz$ 3C), 18.47 (s, 4C).  ${}^{31}P{}^{1}H{}$  NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  155.36 (dd,  ${}^{2}J_{\rm PP}$  = 366.1 Hz,  ${}^{2}J_{\rm PH}$  = 16.9 Hz), 150.18 (dd,  ${}^{2}J_{\rm PP}$  = 366.1 Hz,  ${}^{2}J_{\rm PH}$  = 12.1 Hz). Anal. Calcd for C<sub>30</sub>H<sub>58</sub>Cl<sub>2</sub>Ir<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C, 37.22; H, 6.04. Found C, 37.46, H, 5.92.

**Crystallography.** Intensity data were collected with an Oxford Diffraction Xcalibur 3 system using  $\omega$ -scans and Mo K $\alpha$  ( $\lambda = 0.71073$  Å). The CCD data were extracted and integrated using Crysalis RED.<sup>39</sup> The structures were solved using direct methods and refined by full-matrix least-squares calculations on  $F^2$  using SHELXL<sup>40</sup> and

SIR-92.<sup>41</sup> Non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to parent sites, using a riding model. Crystals of **6** and **13** have residual electron density close to Ir. This is explained by poor crystal quality and a nonmodeled hydride, respectively. Crystals of **8** and **13** have disordered cyclohexyl groups, and these were modeled isotropically. The CCDC deposition numbers are 1474224–1474227.

General Procedure for Transfer Dehydrogenation of Cyclooctane. In a typical experiment, the catalyst (0.0095 mmol) and <sup>1</sup>BuONa (0.0014 g, 0.0142 mmol, 1.5 equiv) were placed into a Straus flask and specified amounts of cyclooctane (COA) and *tert*butylethylene (TBE) were added. The flask was sealed and fully immersed into a preheated oil bath. After completion of the heating, the flask was cooled by a stream of air and the sample was analyzed by NMR spectroscopy.

General Procedure for Acceptorless Dehydrogenation of Alcohols. In a typical experiment, the catalyst (0.0095 mmol) and degassed alcohol (4000 equiv) were placed into a Schlenk flask equipped with magnetic stirring bar and reflux condenser. The reaction mixture was stirred for 0.5 h, and then the flask was placed into an oil bath preheated to the specified temperature. A slow stream of Ar was passed above the reflux condenser to facilitate the escape of H<sub>2</sub>. After the desired reaction time, the Schlenk flask was allowed to reach room temperature, and the sample was analyzed by NMR spectroscopy. To obtain a sample of polystyrene, the reaction mixture was diluted with small amount of acetone, followed by addition of pentane. The precipitate was washed with pentane and dried in vacuum. NMR spectra were in agreement with those reported for polystyrene.<sup>42</sup> Anal. Calcd for  $(C_8H_8)_n$ : C, 92.26; H, 7.74. Found C, 91.81, H, 7.35.

**Computational Details.** The electronic structure calculations were carried out with Gaussian  $09^{43}$  program using the DFT method with the PBE<sup>44</sup> exchange and correlation functionals. The relativistic, small-core ECP and corresponding basis set of Dolg et al.<sup>45</sup> (SDD) was used for the Ir atom; D95(d)<sup>46</sup> basis set was applied to other atoms. This model was previously shown to give accurate results for iridium pincer complexes.<sup>47</sup> All stationary points located on the potential energy surfaces were characterized by normal-mode analysis as minima or transition states. Natural bond occupation (NBO) calculation was done as implemented in the Gaussian program package.<sup>48</sup>

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00846.

Further experimental details, NMR spectra, and computational results (PDF)

Crystallographic information files for compounds 6, 8, 13, and 15 (CIF)

Computed molecule Cartesian coordinates (XYZ)

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# Notes

The authors declare no competing financial interest.

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